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Data Validation Process for the PM2.5 Chemical Speciation Network

Prepared for

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1.0 Introduction

Research Triangle Institute (RTI), under contract with the U.S. Environmental Protection Agency (EPA) Office of Air Quality Planning and Standards (OAQPS) is providing analytical laboratory services for a new program to determine the chemical speciation of fine particulates. Analytical data to be gathered include:

- Total mass
- Sulfate, nitrate, ammonium, sodium, and potassium ions
- Elemental composition (by X-ray Fluorescence)
- Organic, elemental, carbonate and total carbon.

RTI is responsible for the following activities:

- Most laboratory analyses for the program (except XRF, which is subcontracted to Chester LabNet)
- Scheduling the distribution and receipt of sampler components to and from the monitoring agencies that operate the sites
- Entering and managing all field and laboratory data
- Performing preliminary Level 0 and Level 1 data validations
- Reporting the preliminary validated data to the monitoring agencies on a monthly basis
- Finalizing the validated data set based on the monitoring agencies' reviews
- Formatting the data and uploading the validated data to AIRS.

The purpose of this document is to describe the following elements of the data validation process:

- Overall process of validation used by the RTI laboratory, validation criteria, and corresponding flags.
- Process, forms, and formats used by RTI for reporting its data validation results to the Delivery Order/Project officer (DOPO) and the monitoring agencies.
- Forms used by the monitoring agencies to review and revise these validation flags, and to add validation flags based on their internal data validation processes and procedures.

Validating data for the STN requires review of information generated during the entire process, from sample scheduling through receipt of exposed filters, analysis, and data entry. Typical validation requirements include:

- Correct assignment of sampling information including exposure site, date, channel assignments, and filter IDs
- Sampler operating conditions are within prescribed limits
- Holding times for exposed media are observed
- Filter media are received undamaged
- Quality assurance/quality control (QA/QC) criteria such as recoveries, detection limits, and blanks are met in the laboratories
- Within-sample screening checks such as ion ratio tests are satisfactory.

The state monitoring agencies that operate the sampling sites possess the most complete information about the status of each site at the time of sampling. This includes audit and calibration results, detailed operators' notes, meteorological information, and data downloaded from the samplers. RTI works with each agency through the DOPO to complete the validation of each data set before it is uploaded to Airometric Information Retrieval System (AIRS). The mechanisms for transmitting data validation information between RTI and the monitoring agencies is the monthly data report. The monitoring agencies provide their comments and corrections to RTI by filling out the form described in Appendix A. Other formats, such as spreadsheet files can also be accepted, provided that they associate the changes with the necessary identifying information, such as the chain of custody form number.

2.0 The Validation Process

2.1 Validation Levels

The OAQPS has defined several different levels of data validation that are applicable to the chemical speciation program. RTI is responsible for Levels 0 and 1. The monitoring agencies may apply additional Level 0 and 1 checks, as well as checks at higher levels.

Level 0 validation coincides with the customary QA/QC operations normally carried out to ensure reliable environmental data of known origin. Level 0 validation focuses on the correctness of individual operations or analyses independent of other results.

Level 1 validation includes between-analyte data screening within a single sample event, and is useful for identifying suspicious or atypical results. The purpose of Level 1 screening during the initial phases of the program will be to identify samples for further investigation. If investigation of a suspicious result turns up an identifiable problem, appropriate flags can be assigned. In addition, investigation of Level 1 problems might lead to systematic and procedural changes to prevent future occurrences. Level 1 checks that will be used initially include mass balance (total weight of chemical species vs. gravimetric result), ion balance (total anion charge vs. total cation charge). Correlation between analytes will also be investigated as a potential Level 1 screening tool. A fixed percentage (2%) of the highest and lowest values will be identified for examination.

2.2 Types of Flags

The data generated by the STN program will ultimately be delivered, along with validation information, to AIRS. AIRS defines a very limited number of data validation flags that can be used with the PM2.5 chemical speciation data. To better manage the project, and to comply with all the regulatory requirements for PM2.5 sampling, a more elaborate set of internal data flags will be used by RTI in its internal data base. In addition to the AIRS codes and RTI's internal flags, the manufacturers of the chemical speciation samplers have defined error codes that are displayed after each 24-hour sampling event. All three types of flags will be carried throughout the data management system until the monitoring data are uploaded to AIRS along with the validation codes recognized by AIRS.

2.3 Process Description

Data validity is integral to many aspects of the program. The first validation flags for a sample exposure session are generated by the sampler during the exposure. These typically include flags such as flow rate and filter temperature. The site operator also has the opportunity to record events such as power failures and nearby construction which translate directly into AIRS codes. Other post-exposure validation criteria include holding time before retrieval, and shipment temperature. Upon receipt at RTI, the shipping materials, sampler modules, and individual filters are inspected and flags are assigned if damage is seen. The field sampling chain of custody (COC) forms returned to RTI with the sampling modules are examined, and the recorded data are entered into the data base. Any inconsistencies or missing data are noted

during data entry, and may generate other validation flags. The filters are distributed to the different analytical laboratories, which apply their own validation criteria based on QC results generated during the analysis. If a sample is questionable due to poor QC results, the laboratory first attempts to correct the problem and reanalyze the sample to maximize data completeness. However, if this is not possible, the sample data may have to be flagged as suspicious or invalid.

Following analysis, the data set is screened for completeness and automated screening is performed to set validation flags for criteria such as flow rate, exposure time, holding time, etc., that are required to be within specified limits. Level 1 checks, initially limited to cation/anion ratios, and mass balance will be applied to identify atypical samples for further investigation. Data will also be examined manually to identify inconsistencies and unexpected problems. Additional automated screening procedures will be developed later in the program based on experience with Level 1 and manual screening.

The next step is reporting the preliminary validated data set to the monitoring agencies. Each monthly report includes all data that has been processed and validated up to that point, and has not been previously reported. For simplicity, only data sets that have been fully processed and validated will be included in the report. No data for a sample exposure will be reported until all the analysis results have been received and RTI's validation process has been completed. The monitoring agencies then have a specified period of time to examine the data and associated validation flags. A correction form described later in this document is used to indicate changes that the state directs RTI to make before the data are uploaded to AIRS.

2.4 Hierarchy of Validation Flags

In developing the database structure for storing and managing the data and associated validation flags for this program, RTI has defined a logical hierarchy that corresponds to the actual sampling process. This hierarchy is summed up in the following relation:

Sample Session ➜ Flow Channel ➜ Media (filter) ➜ Analysis ➜ Analyte

All flags "flow" to the right in the relationship shown above. For example, flags applied to an entire sample session (e.g., "exposure canceled," "shipping temperature too high," and "retrieval holding time exceeded") apply to all channels, media, analyses, and analytes for that sampling session.

"Flow Channel" refers to a single flow channel of a chemical speciation sampler. All media sampled on that flow channel receive the flags assigned to that flow channel. These flags apply to parameters such as total volume, exposure time, and flow rate.

"Media" currently refers only to filters, although other types of sampling media such as XAD cartridges or denuders might be added to the program in the future. Torn, damaged, contaminated or lost filters are flagged at the media level, and most of these flags propagate to the analyses and analyte records for that filter. NOTE: the seriousness of a damaged-filter flag may depend upon the analysis or analyte; damage that invalidates a gravimetric analysis might be inconsequential for organic and elemental carbon (OC/EC) analysis.

“Analysis” refers to a single type of analysis for a given filter (or other medium). At present, the list includes all those analyses listed in the Introduction section of this document. Any analysis that does not pass all of the particular laboratory's QC checks are flagged, and these flags propagate to each of the analytes for that particular analysis.

"Analyte" refers to analytical results for individual elements, ions, OC/EC species, and filter weight. Validation flags assigned at the analyte level do not propagate further, except in a few instances in which combined results might be reported (e.g., total nitrate from Teflon and nylon filters, or total carbon from OC plus EC results). Where data for two different filters are combined, the validation flags for both filters will be applied to the resulting analyte value.

For example, if the flow rate for a particular flow channel is out of limits, the resulting flag automatically applies to all filters sampled on that flow channel, as well as to the individual analytical results obtained from those filters. A flag is applied at the "media" level would automatically apply to all analytes obtained from that media, but this flag would not apply at the channel or sample level, because these are "upstream" in the flagging hierarchy.

Using the hierarchy of validation flagging described above eliminates redundancy and simplifies the setting and removal of flags; if a filter is torn, only one flag needs to be set in the data base rather than many individual analyte flags. This saves time for both RTI and the monitoring agencies when they validate the data and report the results.

3.0 Level 0 Validation

The various Level 0 validation criteria that will be applied are summarized in Appendix B. Validation flags and codes are generated in several different locations and by several different processes. These include:

- Sampler-Generated Flags -- conditions during the exposure itself
- Operator-Specified Flags -- exposure, filter handling, and other conditions in the field
- Disassembly Flags -- inspection of incoming samples and paperwork
- Laboratory Validation Flags -- primarily based on filter inspection and laboratory QC/QA results
- Range Checking Flags -- automated checks of numerical parameters such as flow rate, exposure time, holding time, etc., that are required to be within a specified range

3.1 Sampler-Generated Flags

Each of the three chemical speciation samplers is programmed to generate certain flags related to sampling conditions. Because the three sampler types vary in design and programming, the flags generated by their software differ. See Appendix B-3 for a list of flags.

3.2 Operator-specified Flags

A Coding Form is sent with every shipment along with the COC. The Coding Form includes a list of conditions that the operator can mark as applying to the exposure session. The specific conditions listed on the Coding Form are directly related to the AIRS null value codes and validation status codes that have been defined for PM2.5 Chemical Speciation data. RTI enters the Coding Form entries into the data base. Although some of the error conditions logically apply to single filters or flow channels, the initial version of the Coding Form only provides a single set of flags applying to the whole event. The person who enters the data into the RTI data base is responsible for applying the flags to the appropriate level in the hierarchy: sampling event, flow channel, or filter.

Operators' comments can be entered in the Comments section of the COC form. These are entered into the data base, and are helpful in assigning or interpreting field validation flags.

3.3 Disassembly Flags

3.3.1 Verification of Correct Identification

When the exposed filter modules, COC sheets, and Coding Forms are returned to RTI from the field, the information recorded on the COC forms must be checked against information generated during the scheduling process. If the modules were interchanged, used on the wrong date, etc., corrections are made in the data base to reflect actual usage.

If a module set is returned unused, the exposure is invalidated using an appropriate code that reflects the reason why the exposure was not performed (e.g., technician not available, unable to reach site). The SHAL Level 0 Check List is used to record this type of information, which is entered into the data base at the same time as the COC. Forms received from the field. If there is a discrepancy that RTI cannot resolve, RTI will notify the monitoring agency's designated contact person of the problem by telephone or e-mail and will attempt to resolve it.

3.3.2 Incoming Inspection and Disassembly

Inspections upon receipt include determining the temperature in the container, inventory of contents, assessment of any external, and internal damage that may have occurred. The modules are disassembled so that the filters can be removed and routed to the laboratories for analysis. Problems such as missing or damaged module components (o-rings, spacers, etc.) or filters are noted on the SHAL Level 0 Check List.

3.3.3 Data Entry

After initial checking by the SHAL personnel, data on the COC and Coding Forms, and the SHAL Level 0 Check List are screened and entered. The COC form provides critical information used for data validation, including holding times, site conditions, instrument internal temperature, flow rate consistency. The data entry person has been trained to look for inconsistencies on the forms and to assign appropriate flags or take other appropriate actions when problems are found.

3.4 Laboratory Validation

The analyses required under the pilot program include OC/EC, anions and cations by ion chromatography (IC), elemental analysis by X-ray Fluorescence (XRF), and total mass. Validation flags and criteria applying to the IC and OC/EC analyses are described in Appendix C. Measurement of semi-volatile organic compounds (SVOCs) is scheduled for the full program, but is not being done for the pilot network. Descriptions of the individual analyses follow:

- Organic and Elemental Carbon (OC/EC) -- This measurement is done using a special thermal analyzer that is programmed to heat a sample (a section from a quartz filter) stepwise to a relatively high temperature in a non-oxidizing atmosphere, then to allow the sample to cool somewhat, and finally to heat the sample in an oxidizing atmosphere. All carbon removed from the filter section during the analysis is converted first to carbon dioxide and then to methane, which is measured using a flame ionization detector. OC is either removed from the filter by thermal desorption or converted to elemental carbon (or char), which remains on the filter, during the initial heating in a non-oxidizing atmosphere. Elemental carbon, including char formed from organic carbon, is pyrolized from the filter during the second heating sequence, which is conducted in an oxidizing atmosphere. The transmittance of the filter, which is measured using a small laser and a photocell, is reduced by the presence of elemental carbon but not by the presence of organic carbon. The transmittance of the filter is used to adjust the

OC/EC split to account for organic carbon that was converted to char in the initial heating sequence of the analysis. QA/QC applicable to the OC/EC analysis includes multi-point calibration using filters spiked with known amounts of sucrose. The response of the FID is checked after each run using an automatic injection of a methane gas standard. Other routine checks include duplicates from field samples, filter lot blanks, lab blanks, trip blanks, and field blanks. No standards for the OC/EC analysis are currently available from outside sources such as NIST.

- Ions by Ion Chromatography (IC) -- The measurement of common ions (Na+, K+, NH4+, SO4-2, and NO3-) contained in the particulate matter. Aside from the initial extraction step, analysis is similar to methods used for other low-level environmental media such as precipitation samples. Both nylon and Teflon® filters are being analyzed for ions, depending on the sampler model. Filters to be analyzed for ions must be cleaned and verified prior to use to remove trace levels of sulfate, nitrate and the other ions. The usual laboratory QA/QC checks are applied during analysis, and the analyst applies Level 0 validation flags as necessary.

- XRF -- Elemental analysis by XRF is being conducted by a subcontractor, Chester LabNet. The Teflon filters used for this analysis are also used for mass determination and, for the URG samplers, for ion analysis, so RTI must expedite these filters through the weighing lab and then send them to LabNet, which, for the URG filters, must return them promptly to RTI for ion analysis. This process must be expedited because of tight holding time and data reporting requirements. Data uncertainty and validity are determined by LabNet and are reported back to RTI.

- Mass -- The gravimetric laboratory follows QA/QC procedures that are identical to those applicable to the PM2.5 national network. These include equilibration of filters at carefully controlled conditions of temperature and humidity prior to each weighing; frequent use of check weights, filter re-weighings, laboratory, trip, and field blanks; and semi-annual balance maintenance.

3.5 Automated Screening

After all the data forming a data set have been finalized, automated procedures are run to ensure that all simple range checks are complete. Automated screens are typically based on fixed limits applicable to a particular channel of data. Examples include flow rates, which are a fixed percentage of the nominal flow rate for each channel, retrieval time after sampling, and temperature upon receipt at the laboratory. Appendix B contains the specific range checks that will be applied.

4.0 Level 1 Data Validation

4.1 Purpose of Level 1 Validation

Initially in the program, Level 1 validation will be primarily used to identify potential problems for further investigation. As experience is gained with applying these checks, further use of the results may be possible, and/or further Level 1 checks may be developed that are more effective in pinpointing analytical problems. The s validation checks will feed in to the final data review that is applied before the monthly data reports are issued. Level 1 results and observations will also be used to prompt corrective actions at a system level. The following sections describe the initial set of Level 1 validation checks that will be used. Additional Level 1 checks will be developed based on experience with the data and suggestions from monitoring agencies, EPA, and data users.

4.2 Mass Balance Level 1 Check

The mass balance check assumes that the sum of the weights of the chemical species should approximate the gravimetric result for an exposure:

$$C_m \overset{?}{=} \sum_{i}^{\text{all species analyzed}} C_i - \sum_{j}^{\text{duplicates}} C_j \times K_j$$

where, C_m = the mass concentration determined by mass/volume
C_i = concentrations of individual chemical analytes
C_j = concentrations of duplicated species (e.g., elemental sulfur and sulfate sulfur)
K_j = a factor to correct for elements measured by two or more analyses (e.g., sulfur in sulfate ion).

Assumptions and potential problems include the following:

- The analytical measurements do not include all the elements, compounds, and ions that may contribute to the total mass.
- All carbon species, including elemental carbon, are measured as methane without regard to other elements (oxygen, nitrogen, etc.) that may be present in the organic molecules on the filter but not measured by any analysis.
- Hydration state of the particulate matter is not taken into account. Water of hydration adds to the total gravimetric mass, but does not affect the chemical analyses; the relative proportion of water can vary from sample to sample.
- Corrections for duplicated elements are only approximations because the elemental sulfur concentration may not correspond precisely with sulfur calculated from sulfate concentration.

Initial acceptance limits for the mass balance check will be defined as percentiles of the distribution of observed values of the difference between gravimetric mass and C_m defined above. Both absolute and relative concentration differences will be investigated initially as

validation metrics. Approximately 1% of the samples with the highest difference (or relative difference) and 1% with the lowest difference will be examined initially. Other screening criteria will be developed as historical data are gathered for this program.

4.3 Ion Ratios

The relative proportions of total positive and negative charges for anions and cations determined by Ion Chromatography will be examined. Total charges will be calculated as follows:

$$Z^{+} = \sum_{i}^{all\ cations} C_i \times z_i \,/\, fw_i \qquad Z^{-} = \sum_{i}^{all\ anions} C_i \times z_i \,/\, fw_i$$

where, Z^+ and Z^- are the total cation and anion charges expressed as concentration in air

C_i = concentration of the i^{th} ion in air (as mass/volume)

z_i = charge on the ith ion

fw_i = formula weight of the i^{th} ion.

Assumptions and potential problems include the following:

- The analytical measurements for this program do not include all anionic or cationic species that might be present in any particular sample
- Species concentrations may vary geographically or by season.

Previous studies such as IMPROVE did not include exactly the same set of ions; consequently, it will be necessary to develop acceptance criteria based on historical data for the current program. Initial screening for further investigation will focus on the extreme values of the actual population. Approximately 1% of the samples with the highest ratios and 1% with the lowest ratios will be examined initially. Other screening criteria will be developed as historical data are gathered for this program.

4.4 Final Data Review

Before the data are finalized for reporting each month, they are reviewed by a senior scientist to look for anomalies and inconsistencies that may not have been captured by routine screening. Microsoft Access will be used to facilitate viewing the data for the following:

- Internal consistency between data, flags, dates, site assignments, etc.
- Visual review of all data marked "invalid"
- Evaluation of data set completeness
- Investigation of anomalous samples, including those identified by Level 1 screening.

5.0 Validation Applied by the Monitoring Agencies

The data reviews performed by the monitoring agencies have two major purposes:

1. To review and assess the data and the validation flags that have been applied by RTI. If the monitoring agency disagrees with any validation criteria or data values, the specific changes are passed back to RTI to be corrected before the data are uploaded to AIRS.

2. To apply additional validation criteria based on knowledge of the site conditions, calibration results, audit reports, etc. Higher Levels of data validation can also be performed by the agencies. Results of additional validation screening are passed back to RTI using the same review form.

The monthly data reports that go to the monitoring agencies and the DOPOs include data that have been analyzed, entered, and validated, together with the validation flags and codes for each item. Data that have previously been reported to the monitoring agencies are not resubmitted unless reprocessing and reapproval is required for some reason. A monitoring agency receives only the data for sites operated by that agency. DOPOs receive the reports for only the monitoring agencies assigned to them. Data reports are organized by exposure sample, flow channel, analysis, and individual analyte. Accompanying each data report is a spreadsheet that reports all measurement values and the associated validation flags.

The validation flags shown in the monthly data reports fall into three general categories:

- Flags that will result in a Null Value Code in AIRS (i.e., data that are completely invalid; the null value code overwrites the numerical value)
- Flags that will result in a Validity Status Code in AIRS (i.e., data that might be considered 'questionable'; Validity Status Codes do not overwrite the numerical value)
- Certain informational flags not reported to AIRS, but which might be used to prompt further investigation by the states (e.g., Level 1 flags showing an unusual mass balance or cation/anion ratio at a particular site might prompt the agency to investigate sample handling procedures).

Typical questions that the agency might ask during its review of the monthly data report include the following:

- Do the agency's operating records confirm the site, date, and explanation when exposure sessions are flagged as invalid?
- Do other invalidated or flagged data appear reasonable based on operations records?
- Are there other QA/QC data available that could affect the validity status of any data? For example:
- Calibration factors obtained during regular field checks or periodic audits that could be applied to bring measurements into compliance (e.g., flow rate)

- Calibration or audit results that might invalidate exposures performed at a particular site over a certain period of time
- Operator's notes containing information relevant to data questioned by RTI, including Level 1 screening results.

All corrections, changes, and questions should be entered using a Correction Form that accompanies each monthly data report, a copy of which is shown in Appendix A. The monitoring agency can use the Correction Form to indicate changes to validation codes by individual analyte, by analysis, or for an entire exposure session. Comments should be included to document why codes have been changed; however, these comments do not go to AIRS.

The final step in preparing the validated and corrected data set to AIRS is mapping all of the validation flags generated by many different processes onto the limited set of flags that AIRS will accept. The logic of this mapping process is described in Appendix D.

Appendix A
Data Review and Change Submission Form

This Appendix contains the following:

- Instructions
- Tables of AIRS flags to be used
- Blank Form
- Example of Properly Completed Form

A.1 Instructions for Completing the Review and Change Form

These instructions describe the columns on the Data Review and Change Submission Form used to transmit changes in validation flags from monitoring agencies to RTI prior to submission of data to AIRS. Please examine the attached sheet for several typical examples. Brief instructions on filling out each section of the Change Submission Form are given below:

Header - Please fill out the material in the header completely. It is very important to know the date of the original report. Pages after the first should be numbered sequentially.

Chain of Custody ID Number - This is the number that uniquely identifies the set of filters exposed at a particular site, on a particular date. This number is critically important for identifying the correct data. If you believe that this number is incorrect in the data report, please contact RTI at once.

Analysis - This is the name of one or more analyses that are to be changed. Possibilities are as follows:

- IC
- OC/EC (includes total and carbonate carbon)
- Mass
- Elements (by XRF)
- If all analyses for the exposure session are equally affected by the change, write "all."

Analytes -- This is the name of one or more analytes to be changed. If all the analytes for an analysis receive the same change, write "all." If only cations are affected for an IC analysis, write "cations only." For nitrate, specify which type of nitrate (particulate, volatile, etc.); otherwise, all nitrate analyses will be flagged the same way.

Data Flag(s) -- This is divided into two columns, Delete and Add. Under Delete, list the flags that are to be deleted or over-written by a flag to be added. Under Add, list the flag that is to be inserted. All added flags must be valid AIRS Null Value Codes or Validity Status Codes. The table of all AIRS codes that are defined for PM2.5 chemical speciation is shown below.

Comment -- The comment is not reported to AIRS; however, it is important to explain the reason for a change in case RTI QA and data entry personnel have any questions. Having the comments on file will also facilitate answering questions from EPA and other data users.

AIRS NULL VALUE CODES

AA	9967	SAMPLE PRESSURE OUT OF LIMITS
AB	9968	TECHNICIAN UNAVAILABLE
AC	9969	CONSTRUCTION/REPAIRS IN AREA
AD	9970	SHELTER STORM DAMAGE
AE	9971	SHELTER TEMPERATURE OUTSIDE LIMITS
AF	9972	SCHEDULED BUT NOT COLLECTED
AG	9943	SAMPLE TIME OUT OF LIMITS
AH	9974	SAMPLE FLOW RATE OUT OF LIMITS
AI	9975	INSUFFICIENT DATA (CAN'T CALCULATE)
AJ	9976	FILTER DAMAGE
AK	9977	FILTER LEAK
AL	9978	VOIDED BY OPERATOR
AM	9979	MISCELLANEOUS VOID
AN	9980	MACHINE MALFUNCTION
AO	9981	BAD WEATHER
AP	9982	VANDALISM
AQ	9983	COLLECTION ERROR
AR	9984	LAB ERROR
AS	9985	POOR QUALITY ASSURANCE RESULTS
AT	9986	CALIBRATION
AU	9987	MONITORING WAIVED
AV	9988	POWER FAILURE (POWR)
AW	9989	WILDLIFE DAMAGE
BA	9990	MAINTENANCE/ROUTINE REPAIRS
BB	9994	UNABLE TO REACH SITE
BC	9995	MULTI-POINT CALIBRATION
BD	9996	AUTO CALIBRATION
BE	9997	BUILDING/SITE REPAIR
BG	9966	MISSING OZONE DATA
BI	9964	LOST OR DAMAGED IN TRANSIT

AIRS VALIDATION STATUS CODES

A	HIGH WINDS
C	VOLCANIC ERUPTIONS
D	SANDBLASTING
E	FOREST FIRE
F	STRUCTURAL FIRE
G	HIGH POLLEN COUNT
H	CHEMICAL SPILLS & INDUST. ACCIDENTS
I	UNUSUAL TRAFFIC CONGESTION
J	CONSTRUCTION/DEMOLITION
K	AGRICULTURAL TILLING
L	HIGHWAY CONSTRUCTION
M	REROUTING OF TRAFFIC
N	SANDING/SALTING OF STREETS
O	INFREQUENT LARGE GATHERINGS
P	ROOFING OPERATIONS
Q	PRESCRIBED BURNING
R	CLEAN UP AFTER A MAJOR DISASTER
S	SEISMIC ACTIVITY
T	MULTIPLE FLAGS; MISC.
W	FLOW RATE AVERAGE OUT OF SPEC.
X	FILTER TEMPERATURE DIFFERENCE OUT OF SPEC.
Y	ELAPSED SAMPLE TIME OUT OF SPEC.

Chemical Speciation Trends Network
Data Review and Change Submission Form

Page _____ of _____

Monitoring Agency Name _____ Date of Original Report_____

Reviewed by _____ Review Completed, Date_____

Instructions: *Please indicate changes to be made before the data are submitted to AIRS. Only valid AIRS Null Value or Status Codes can be accepted. Alternative formats such as spreadsheet files may also be acceptable. Return this form to RTI through the DOPO.*

Chain of Custody ID Number	**Analysis**	**Analyte(s)**	**Data Codes(s)**		**Comment (optional)**
			Delete	**Add (see table)**	

Chemical Speciation Trends Network
Data Review and Change Submission Form

Page _____ of _____

Monitoring Agency Name _____ Date of Original Report_____

Reviewed by _____ Review Completed, Date_____

Instructions: *Please indicate changes to be made before the data are submitted to AIRS. Only valid AIRS Null Value or Status Codes can be accepted. Alternative formats such as spreadsheet files are acceptable. Return this form to RTI through the DOPO.*

COC ID	Analysis	Analyte(s)	Data Codes(s)		Comment (optional)
			Delete	Add (see table)	
Q1234V	elements (XRF), mass	all		AH	Channel 1 flow rate sensor was seriously out of calibration during internal audit on 3/15/2000. All data for channel retroactively invalidated.
Q3245R	all analyses, all filters	all		K	Operator noted agricultural tilling in the area, which may explain high loadings on all filters for this sample exposure.
Q5432M	all analyses, all filters	all		AQ	Internal Systems Audit found the site operator to be using improper filter handling procedures. All samples handled by this operator are invalidated.
Q9993A	XRF, mass	all elements, mass		AM	The reported masses indicate that this filter module may have been interchanged with a trip blank that was used at the same time (Q1877Y).
Q4988J	all	all	AI	--	Volume data omitted from the original COC form has been supplied to RTI. Recalculate PM concentrations and remove AI null value code.
Q1112U	all	all	AM	change to T	Shipment was received by the lab at 8ºC and all data was marked Invalid (AH). EPA has granted a waiver to change this to status code T. (multiple/misc.) flags).
Q2233M	XRF	all elements		AM	Elemental XRF results failed Level 2 outlier tests at p<0.001 when compared with other samples taken at this site.
Q1004H	IC	nitrate		T	Nitrate data failed Level 2 outlier tests at p<0.01. Other analytes appear to be OK. The lab should review the nitrate data.
Q4657P	IC	anions, cations, nitrate		T	Site audit found that this Channel was being used without the required MgO denuder.
Q5555T	OC/EC	all carbon species		E	All carbon species were outliers at p<0.01 in Level 2 validation. There was a forest fire approximately 30 miles upwind.

Appendix B
Field Sampling Data Validation Criteria

B.1 Criteria Applying to Individual Sampling Exposures

Criteria	Acceptable Range	Frequency	AIRS Code
Sample Recovery Time	96 hours from sample end date until retrieval and storage at < 4° C	all filters	AQ
Sampling Period (including multiple power failures)	1380-1500 minutes	all filters	AG
Filter Temp Sensor	no excursions of > 5°C lasting longer than 30 min (3° C for MetOne SASS)	each 24 hour exposure	X
Average Flow Rate	indicated average within ±10% of nominal flow rate	each 24 hour exposure	AH
Variability in Flow Rate	average 24-hour CV* ≤ 2% (this value may not be provided by all samplers)	each 24 hour exposure	W
Individual Flow Rates	no flow rate excursions > ±5% for > 5 min. (this flag may not be provided by all samplers)	each 24 hour exposure	W

*CV= coefficient of variation = 100 x standard deviation/average of the 5-minute averages

B.2 Criteria based on Periodic Calibration, Verification, and Audit Results

Assessing data quality based on these criteria is the responsibility of the monitoring agency, not the laboratory. Audits, calibrations, and other periodic checks are typically not done in association with a particular exposure session and may affect the validity of multiple exposures. The flags in the last column are suggested for use when samples need to be flagged retroactively due to problems detected during calibrations and audits. The Chain of Custody numbers of samples to be flagged should be sent to RTI using the Data Review form or in another acceptable format. The criteria and acceptance ranges provided in the most recent version of the Chemical Speciation QAPP supercede those provided in this table.

Criteria	Acceptance Range*	Frequency*	AIRS Code
Calibration/Verification			
Internal External Leak Checks	< 80 mL/min (or equivalent pressure change)	every 5 sampling events	T or AK
One-point Temp Check	± 4°C of standard	1/4 weeks	T or AS
Temp Multi-point Verification	± 2°C of standard	on installation, then 1/yr	T or AS
Pressure Calibration	± 10 mm Hg	on installation, then 1/yr	T or AS
Pressure Verification	± 10 mm Hg	1/4 weeks	T or AS

Criteria	Acceptance Range*	Frequency*	AIRS Code
Other Monitor Calibrations	per manufacturers' operating manual	--	T or AS
One-point Flow Rate Check	± 4% of transfer standard	1/4 weeks	T or AS
Flow Rate Multi-point Verification	± 2% of transfer standard	1/yr	T or AS
Accuracy Audits			
Temperature Audit	± 2°C	4/yr	T or AS
Pressure Audit	±10 mm Hg	4/yr	T or AS
Flow Rate Audit	± 4% of audit standard	1/2wk	T or AS

*Based on criteria for the national PM2.5 FRM program.

B.3 Flags Applied by the PM2.5 Chemical Speciation Samplers

Sampler flags are displayed on the LCD readout screen and copied onto the COC form by the site operator. These flags apply either to the entire exposure (e.g., sample time out of limits), or to an individual flow channel (e.g., average flow rate out of limits).

URG Corporation - MASS Model 400 and 450

The URG MASS chemical speciation samplers (Models 400 and 450) are very similar to the Federal Reference Method gravimetric samplers currently used in the national PM2.5 network, and inherit their flags from the FRM program. The URG MASS 400 and 450 sampler-generated flags are as follows:

Flag	Description	Applies to
Tm	Sample Time Out of Limits - Set if the total sampling time for the test is less than 23 hours or greater than 25 hours.	Sample Event
PF	Power Fail - Set if a power failure lasting 1 minute or longer occurs.	Sample Event
FIV	Flow Variation Out of Limits - Set if the absolute value of flow rate minus the average flow rate exceeds 5% of the average flow rate for 5 minutes or longer.	- not used -*
FTp	Filter Temperature Difference Out of Limits - Set if the filter temperature exceeds 5 degrees above the ambient temperature for a period of at least 30 minutes.	Sample Event
ITP	The Inactive Temperature Out of Limits - Set if the inactive temperature exceeds 5 degrees above the ambient temperature for a period of at least 30 minutes.	Sample Event
Flo	Flow Out of Range - Set if the flow rate varies by more than 10% of the setpoint for at least 60 seconds.	- not used -*

Graesby-Andersen Corporation - RAAS

The set of flags produced by the RAAS samplers is not completely described in the most recent available Users Manual. RTI is prepared to process flags that correspond to the FRM flags shown in the table above.

MetOne Corporation - SASS

The only flag available on the readout screen of the SASS sampler is the filter delta-temperature flag. This is set when the 5-minute filter temperature average differs by 3°C or more from the ambient temperature average for the corresponding time period. MetOne decided to use the tighter 3 degree specification rather than 5 degrees used in the FRM program because the SASS is a fundamentally different design which produces much less temperature variation.

Flag	Description	Applies to
FTp	Filter Temperature Difference - Set if the filter temperature exceeds 3 degrees above the ambient	Flow Channel

Appendix C
Laboratory Validation Flagging

C.1 OC/EC Laboratory Validation Criteria

Internal Flag	Description	Criteria or Limits	Comments
LFP LFL LFS LFD LFT LFU LFO	Filter inspection flags*	• P - Pinholes • L - Loose Material • S - Separation of reinforcing ring • D - Discoloration • T - Tear • U - Non-uniformity • O - Other (wrinkling, warping, etc.)	Separation of reinforcing ring may not be considered serious for OC/EC analysis.
LCA	Analyzer Calibration out of limits	$R^2 > 0.98$; 3-sigma control chart criteria for mean and standard deviation	Do not analyze until instrument problem is corrected
LBL	Daily Blank	< 1 ugC/cm^2	Do not analyze until problem is corrected.
LST	Daily Calibration Check Standard	within 10% of calibrated value	Do not analyze until problem is corrected.
LLP	Calibration loop response (area counts)	within 10% of calibrated value	Troubleshoot and reanalyze; should seldom generate a flag.
LDU	Filter Duplicates (reanalysis of a field sample)	within $\pm$10% *	*Duplicate data is not normally used as a validation criterion. Analyst should investigate and decide what data to flag or invalidate.

C.2 Ion Chromatography Laboratory Validation

Flag	Description	Criteria or Limits	Comments
LFP LFL LFS LFD LFT LFU LFO	Filter inspection	• P - Pinholes • L - Loose Material • S - Separation of reinforcing ring • D - Discoloration • T - Tear • U - Non-uniformity • O - Other (wrinkling, warping, etc.)	*See SOP for list of filter defects and codes
LCA	Calibration out of limits	statistical control limits	Analyst should attempt to reanalyze all aliquots affected by unacceptable QC results
LBL	Blanks out of limits	blank < MDL	
LST	Standards out of limits	recovery >90% and <110%	
LDU	Duplicates out of limits	< 15 µg difference	

C.3 Gravimetric Analysis Laboratory Validation

Flag	Description	Criteria	Comments
LCA	mass reference standard out of limits	Verified value ± 3 µg	Weigh at least one working standard every 10th filter.
LBL	Lab (filter) blank out of limits	Initial weight ± 15 µg	Weigh at least one lab blank every session.
LBF	Field (filter) blank out of limits	Initial weight ± 30 µg	Field blanks are not identified as such to the analyst. Field blank data are evaluated during data review.
LBD	Duplicate out of limits	Initial weight ± 15 µg	Reweigh every 10th filter.

Appendix D
Mapping of Validation Criteria onto AIRS Codes

Because very few AIRS flags are defined relative to the number of official and unofficial criteria that are applied to the data during data processing, it is necessary to "map" the various internal flags onto a final set of AIRS codes. This Appendix shows how this mapping is done.

Since only one final code is allowed in AIRS, a Priority Order for flagging is also provided. The flag related to the most serious condition is used, unless there are multiple flags at the same level, in which case the AIRS code for multiple or miscellaneous is used. This Appendix is divided into several sections to reflect the seriousness of the flagging conditions.

D.1 INVALID - Not Exposed

These flags result when a filter, module, or shipment is returned unexposed. No exposure information or analytical data is generated; however, records for individual analytes, each marked with a Null Value Code, will be uploaded to AIRS.

Field Operator Flags:

- AM - multiple or miscellaneous voids
- AB, AF, AL, AN, AO, AP, AQ, AU, AV, BA, BB, BE, BI - not exposed or not analyzed.

Sampler Flags:

- None - sampler was not run; therefore, there are no flags to report.

Internal Flags:

Internal Flag	Description	AIRS Code
DFM	Filter missing	AM
DSI	Shipment invalid	AM
DCI	Channel invalid	AM
DMC	Module condition invalid (not exposed)	AM
FIC	Exposure session canceled or modules returned unexposed	AF
FSL	Field Sample Lost in Transit	BI

AIRS Flag Priority:

- AM (multiple flags) > single Null Value Codes in alphabetical order.

D.2 INVALID - Filters Exposed and Returned

The second category of invalidation is when filters are exposed and returned, but there are serious problems with a filter, module, or flow channel that require Null Value Codes to be reported to AIRS.

Flags Assigned by Field Operator:

- AM - multiple or miscellaneous voids
- AC, AG, AH, AI, AJ, AK, AR, AS, AW
- W, X, Y, may be reassigned as AF, AM, AG if the data are to be invalidated.

Sampler Flags:

Flag	Description	AIRS Code
Tm	Sample Time: samp. time <23 hours or >25 hours	AG

Internal Flags:

Flag	Description	AIRS Code
DEC	Module end cap missing (filter contaminated)	AM
DFM	Filter missing	AM
FDT	Field delta temperature out of limits	AN
FEX	Exposure duration outside limits	AM
FFL	Filter Leak	AK
FHT	Pickup holding time exceeded	AM
FVL	Total volume sampled out of limits	AM
LBD	Laboratory blank duplicate outside limits	AR*
LBF	Field blank reweighing outside specs	AR*
LBL	Laboratory blank values outside limits	AR*
LCA	Laboratory calibration outside limits	AR*
LDU	Lab duplicate outside limits	AR*
LEQ	Lab environmental criteria outside limits	AR*
LLI	Analysis invalid - Other	AM
LLM	Laboratory maintenance outside limits	AR*
LLP	Calibration loop response (area counts)	AR*
LST	Daily calibration check standard outside limits	AR*
QLI	Outlier invalidated by QAO based on Level 1 check	AM

*Filters should not be weighed or analyzed until the condition is rectified.

AIRS Flag Priority:

- AM (multiple flags) > null value codes in alphabetical order

D.3 Range Checks

The following simple range criteria are applied using automated queries after the data have been entered into the data base. The corresponding AIRS Null Value Codes are given in the last column. The criteria and acceptance ranges provided in the most recent version of the Chemical Speciation QAPP supercede those provided in this table.

Check Type	Nominal Value	Upper Limit	Lower Limit	AIRS Code
Avg. Flow Rate, LPM (acceptance limits ±10% of nominal flow)				
Andersen				
• Ch 1	16.7	18.33	15.00	AH
• Ch 2	7.3	8.03	6.57	AH
• Ch 5	7.3	8.03	6.57	AH
• Ch 4+5	24.0	26.4	21.6	AH (both)
MetOne				
• Ch1, 2, 3 (and 4, if used)	6.7	7.37	6.03	AH
URG				
• Ch 1 (400)	16.7	18.33	15.00	AH
• Ch 2 (450)	16.7	18.33	15.00	AH
Filter Delta-T, degrees C (filter minus ambient)				
Andersen	--	--	--	--
URG	--	±5ºC	±5ºC	AN
MetOne	--	±3ºC	±3ºC	AN
Flow CV, percent				
All models (if provided)	--	2%	--	AN
Sampling Time (hours):				
All models	24	25	23	AG
Holding Time before filters are picked up and placed in storage at <4ºC (hours):				
All models	--	96	--	AM
Holding Time between pre-weighing and start of sampling (days):				
All weighed filters	--	30	--	AM
Holding Time between return to RTI and final weighing or analysis (days):				
All filters	--	30 (stored <4ºC) 10 (stored >4ºC)	--	AM

AIRS Flag Priority:

- AM (multiple flags) > null value codes in alphabetical order

D.4 AIRS Validation Status Codes (Questionable Results)

The validation criteria described in this section result in AIRS Validation Status Codes, which do not overwrite the numerical data in the AIRS records; data values are transmitted to AIRS along with the single-digit code shown.

Field Operator Flags:

All of the operator-assigned codes are already defined in AIRS and do not have to be changed. The T, W, X, and Y flags will be most common; all of the following flags are defined in Appendix A:

- T - multiple or miscellaneous status flags
- W, X, Y
- A, B, C, D, E, F, G, H, I, J, K, L, M, N, O, P, Q, R, S.

Sampler Flags:

Sampler Flag	Description	AIRS Code
FIV	Flow Variation Flag: flow error > 5% for >5 minutes	W
FTp	Filter Temperature Diff: dT > 5ºC for > 30 minutes	X

Internal Flags:

Internal Flag	Description	AIRS Code
LFD, LFL, LFO, LFP, LFS, LFT, LFU	Filter inspection flags	T

AIRS Flag Priority:

- T (multiple) > W, X > Other AIRS status codes

D.5 Informational Flags; Not Flagged in AIRS

The flags in this section are retained in the RTI data base for informational purposes. They are usually not translated directly into AIRS codes.

Sampler Flags:

Flag	Description	Comment
PF	Power Fail: set if power fail duration > 1 minute	check operator's notes and sampling duration

Internal Flags:

Internal Flag	Description	Comment
APB	Analysis partially billable	data processing information; not used for validation
FC2, FC4, FC6, etc.	Actual channel number used for sampling (when sampled on a different channel than scheduled)	data processing information; not used for validation (however, accurate attribution of channel information is subject to internal verification by RTI)
LFW	Upside-down filter	to be investigated further; the effect on analytical validity is currently unknown
LPW	Pre-exposure filter weight outside specs	very rare; filter should not have been used
QAC	Cation/anion total charge ratio outside limits	Level 1 QA investigation
QCR	Between-analyte correlations outside limits	Level 1 QA investigation
QMB	Total mass balance outside limits	Level 1 QA investigation
FCE	Information on Chain of Custody form corrected by RTI	Includes minor corrections such as columns interchanged, and average flow computed from volume/time
SNB	Sample not billable	(self-explanatory)

Priority:

Not Applicable.

D.6 AIRS Codes Not Used for PM2.5 Chemical Speciation Data Reporting

The flags in this section are defined in AIRS or by one or more of the Chemical Speciation samplers, but are not considered applicable to PM2.5 Chemical Speciation monitoring.

AIRS Null Value Codes Assigned but Not Used:

AIRS Code	Description	Comment
AT	Calibration	Continuous monitor flag
AA	Sample Pressure out of Limits	Continuous monitor flag
BF	Precision/zero/span	Continuous monitor flag
BD	Auto Calibration	Continuous monitor flag
BC	Multi-point Calibration	Continuous monitor flag
AY	Q C Control Points (Zero/span)	Continuous monitor flag
AZ	Q C Audit	Continuous monitor flag
AX	Precision Check	Continuous monitor flag

Sampler Flags Not Used:

Flag	Description	Comment
ITp	Inactive Temperature Difference - not used	FRM flag
Flo	Flow Rate: set if FR > 10% out of spec. for > 1 minute	FRM flag

Priority:

Not Applicable

Appendix E
Examples of Data Validation and Quality Assessment for the Chemical Speciation Trends Network

From: J. B. Flanagan, J.A. Deal, E. E. Rickman, Jr., J.A. O'Rourke. 2003. *Data Validation and Quality Assessment for the Chemical Speciation Trends Network.* Presented at the American Association for Aerosol Research Particulate Matter: Atmospheric Sciences, Exposure and Fourth Colloquium on PM and Human Health, Pittsburgh, PA.

Abstract

The PM2.5 Chemical Speciation program has very tight data turnaround requirements -- fully-validated data are currently being uploaded to AQS in an average of <120 days after sampling for approximately 59 analytical values that are reported for each sampling event.

Data for approximately 225 field monitoring sites (approximately 1800 separate monitoring events per month) are validated and reported at monthly intervals to the state and local air monitoring agencies which operate the samplers. An efficient system for data validation has contributed to RTI's ability to meet EPA's stringent requirements.

This presentation will provide an overview of the steps used to validate the data for the PM2.5 Chemical Speciation program and the different kinds of data comparisons that are used to identify questionable data. Some of the routine validation steps include checks of exposure dates and range checks on various parameters; and verification of mass balance, anion/cation charge balance, and sulfur/sulfate balance.

The high degree of integration with the laboratory database has enabled many data entry, validation, and reporting functions to be automated, and also allows human data reviewers to assess overall trends easily. Monthly validation procedures sometimes help to identify problems with individual samplers in the field (such as a leaking flow channel), which can then be brought to the attention of the agency that operates the field site.

Introduction

Research Triangle Institute (RTI) is the prime contractor for the PM2.5 Chemical Speciation Program sponsored by EPA/ OAQPS. RTI has overall responsibility for scheduling, shipping, analysis, data validation, quality assurance, and data reporting, including the following activities:

- Preparing sampling media
- Scheduling and coordinating shipments of sampling media
- Maintaining chain of custody for all shipments, filters,
- and laboratory aliquots

- Conducting laboratory analyses, with associated laboratory QC and data validation
- Validating field and laboratory data for the monthly reports using the data base and hard copy information:
  - Level 0 data validation
  - Level 1 data validation
- Reporting the data monthly to state and local monitoring agencies to complete the validation of the data
- Reporting the validated data sets to AIRS
- Corrective Actions

Speciation Analyses

The following are the routine analyses that are performed for speciation events:

- Total PM2.5 Mass by gravimetry
- Elemental, Organic, and Total Carbon by Thermal Desorption / FID
- Anions and Cations by Ion Chromatography
- Elemental Analysis by X-Ray Fluorescence (48 elements)

Laboratory QA/QC Activities Related to Data Validation

Verification of Sampling Media. All filter media are checked prior to use, as appropriate for the filter material:

- Quartz filters from the manufacturer are fired and checked for residual carbon
- Teflon filters equilibrated, weighed, and checked for weight stability
- Nylon filters are individually washed; new filter lots are checked for contamination prior to use

Data flagging and corrective actions based on laboratory QC results are the responsibility of the individual laboratories. Flags are passed to the data base along with analytical results. Laboratory QC operations consist of the following general categories for most analyses:

- Spikes, blanks, duplicates
- Multi-point calibrations
- Analysis of standard materials
- Periodic detection limit determinations

When sampler problems are suspected based on validation results, RTI informs the EPA Delivery Order Project Officer so that the monitoring agency can be informed.

Level 0 Data Validation

Level 0 validation checks are objective tests that include all laboratory checks as well as basic screening of the data base prior to each monthly data delivery. These include the following:

Internal consistency checks:

- Correct number and type of samples by date and site
- Verification of scheduled vs. actual exposure information
- Outlier tests based on prescribed acceptance ranges:
  - flow rate by sampler type and channel
  - elapsed sample time
  - holding time(s)
  - temperatures: exposure and shipping
  - routine (exposed) sample mass should be greater than a lower limit of 3.0 micrograms per cubic meter

Data records identified by Level 0 data validation are treated in one of three ways:

- Investigate the source of the problem, and correct the data
- Flag the data as suspicious using an appropriate AIRS validity status code when the underlying problem cannot be identified.
- Invalidate the data when the data are clearly wrong, and cannot be corrected

Level 1 Data Validation

Level 1 checks are statistical procedures that have been devised to help identify sampling events that may have undiagnosed problems of various types such as:

- Filter misidentification, or filters that have been "swapped" between different events, or between a Routine and a Blank sample.
- Laboratory analytical problems
- Problems at the site, such as a defective flow channel

Three main Level 1 checks are done for the Chemical Speciation program:

- Reconstructed Mass Balance - the sum of concentrations for all chemical analytes is compared against the concentration from the gravimetric mass
- Anion - Cation Balance - the total concentration (on a mole basis) of anions and cations from ion chromatography are compared to each other
- Sulfur - Sulfate Balance - Sulfur measured using XRF is compared against Sulfate measured using ion chromatography.

Limits for identifying outliers were established early in the STN program as the lower 2% and the upper 98% of the distribution of the values at that time. The numerical values of the control limits for these checks are given in the sections below. An AQS validity status flag of '5' - outlier cause unknown is applied whenever a Level 1 validation limit is exceeded.

Reconstructed Mass

Reconstructed mass is simply the summation of the concentration of all the chemical analytes divided by the gravimetric mass. Duplicated analytes such as sodium, potassium, and sulfur/sulfate are deducted from the analyte summation, and volume variations are taken into account for samplers that use different flow rates on different samples. Limits used for identifying reconstructed mass outliers are as follows:

Lower Limit: [Sum of Analytes]/[Grav. Mass] < 0.60

Upper Limit: [Sum of Analytes]/[Grav. Mass] > 1.32

Comparing the reconstructed mass, which includes all chemical analytes, vs. the gravimetric mass is helpful to identify samples for which filters may have been switched. Since most samplers use three different filters (nylon, Teflon, and quartz) for the various analyses, any outliers can sometimes indicate assignment problems such as filters that have been switched between events. Note, that concentration is used instead of filter mass because the flow rates for all filters are not the same in some analyzers.

Due to the lower level of filter loading, reconstructed mass balance has been found less useful for very clean non-urban sites such as national parks, and RTI will remove flags at the request of the monitoring agencies in such cases. However, the test is helpful for the "core" urban sites and other sites with appreciable filter loadings.

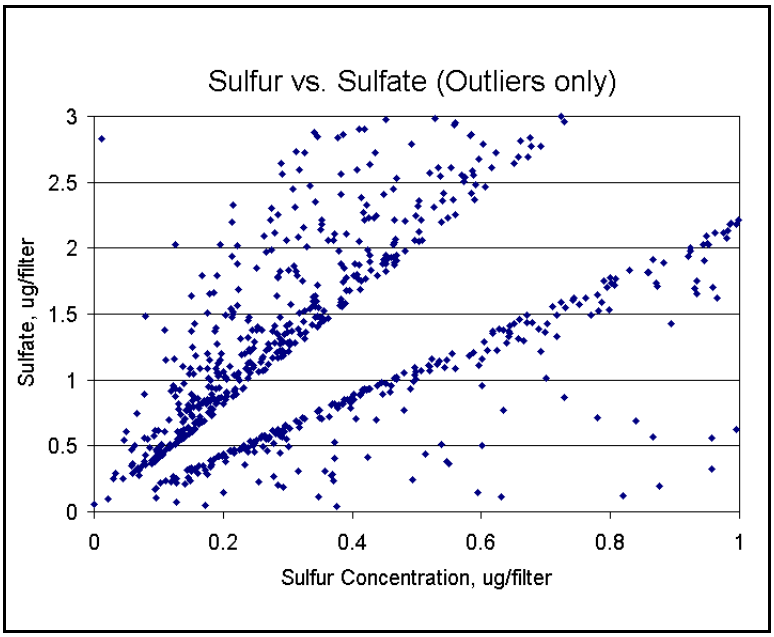
Anion - Cation Balance

The theoretical value of the anion/cation balance, expressed as equivalent charges, is 1.00. The limits used for identifying outliers were determined early in the program from sites in the "minitrends" program, and are as follows:

Lower Limit: [Sum of Anions]/[Sum of Cations] < 0.86

Upper Limit: [Sum of Anions]/[Sum of Cations] > 2.82

Anions and cations are captured on the same filter (nylon and/or Teflon) for the most common sampler type. Consequently, the Anion-Cation balance is generally less useful for diagnosing specific problems between filter channels compared with other Level 1 validation tests such as sulfur/sulfate ratio. Furthermore, "missing" anions or cations that are not included



in the standard set of STN ion analyses can upset the balance -- for example, excess chlorine may be present at sites near the ocean due to salt spray. As with the reconstructed mass balance, this test is less effective at low-level sites such as national parks.

Sulfur - Sulfate Ratio

The theoretical ratio of Sulfur/Sulfate is 0.33, based on their molecular weights of 32 and 96, respectively. Limits for outliers are as follows:

Lower Limit: [S]/[SO4] < 0.25

Upper Limit: [S]/[SO4] > 0.45

Sulfur is determined by XRF and Sulfate is analyzed by Ion Chromatography. In most cases, they are collected on different filters - sulfur on Teflon and sulfate on nylon. Thus, this ratio is often very useful for diagnosing flow rate problems in either one of the sampler's channels. Leaks are most often the cause of such problems, and RTI will notify a site of a potential problem when repeated outliers are observed for the same site.

The graph below shows a typical set of outliers from the sulfur/sulfate ratio test. Note that the upper and lower outliers are roughly similar in number, indicating that the limits are symmetrical. Approximately 4-5% of the total values are flagged in each monthly report.

Conclusion

The data validation program for the PM 2.5 Chemical Speciation Program has been effective in preventing identifying atypical and erroneous data through a comprehensive program that includes:

- Ensuring accurate input of data
- Validation of data in the analytical laboratories using QC information to identify problems
- Level 0 validation checks that include laboratory QA/QC, and attribution and range checks for data in the data base
- A set of "Level 1" validation checks to identify values that are not typical of historical results, or which violate expected relationships
- Review by the state monitoring agencies both to verify and approve the data flagging that RTI has done, as well as to identify problems based on their own information
- Follow-up with monitoring agencies where possible systematic problems at the monitoring sites have been detected