Chapter 6

MCK131, KY

Data Quality

Data quality indicators (DQI) have been formulated to gauge achievement of CASTNet objectives. DQI are quantitative and qualitative descriptors used in interpreting the degree of acceptability and utility of the data collected. The DQI for CASTNet are precision, accuracy, completeness, bias, representativeness, and comparability. Precision, accuracy, and completeness for CASTNet 2002 data were analyzed as well as some historical data over the period 1990 through 2001. Results from independent audits for 2002, interlaboratory comparisons, and analysis of blank filters were also analyzed. These analyses demonstrate that CASTNet data can be used with confidence since CASTNet data are continually verified through the use of the DQI. In short, CASTNet has produced and continues to produce data of the highest quality.

Overview

The CASTNet QA program was designed to ensure that all reported data are of known and documented quality in order to meet CASTNet objectives and to be reproducible and comparable with data from other monitoring networks and laboratories. The QA program elements are documented in the CASTNet Quality Assurance Project Plan (QAPP) (Harding ESE, 2002c). The QAPP is comprehensive and includes standards and policies for all components of project operation from site selection through final data reporting.

As discussed in Chapter 1, the primary objectives for CASTNet are to (1) monitor the status and trends in regional air quality and atmospheric deposition; (2) provide information on the dry deposition component of total acid deposition, ground-level O_3, and other forms of atmospheric gaseous and aerosol pollution; and (3) assess and report on geographic patterns and long-term, temporal trends in ambient air pollution and acid deposition. The CASTNet data collection processes and QA efforts were designed to meet these objectives.

DQI have been formulated to gauge achievement of CASTNet objectives. DQI are quantitative and qualitative descriptors used in interpreting the degree of acceptability and utility of the data collected. The DQI for CASTNet are precision, accuracy, completeness, bias, representativeness, and comparability. In this chapter, the quantitative DQI precision, accuracy, and completeness are presented for CASTNet 2002 data. Some historical data over the period 1990 through 2001 are also presented. Three other topics are discussed in this chapter: independent audit results for 2002, results from interlaboratory comparisons, and analysis of blank filters. A more complete assessment of the CASTNet DQI and related QA information are provided in a companion document – CASTNet 2002 QA Report (MACTEC, in press).

CASTNet data can be used with confidence since CASTNet data are verified as high-quality through the use of DQI. Quantitative DQI are assessed by calculating statistical estimates of the precision, accuracy, and completeness of CASTNet measurements for both discrete and continuous data. Continual verification that the data obtained from both field and laboratory measurements meet specific criteria ensures that the data reliably present a true picture of the quantity of those pollutants in the air sampled and of the meteorological conditions used in the MLM. The historical statistics have demonstrated that the QA program is adequate and followed strictly. The results show that the selected DQI parameters are within control and that the long-term database satisfies CASTNet objectives.

Precision

Precision is defined as the closeness of agreement between independent test results obtained under prescribed similar conditions. The primary assessment of overall precision of CASTNet field measurements is obtained by calculating the difference between simultaneous measurements taken from separate, duplicate instruments at collocated sites. These measurements (i.e., filter concentration measurements and continuous field measurements) are compared using the same protocol. In addition, all laboratory measurements require an assessment of analytical precision via replicate analysis. This guarantees that the analytical methods provide reproducible results from sample to sample.

The collocated sampling program of CASTNet is accomplished by operating a duplicate set of monitoring equipment adjacent to a complete set of existing CASTNet sampling instruments. All instruments are installed in identical configurations. Sensors are located so as not to interfere with each other's operation or response (e.g., wind speed and direction sensors are separated so as not to create turbulent disturbances). Collocated sampling systems were operated at an eastern location in Kentucky (MCK131/231, KY) and at a western location in Colorado (ROM206/406, CO) during 2002. The systems in Kentucky are both operated by EPA. The site at Rocky

Mountain National Park, CO has two independent systems. EPA operates ROM206 while NPS operates ROM406. While two collocated sites cannot represent the network as a whole (with sites from the Virgin Islands to Alaska), 11 collocated sites have been operated over the history of the network. These 11 sites represent a wide variety of pollutant concentrations and land use/terrain settings.

Determination of the degree of precision of CASTNet measurements at collocated sites indicates the likelihood that data obtained from one CASTNet site can be confidently compared with data obtained from any other CASTNet site in any other location. The overall precision of meteorological variables, flow rate, and O_3 is assessed quarterly by calculating the difference between simultaneous measurements (i.e., hourly averages) taken by the duplicate, separate instruments at collocated sites. The overall precision of filter concentration and dry deposition data is assessed quarterly by calculating the absolute relative percent difference (ARPD) of values for simultaneous weekly samples at collocated sites and averaging these values to produce the MARPD. Tables 6-1 and 6-2 summarize criteria used to gauge precision and accuracy of CASTNet continuous and discrete measurements, respectively.

Analytical precision within sample batches is assessed by replicating five percent of the samples within a run and by calculating the relative percent difference (RPD). Samples to be replicated are selected at random.

Producing precise weekly pollutant concentrations from two collocated sampling systems challenges every element of the measurement system, e.g., field sampling, sample flow, flow controllers, data loggers, shipping, receiving, chain-of-custody, sample preparation, extraction, chemical analysis, QC, data processing, and data management. Indeed, consistently producing pollutant concentrations with a 5 to 10 percent precision indicates successful operation of every element of the filter pack monitoring process.

Mathematical formulas for calculating DQI criteria are provided and discussed in Appendix A of the 2002 companion document – 2002 CASTNet QA Report (MACTEC, in press).

Accuracy

Accuracy is defined as the closeness of agreement between a true or reference value and an associated measurement result. The difference between the two is expected to be within a prescribed precision interval for the measurement to be deemed accurate. Accuracy of the field measurements is determined by challenging instruments with standards that are traceable to the NIST. Continuing accuracy is verified through semiannual calibrations by MACTEC personnel and audits every other year by an independent auditor. Accuracy objectives for field measurements are listed in Table 6-1.

Table 6-1. Data Quality Indicators for CASTNet Field Measurements

Measurement		Criteria*	
Parameter	**Method**	**Precision**	**Accuracy**
Wind Speed	Anemometer	± 0.5 m/s	The greater of ± 0.5 m/s for winds < 5 m/s or ± 5% for winds ≥ 5 m/s
Wind Direction	Wind Vane	± 5°	± 5°
Sigma Theta	Wind Vane	Undefined	Undefined
Relative Humidity	Thin Film Capacitor	± 10% (of full scale)	± 5%, rel. hum. > 85% ± 20%, rel. hum. ≤ 85%
Solar Radiation	Pyranometer	± 10% (of reading taken at local noon)	± 10%
Precipitation	Tipping Bucket Rain Gauge	± 10% (of reading)	± 0.05 inch†
Ambient Temperature	Platinum RTD	± 1.0°C	± 0.5°C
Delta Temperature	Platinum RTD	± 0.5°C	± 0.5°C
Surface Wetness	Conductivity Bridge	Undefined	Undefined
O_3	UV Absorbance	± 10% (of reading)	± 10%
Filter Pack Flow	Mass Flow Controller	± 10%	± 5%

Note:

°C = degrees Celsius
m/s = meters per second
rel. hum. = relative humidity
RTD = resistance-temperature device
UV = ultraviolet

* Precision criteria apply to collocated instruments and accuracy criteria apply to calibration of instruments.
† For target value of 0.50 inch.

Table 6-2. Data Quality Indicators for CASTNet Laboratory Measurements

Analyte	Medium	Method	Precision (MARPD)*	Accuracy (%)	Nominal Detection Limits
Ammonium (NH_4^+)	F	Automated colorimetry	10	90 - 110	0.02 mg-N/L
Sodium (Na^+)	F	ICP-AES	10	90 - 110	0.005 mg/L
Potassium (K^+)	F	ICP-AES	10	90 - 110	0.005 mg/L
Magnesium (Mg^{2+})	F	ICP-AES	10	90 - 110	0.003 mg/L
Calcium (Ca^{2+})	F	ICP-AES	10	90 - 110	0.003 mg/L
Nitrate (NO_3^-)	F	Ion chromatography	5	95 - 105	0.008 mg-N/L
Sulfate (SO_4^{2-})	F	Ion chromatography	5	95 - 105	0.04 mg/L

Note:

F = filter pack samples
ICP-AES = inductively coupled plasma-atomic emission spectrometry
MARPD = mean absolute relative percent difference
N = nitrogen

* This column lists precision goals for both network precision calculated from collocated filter samples and laboratory precision based on replicate samples.

For more information on analytical methods and associated precision and accuracy criteria, see the CASTNet QAPP (Harding ESE, 2002c).

Accuracy of laboratory measurements is determined by analyzing an independently prepared reference sample in each batch and calculating the percent recovery relative to the target (theoretical) value. The percent recovery must meet the acceptance criteria listed in Table 6-2. Reference samples are traceable to NIST or obtained directly from NIST (when available) as a standard reference material. Accuracy is also estimated by calculating the percent recovery of continuing verification samples (CVS) for each batch of samples analyzed. CVS are independently produced standards that approximate the midpoint of the analytical range for an analyte and are run after every tenth environmental sample. Maintaining measurement accuracy levels that meet or exceed DQI ensures that the data obtained have an assessable utility level and contain minimal field sampling and/or analytical errors. Additional information on CASTNet measurement accuracy can be found in the CASTNet QAPP (Harding ESE, 2002c).

Completeness

Completeness is defined as the percentage of valid data points obtained from a measurement system relative to the total possible data points that were expected to be obtained. Completeness is an indicator of systematic or isolated problems during data collection/processing that result in loss of data. Completeness data may also indicate whether conclusions should be drawn from collected data (i.e., low completeness may obviate subsequent interpretation). The minimum completeness objective for CASTNet measured parameters is 90 percent (by parameter) for each calendar quarter. Any period with valid data completeness that is less than 75 percent is reported as an invalid sampling period. Historically, the program has produced excellent data capture rates and has exceeded the 90 percent completeness objective for concentration and meteorological parameters. For 2002, completeness of the measured parameters was 96 percent.

The criterion for modeled values is approximately 70 percent. The completeness criterion for the modeled values is lower than that for the measured parameters because the modeled parameters depend on the completeness of several simultaneous measurements. For example, hourly dry deposition fluxes are calculated from modeled V_d that depend on several measured meteorological variables. One missing meteorological parameter or LAI value invalidates a V_d value. Similarly, data aggregation procedures require approximately 70 percent data completeness for hourly fluxes and weekly concentrations/fluxes in order to calculate the weekly and quarterly values. Historically, completeness of the annual mean concentrations, V_d, and flux estimates all met their respective criteria and exceeded objectives by achieving better than 80 percent completeness for modeled values (flux and deposition velocities). Completeness of the modeled values for 2002 was 91 percent.

Precision

Exposed Filter Concentrations

Figure 6-1 provides a bar chart in which the bars represent precision statistics for each CASTNet analyte in terms of MARPD for both the historical (1990 through 2001) and the 2002 data for MCK131/231, KY and ROM206/ROM406, CO. Trace cations are excluded from this analysis and are discussed later. The historical results vary from about 5 percent for particulate SO_4^{2-} to about 12 percent for particulate NO_3^-. The historical MARPD for SO_4^{2-} and NH_4^+ met the criteria in Table 6-2. The results for SO_2 and HNO_3 were above the 5 percent criterion but were considered reasonable. The results for NO_3^- were significantly above the 5 percent goal. Historically, the precision of particulate NO_3^- measurements has been consistently worse than for the other analytes, possibly because 1) nitrate concentrations are the lowest of all the pollutants and 2) nitrate species are in a dynamic equilibrium on and between filters involving gas and particle phases. This equilibrium is affected by changes in temperature and humidity. For example, ammonium nitrate aerosol collected on the Teflon® filter could volatize and form gaseous HNO_3, which in turn could migrate to the nylon filter, thereby changing concentrations of NO_3^-, NH_4^+, and HNO_3. In other words, NO_3^- and NH_4^+ concentrations could be underestimated and HNO_3 overestimated.

The 2002 precision results shown in Figure 6-1 indicate that the results for MCK131/231 were below historical results and generally met DQI criteria. NO_3^- was the only parameter above the DQI criterion, which for NO_3^- is 5 percent. Similarly, the precision results for ROM206/406 were below historical results (except for SO_2) and met the DQI criteria for SO_4^{2-}, NH_4^+, and HNO_3.

Precision statistics for 2002 for cations, based on collocated ambient concentrations, are summarized in Figure 6-2. The MARPD statistics for MCK131/231 met the 10 percent criterion for all cations except for Na^+. The results for ROM206/406 show that the DQI criterion was met for Mg^{2+} and K^+, but not for Ca^{2+} and Na^+. Table 6-3 summarizes precision results by quarter for the two collocated sites. The data show the precision data were well above the 10 percent goal for Na^+ for both the Kentucky and Colorado sites during the first quarter. An investigation indicated the source of contamination was the laboratory sample bottles purchased from a certain manufacturer (Harding ESE, 2003). The bottles showing contamination were used between March 1999 and March 2002. Bottles are no longer purchased from this manufacturer. The acceptance testing program for filter media previously only performed tests for anion and NH_4^+ parameters. As a result of this investigation, the program now includes acceptance testing for Na^+, K^+, Mg^{2+}, and Ca^{2+}. If test results exceed the reporting limits shown in Table 6-2, the associated box of filters is rejected.

The 2002 analytical precision results for five analytes and the three filter types are

presented in Figure 6-3 using a scale of zero to 14 percent to match the scale shown in Figure 6-1. The results presented in Figure 6-3 were based on analysis of 5 percent of the samples that were randomly selected for replication in each batch. The results of the analysis of the in-run replicates were compared to the results of the original concentrations. The laboratory precision data met the 5 percent measurement criterion listed in Table 6-2.

Ozone Concentrations

As discussed in Chapter 1, CASTNet QA procedures for the EPA-sponsored O_3 analyzers are different from the EPA requirements for SLAMS monitoring while the QA procedures for the O_3 analyzers at the NPS-sponsored sites meet the requirements. The operation of the collocated O_3 analyzers at ROM206/406 provides an opportunity to evaluate the precision of the independent systems. Table 6-1 provides the DQI criteria for the CASTNet continuous measurements. The precision criterion for O_3 is 10 percent.

MARPD statistics were calculated from hourly O_3 measurements obtained from ROM206/406, CO and MCK131/231, KY during 2002. In addition, quarterly historical precision statistics were compiled for all collocated sites. Quarterly precision results are summarized in Figure 6-4. The data show the historical and 2002 results met the 10 percent criterion. The annual MARPD for ROM206/406 was approximately 4.5 percent, indicating that the two independently operated O_3 analyzers with different QA/QC procedures produce virtually identical results.

MLM Simulations of Weekly Fluxes

The collocated sampling stations at ROM206/ROM406, CO provide an excellent opportunity to estimate the precision of weekly modeled dry deposition (flux) rates. Figures 6-5 through 6-7 illustrate weekly flux estimates for SO_2, HNO_3, and SO_4^{2-}, respectively, for the two monitoring stations. The bar charts show excellent comparability between the sets of results for each of the three pollutants. The respective MARPD values are 11 percent, 8 percent, and 7 percent.

Accuracy

Laboratory Filter Concentrations

Accuracy of laboratory measurements is assessed through the analysis of reference samples and CVS. Reference samples and CVS are procured from independent suppliers and are NIST traceable. Reference samples are analyzed at the beginning and end of each analytical batch to verify the accuracy and stability of the calibration curve. The target value of the CVS solution is set to the midrange of the calibration curve. The CVS in 2002 were analyzed every tenth sample to verify no drift in the calibration curve. Table 6-4 presents the percent recoveries and standard deviations for reference samples and CVS relative to target concentrations. The table shows that the DQI goals (see Table 6-2) were met in 2002. The table also lists the precision results that were shown in Figure 6-3.

Continuous Measurements

CASTNet sites were calibrated every six months with NIST-traceable standards during 2002. Table 6-5 shows that all continuous parameters were within DQI criteria (Table 6-1) more than 90 percent of the time, except for relative humidity > 85 percent and solar radiation. These parameters met established criteria 81 percent and 88 percent of the time, respectively. According to CASTNet project protocols, associated data are still considered valid if the calibration criterion is not exceeded by more than its magnitude (i.e., if within 2x the criterion). The percent within 2x criterion for these parameters was 97 percent and 100 percent, respectively. Therefore, the completeness values for these parameters were not adversely affected.

Beginning in 2000, the frequency of site calibration was reduced from a quarterly to a semiannual schedule, and tighter measurement criteria limits were established for relative humidity > 85 percent and filter pack flow rate. The average percentage of sites meeting the criteria for these two parameters before 2000 was in the high 90's. The average percentage after 2000 is 85 percent for relative humidity > 85 percent and 91 percent for filter pack flow rate.

Historically, solar radiation has met the criterion at a lower frequency than any other parameter. The average percentage meeting the criterion before 2000 was 93 percent. The average percentage after 2000 is 90 percent.

Completeness

Completeness is defined as the percentage of valid data points obtained from a measurement system relative to total possible data points expected to be obtained. The CASTNet DQI requires a minimum completeness of 90 percent for every measurement for each quarter. In addition, the data aggregation procedures summarized in Chapter 1 require approximately 70 percent completeness for hourly fluxes and weekly concentrations/ fluxes. Figure 6-8 presents 2002 completeness data for all sites for measured filter concentrations, continuous measurements, and calculated parameters. The figure shows that the 2002 direct measurements met the 90 percent goal. The 2002 results show filter concentrations and flow values exceeded 95 percent, and ozone data completeness was approximately 94 percent. The four parameters derived from MLM results exceeded 85 percent completeness.

Interlaboratory Comparisons

NIST-traceable standards are utilized by the MACTEC laboratory and data are reported in standard units in order to ensure comparability of CASTNet laboratory results with results from other national monitoring programs. The CASTNet laboratory participates regularly in laboratory intercomparison studies. In these studies, blind samples are supplied to a group of participating laboratories, and the results from the various laboratories are collected and reported. Figure 6-9 summarizes the U.S. Geological Survey (USGS) Interlab program from 1999

through 2002. The average reference sample recoveries for the CASTNet laboratory (denoted "ESE") were between 95 and 103 percent. Only three laboratories – including MACTEC's CASTNet laboratory – exhibited average reference sample recoveries that never deviated by more than 5 percent from recovery goals (95 to 105 percent).

Analysis of Filter Blanks

MACTEC switched to a different manufacturer to supply Teflon® filters in August 1998. This decision was made due to recurring problems with high background levels of NO_3^- on the filters. This problem was first experienced in October 1997. CAPMoN had also experienced high background levels on their Teflon® filters. Because of these problems, MACTEC decided to review the historical record of measured concentrations (i.e., background) on various blank filters for any trends or biases in background levels. That analysis was reported in the CASTNet 1998 Annual Report (ESE, 1999). This report presents a continuation of the analysis of filter blanks through 2002.

MACTEC uses three types of filter blanks: unused filters for acceptance tests, laboratory blanks, and trip blanks. Prior to sampling, five percent of new Teflon® and nylon filters and two percent of Whatman impregnated filters are tested for background levels of target analytes. If background levels on the tested filters exceed detection limits, that lot of filters is rejected for use in sampling and is stored in a location separate from the other filters. Prior to late 1997, two percent of all filter types were tested. Currently, two laboratory blanks are tested per week. As an additional QC test, trip (field) blanks are sent quarterly to each monitoring site. The trip blanks are not exposed to the ambient air, but are analyzed and processed following exactly the same protocol as used for the exposed filters. Trip blanks are used as a means of measuring background contamination introduced during filter pack preparation, transport, and storage. Until 1996, trip blanks were shipped monthly to each site.

Table 6-6 summarizes the historical record of filter blanks. The average concentrations from the trip and laboratory blanks are almost equivalent to the detection limits. The data from the acceptance tests illustrate the past problem with the NO_3^- concentrations [e.g., a maximum concentration of 32.18 µg (as N)] on Teflon® filters. However, lots of filters with background above the detection limits are not used for field sampling.

As a result of the past problems with high NO_3^- background on Teflon® filters, the field and laboratory blanks were analyzed in more detail. Figure 6-10 shows the background NO_3^- concentrations on Teflon® trip blanks for the period 1990 through 2002. Figure 6-11 shows laboratory blank results. These data show no change in average background concentrations over the 13-year period. A level of quantitation (LOQ) can be defined as the average concentration plus three times its standard deviation. The trip blank results shown in Figure 6-1 have been used to

calculate an LOQ. Typical LOQ values are approximately 0.1 $\mu g/m^3$. Many western sites measure concentrations only 2 to 3 times higher than LOQ values, introducing uncertainty in these lower NO_3^- concentrations. Typically, four to six sites per year have 20 weeks or more with concentrations less than the LOQ. In general, however, these analyses of filter blanks show that background contamination of CASTNet filters is not a significant problem, and no trends or biases in background levels are evident, except for the sites with very low NO_3^- concentrations.

Results from Independent Audits

Independent systems and performance audits of 20 EPA-sponsored sites were conducted by ARS, a subcontracted auditor possessing the appropriate skills and knowledge. NPS-sponsored sites were not audited by an independent party. Complete audit findings are discussed in the CASTNet 2002 QA Report (MACTEC, in press).

Audit results for 2002 are summarized in Table 6-7 for nine sites. No problems were found for the other 11 sites. The table shows audit findings, their resolution, and the resultant effect on data. For example, at ANA115, MI, the wind direction sensor was discovered to be misaligned by 27.5 degrees. The sensor was replaced seven days after the audit. Since the wind direction data were misaligned by a fixed quantity, the data were adjusted and replaced in the CASTNet database. Sometimes, however, data cannot be adjusted. An audit of PED108, VA indicated a flow problem. The system was replaced 14 days after the audit; but, unlike the problem with the wind direction sensor at ANA115, the flow problem was beyond adjustable parameters. As a result, the flow data were invalidated for the period January 26 through May 31, 2002.

Whenever ARS documented measurements outside of DQI criteria, MACTEC personnel investigated the findings by performing an additional instrument challenge for confirmation. In some instances, the audit finding was not confirmed. Problems with the relative humidity parameter were not confirmed on several occasions. Relative humidity readings take considerable time to properly stabilize. MACTEC's inability to confirm relative humidity audit failures was most likely caused by the auditor's lack of familiarity with the stabilization time required for auditing the relative humidity sensors used in the CASTNet program.

Conclusion

DQI results demonstrate that field and laboratory processes were adequately monitored through QA/QC procedures and generally free of systematic bias during 2002. Accuracy data met the established criteria for field and laboratory parameters with the exception of solar radiation and relative humidity > 85 percent. However, since each criterion was exceeded by a value less than its own magnitude, the associated continuous data collection is considered valid. The increase in the frequency of calibration results exceeding established criteria since 2000 is most likely due to the reduction in frequency of site calibrations

and to the tightening of measurement criteria limits.

Precision data for sulfur constituents and ammonia are considered acceptable. Precision data for nitrate analyses of collocated field samples have not met the established criterion due most likely to the low concentrations generally measured and the unpredictable nature of the gas-particle equilibrium of the nitrate species. Completeness criteria were met for all parameters in 2002.

Table 6-3. Precision Results by Quarter for 2002

Site Pairs	SO_4^{2-}	NO_3^-	NH_4^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	HNO_3	SO_2	Total NO_3^-
MCK 131/231										
Q1	5.27	3.83	5.33	5.15	5.98	41.79	4.00	4.21	6.14	3.75
Q2	1.34	10.86	1.32	4.76	4.81	2.30	3.68	3.68	3.31	3.49
Q3	2.32	9.16	3.35	5.75	4.51	2.81	6.44	3.59	2.98	3.73
Q4	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
2002	2.98	7.95	3.33	5.22	5.10	15.63	4.71	3.83	4.14	3.66
ROM 406/206										
Q1	2.54	9.99	5.01	4.95	4.94	57.86	8.39	4.48	7.97	2.44
Q2	4.18	6.87	4.71	4.21	5.46	9.74	8.00	7.16	10.13	4.21
Q3	5.25	9.66	7.08	17.46	7.60	6.38	5.91	4.10	11.35	4.26
Q4	3.42	14.05	5.55	25.84	12.29	8.21	12.69	4.94	11.86	5.69
2002	3.85	10.14	5.59	13.12	7.57	20.55	8.75	5.17	10.33	4.15

Note:

25 out of 70 site-quarters by parameter were outside criterion.
N/A Not available because of incomplete data

Table 6-4. Filter Pack QC Summary for 2002

Filter Type	Parameter	Reference Sample[1] Recovery (% R) Mean	Reference Sample[1] Recovery (% R) Standard Deviation	Continuing Verification Samples (% R) Mean	Continuing Verification Samples (% R) Standard Deviation	In-Run Replicate[2] Percent Difference Mean	In-Run Replicate[2] Percent Difference Standard Deviation
Teflon®	SO_4^{2-}	99.83	1.71	99.19	1.23	0.63	0.91
	NO_3^-	101.11	1.35	99.47	1.13	1.21	1.83
	NH_4^+	101.74	1.70	98.85	1.50	1.08	1.81
	Ca^{2+}	102.56	3.60	100.83	1.26	2.50	3.64
	Mg^{2+}	101.40	1.16	99.60	0.98	1.84	2.44
	Na^+	96.53	1.72	99.91	1.10	0.95	1.05
	K^+	100.18	2.54	100.20	1.07	2.32	2.42
Nylon	SO_4^{2-}	98.80	1.64	99.49	1.21	2.67	3.28
	NO_3^-	100.34	1.47	99.75	1.19	1.28	1.36
Whatman	SO_4^{2-}	100.72	0.67	98.56	0.65	3.81	6.60

Note: % R = percent recovery

[1] Results of reference sample analyses provide accuracy estimates
[2] Results of replicate analyses provide precision estimates

Table 6-5. Accuracy Results for 2002 Field Measurements

Parameter	Percent Within Criterion
Temperature (0°C)	96 percent
Temperature (ambient)	96 percent
Delta Temperature (0°C)	97 percent
Delta Temperature (ambient)	98 percent
*Relative Humidity > 85%	81 percent
Relative Humidity ≤ 50%	99 percent
*Solar Radiation	88 percent
Wind Direction North	91 percent
Wind Direction South	94 percent
Wind Speed < 5 m/s	100 percent
Wind Speed ≥ 5 m/s	99 percent
Precipitation	99 percent
Wetness (w/in 0.5 volts)	98 percent
Ozone Slope	97 percent
Ozone Intercept	99 percent
Flow Rate	92 percent

Note: °C = degrees Celsius.
m/s = meters per second.
* = Per CASTNet project protocols, data are flagged as "suspect" (S) but still considered valid if the calibration criterion is not exceeded by more than its magnitude (i.e., if within 2x the criterion). The percent within 2x criterion for these parameters was 97 percent and 100 percent, respectively.

Table 6-6. Summary of Filter Blanks 1990 – 2002

TRIP BLANKS						
Parameter Name	**Detection Limit Total µg**	**Total Number**	**Number Above Detection Limit**	**Average Total µg**	**Standard Deviation**	**Maximum Total µg**
Teflon®-NH_4^+-N	0.50	1536	36	0.51	0.06	1.80
Teflon®- NO_3^--N	0.20	1539	161	0.21	0.05	0.97
Teflon®- SO_4^{2-}	1.00	1539	19	1.02	0.49	19.93
Ca^{2+}	0.075	997	501	0.109	0.066	0.613
Mg^{2+}	0.075	997	5	0.075	0.005	0.205
Na^+	0.125	997	259	0.351	0.053	0.526
K^+	0.125	997	57	0.140	0.132	2.710
Nylon- NO_3^--N	0.20	1540	81	0.23	0.36	9.94
Nylon - SO_4^{2-}	1.00	1540	164	1.04	0.43	15.17
Whatman - SO_4^{2-}	2.00	1539	338	2.32	1.48	36.75
LABORATORY BLANKS						
Parameter Name	**Detection Limit Total µg**	**Total Number**	**Number Above Detection Limit**	**Average Total µg**	**Standard Deviation**	**Maximum Total µg**
Teflon®-NH_4^+-N	0.50	498	24	0.51	0.10	1.84
Teflon®- NO_3^--N	0.20	500	3	0.21	0.04	0.61
Teflon®- SO_4^{2-}	1.00	500	6	1.01	0.07	2.28
Ca^{2+}	0.750	493	101	0.090	0.071	1.280
Mg^{2+}	0.075	493	4	0.076	0.014	0.359
Na^+	0.125	493	81	0.258	0.402	5.070
K^+	0.125	493	21	0.139	0.129	2.386
Nylon- NO_3^--N	0.20	499	9	0.20	0.03	0.64
Nylon -SO_4^{2-}	1.00	499	29	1.02	0.19	4.96
Whatman -SO_4^{2-}	2.00	499	41	2.12	0.77	16.27
ACCEPTANCE TEST VALUES						
Parameter Name	**Detection Limit Total µg**	**Total Number**	**Number Above Detection Limit**	**Average Total µg**	**Standard Deviation**	**Maximum Total µg**
Teflon®-NH_4^+-N	0.50	1680	69	0.51	0.05	1.84
Teflon®-NO_3^--N	0.20	1680	59	0.24	0.83	32.18
Teflon®-SO_4^{2-}	1.00	1680	0	1.00	0.00	1.00
Nylon- NO_3^--N	0.20	1501	29	0.20	0.04	0.63
Nylon - SO_4^{2-}	1.00	1501	39	1.01	0.16	3.90
Whatman - SO_4^{2-}	2.00	1344	66	2.14	1.21	25.65

Note: Whatman filters are not analyzed for ambient NO_3^-. The blank results are used only for QC.

Table 6-7. ARS Audit Findings and Responses

Site ID	Audit Date	Audited Parameter	Max. or Avg. Error	Resolution	Data Affected? (Y/N)	Describe Affect on Data
ANA115, MI	8/22/02	Wind Direction Orientation	30.2	A replacement system was sent to the site and the auditor installed it on 8/29/02.	Y	The sensor base was determined to be misaligned by approximately 27.5°. Since the data were off by a fixed amount, data from the installation of the system on 4/26/02 through the audit on 8/22/02 were corrected by 22.5°.
BWR139, MD	4/19/02	**RH > 85%	9	The system was replaced on 7/5/02.	Y	Data flagged 'S' from the previous calibration on 2/2/02 to the 7/5/02 repair visit.***
CAD150, AK	6/11/02	Wind Direction Orientation	13	Not confirmed during 9/9/02 calibration visit.	N	NA
		Wind Direction Linearity	-16.4	Not confirmed during 9/9/02 calibration visit.	N	NA
LYK123, OH	8/29/02	RH > 85%	7.6	The system was replaced on 10/8/02.	Y	Data flagged 'S' from the previous calibration on 4/24/02 through 9/20/02 whereupon the data were invalidated per site operator observation through the 10/8/02 system replacement.***
PED108, VA	5/17/02	Flow Rate	22.6	The system was replaced on 5/31/02.	Y	Data flagged 'I' from the previous calibration on 1/26/02 to the 5/31/02 repair visit.†
PNF126, NC	5/19/02	Solar Radiation	-11.8	The system was damaged by lightning on 6/3/02 and replaced on 6/16/02.	Y	Data flagged 'S' from 4/30/02 to the 5/19/02 audit. ***, ††
VPI120, VA	5/18/02	Ozone Slope	1.22	Not confirmed during 6/1/02 site repair visit or 6/30/02 site calibration.	N	NA
UVL124, MI	8/23/02	RH > 85%	15.70	Confirmed at 5.6 (not 15.7) during 10/25/02 calibration visit.	Y	Data flagged 'S' from the previous calibration on 4/28/02 to the 10/25/02 site calibration.***
		RH ≤ 85%	22.1	Not confirmed during 10/25/02 calibration visit.	N	NA
WSP144, NJ	4/20/02	RH > 85%	15.40	Not confirmed during 6/27/02 site repair visit.	N	NA

Notes:

Y = yes
N = no
NA = not applicable

** Relative humidity (RH) readings take a considerable time to properly stabilize. The unconfirmed RH audit failures appear to be due to the technicians' lack of familiarity with the stabilization time required for CASTNet RH sensors.

*** The "S" flag identifies meteorological data that fall between 1x and 2x the associated measurement criterion for a given parameter. Data with no flags and data with "S" flags are treated identically in all data analyses and by the MLM.

† The "I" flag identifies data that did not pass verification and/or validation criteria.

†† Data from 5/19/02 through 6/3/02 still require flagging. These data will be flagged and resubmitted with a subsequent data transmittal package.

Figure 6-1. Historical and 2002 Precision Data for Atmospheric Concentrations

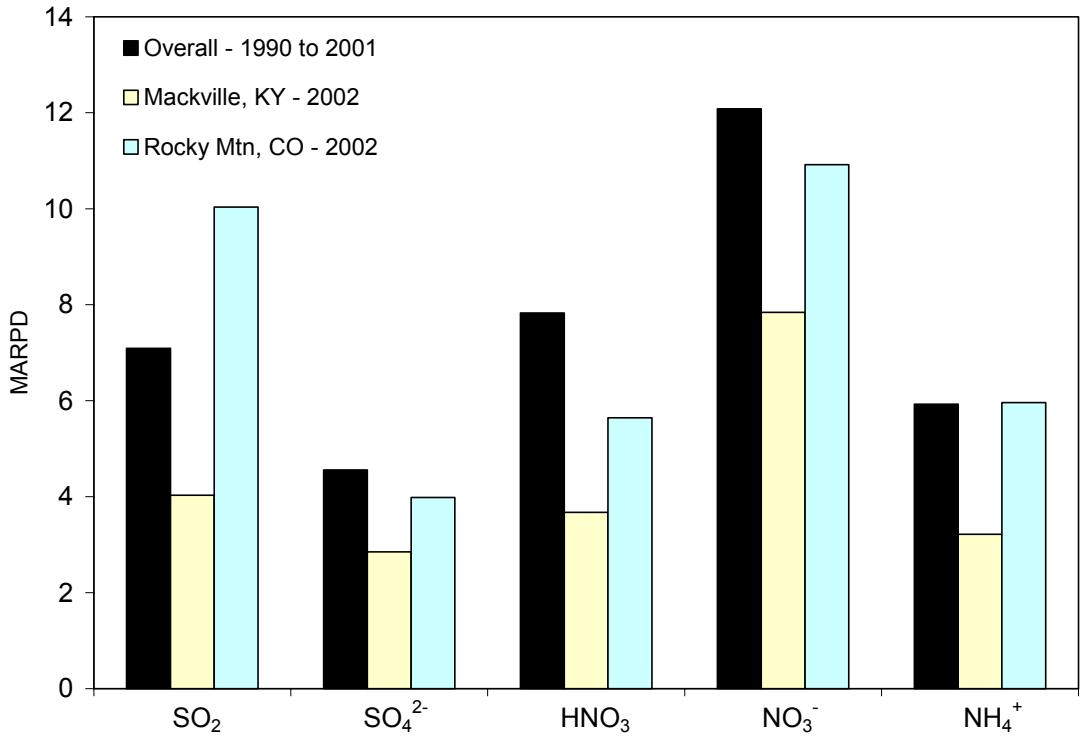


Figure 6-2. Precision Data for Cation Concentrations for 2002

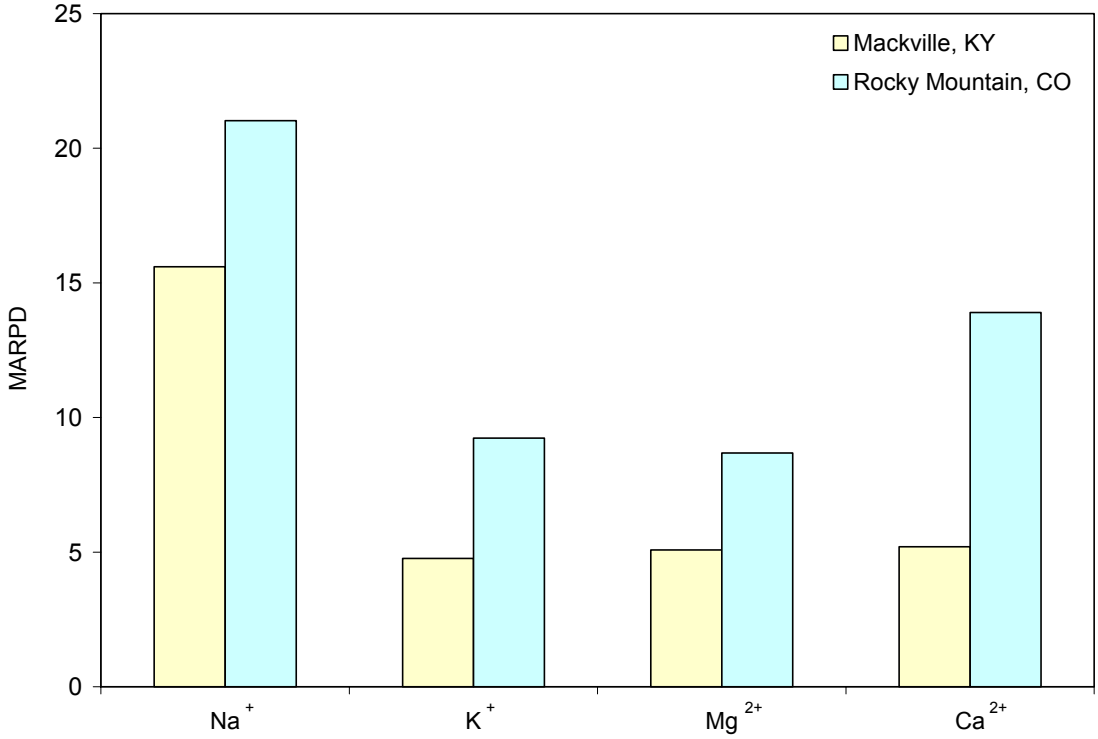


Figure 6-3. Precision Results for Laboratory Replicate Samples (2002)

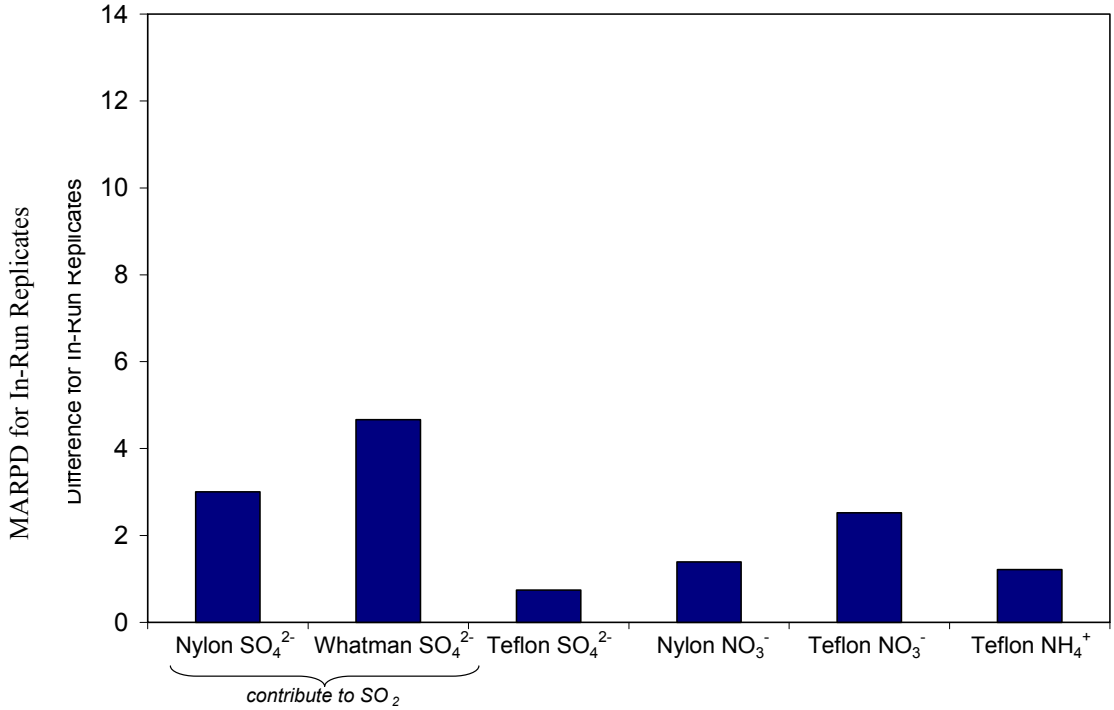


Figure 6-4. Historical and 2002 Precision Data by Quarter for Ozone Concentrations

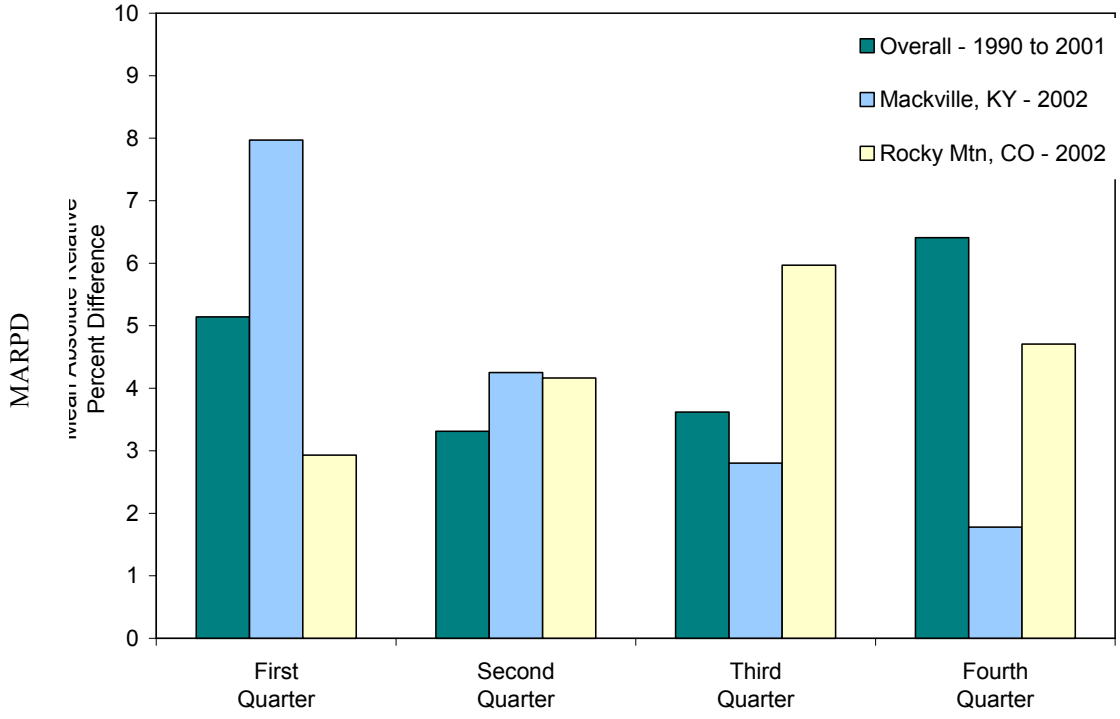


Figure 6-5. Weekly SO_2 Flux Comparison for 2002 for ROM206/406, Colorado

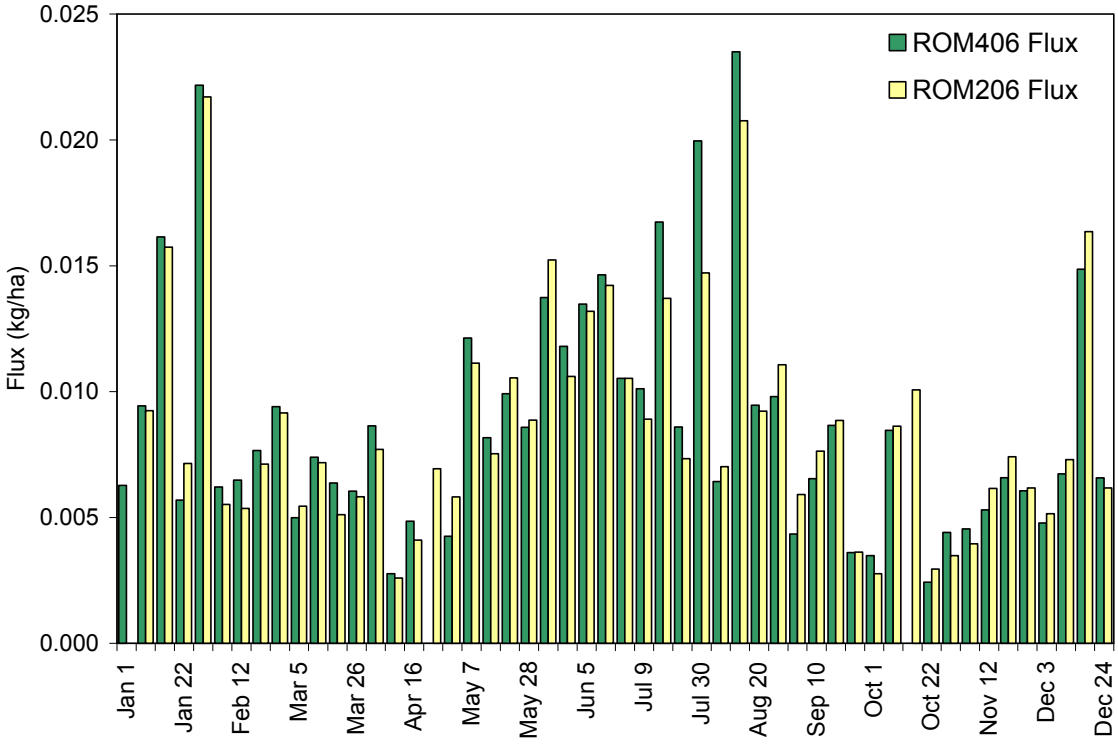
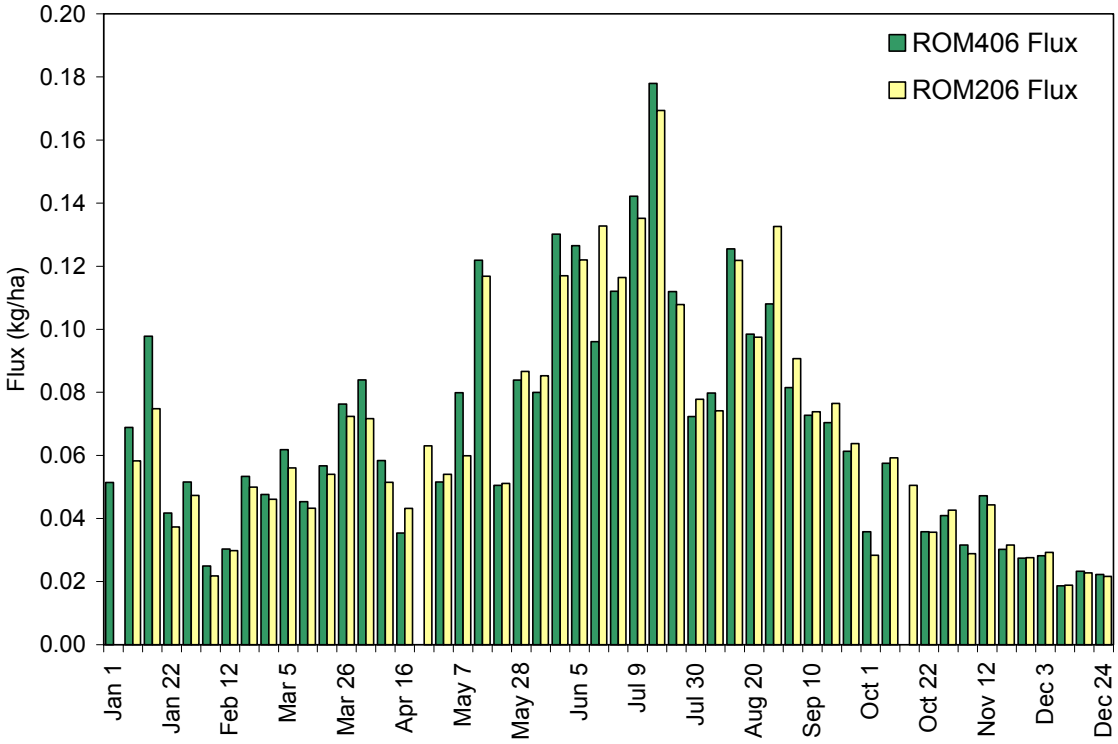


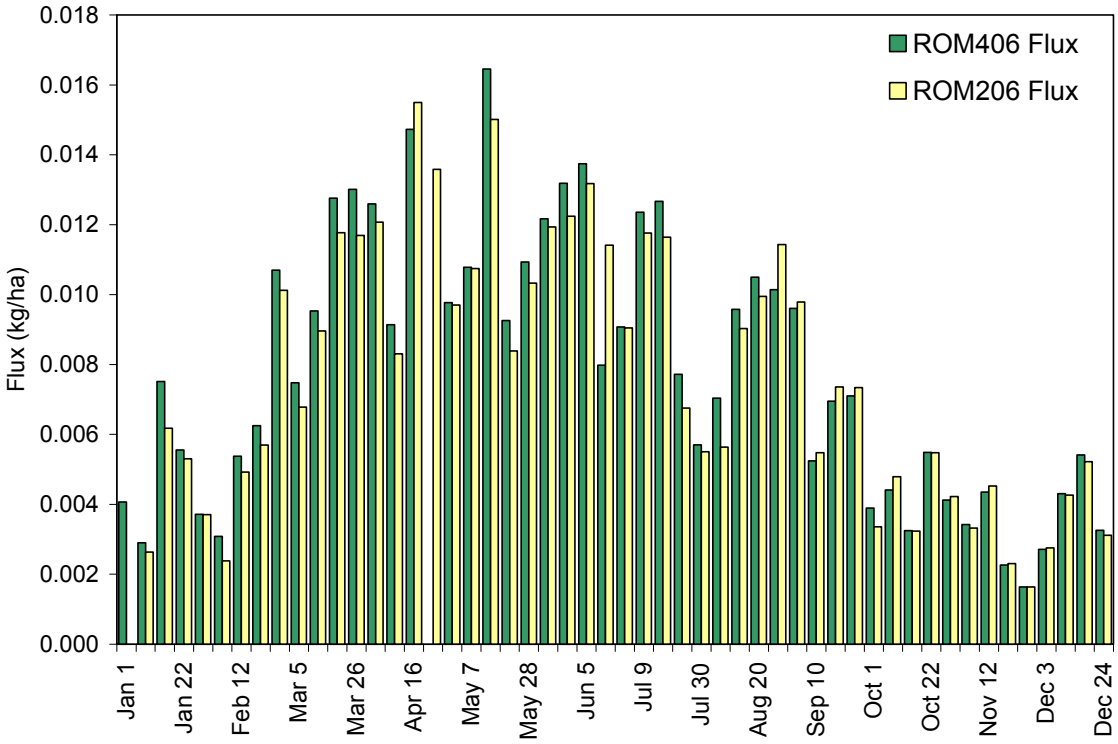
Figure 6-6. Weekly HNO_3 Flux Comparison for 2002 for ROM206/406, Colorado



Note:

406 = NPS-sponsored site
206 = EPA-sponsored site

Figure 6-7. Weekly SO_4^{2-} Flux Comparison for 2002 for ROM206/406, Colorado



Note:

406 = NPS-sponsored site
206 = EPA-sponsored site

Figure 6-8. Percent Completeness of Measurements and Modeled Estimates for 2002

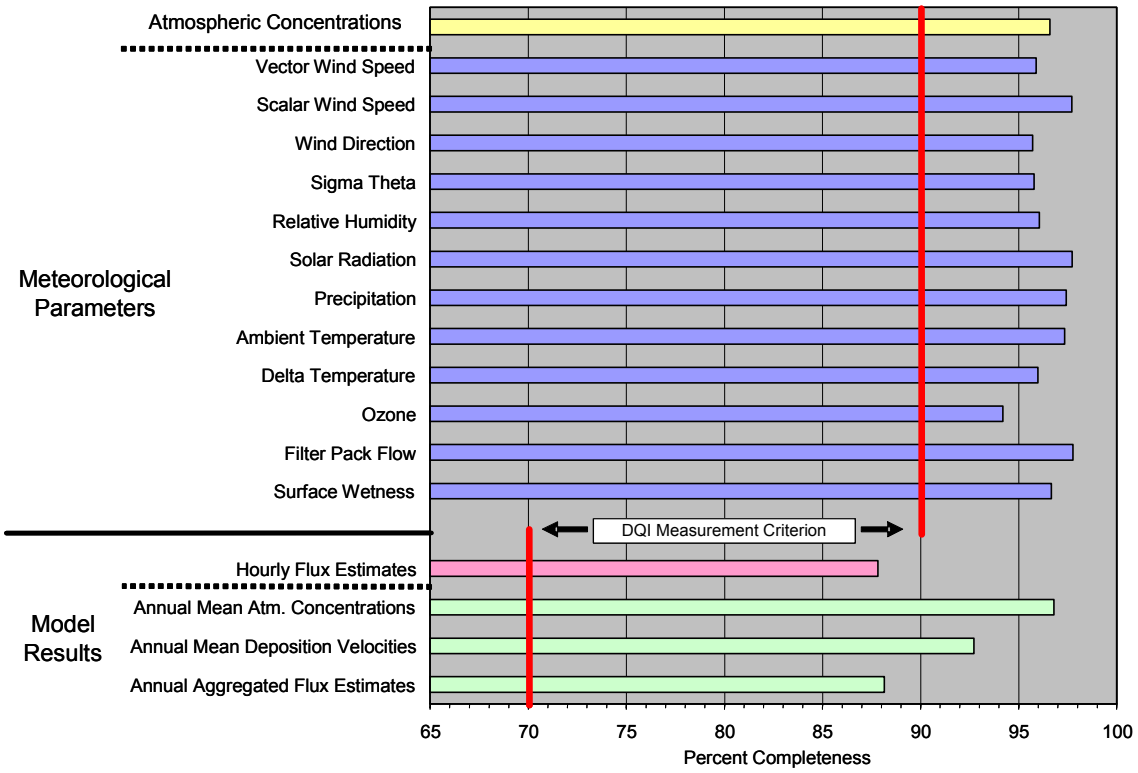
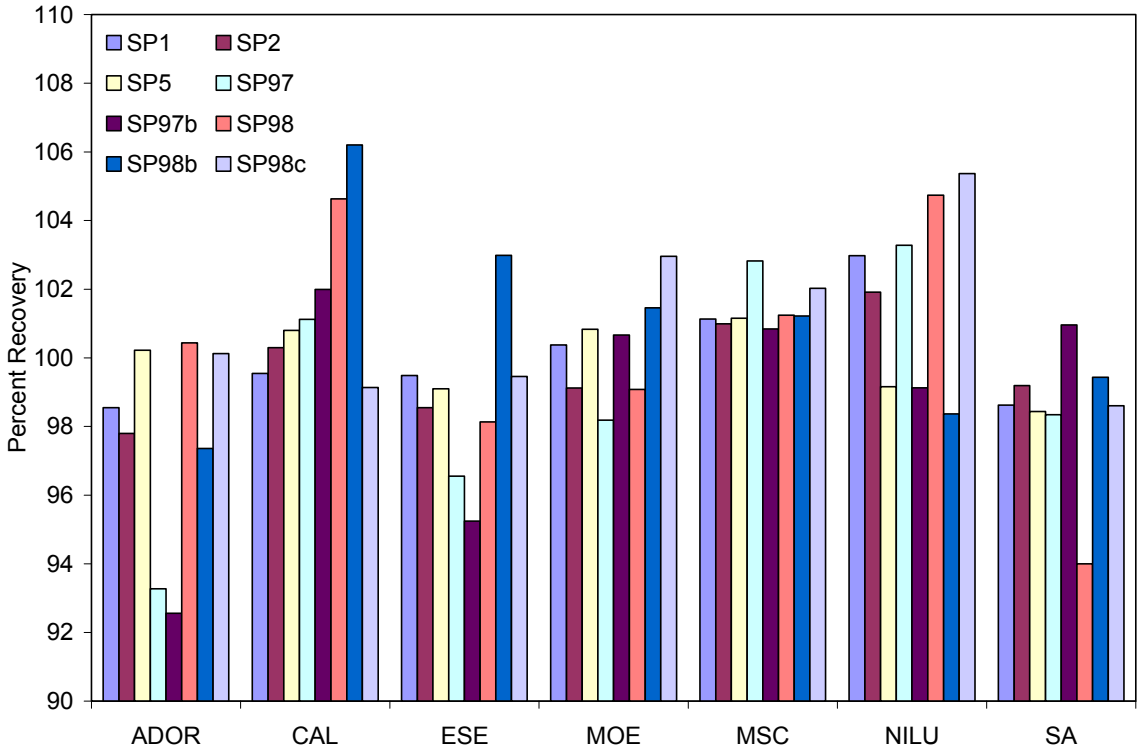


Figure 6-9. Summary of Laboratory Intercomparison Results (1999 through 2002*)

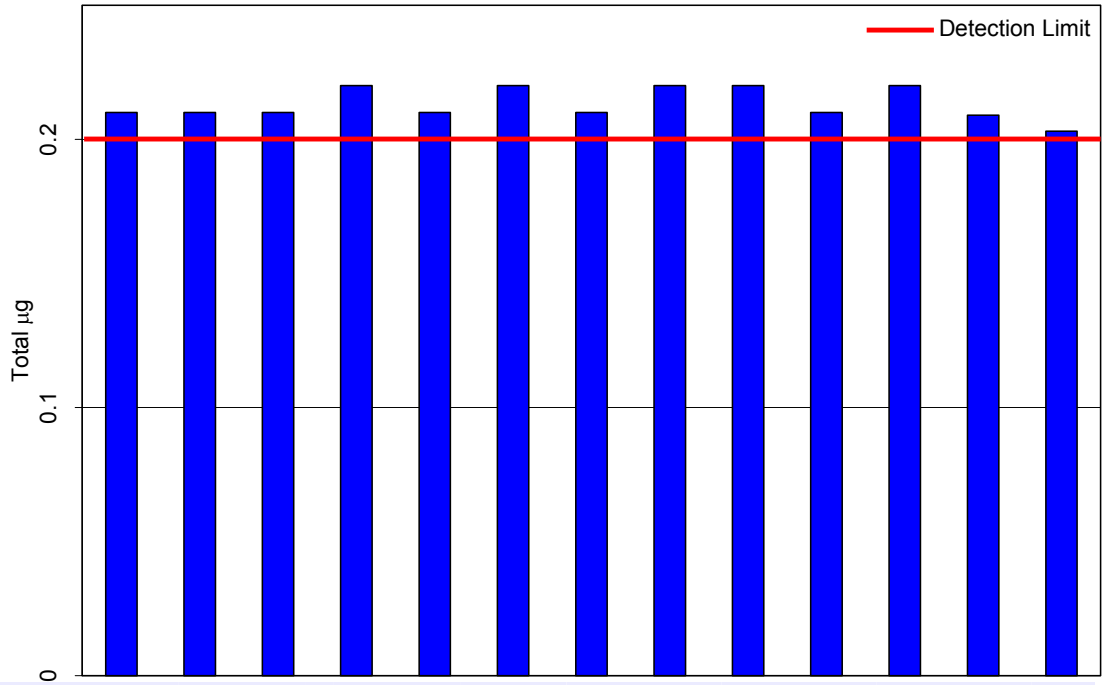


Note:

ADOR = Acid Deposition and Oxidant Research Center, Japan
CAL = Central Analytical Lab
ESE = MACTEC CASTNet Laboratory
MOE = Ministry of Environment and Energy, Canada
MSC = Meteorological Service of Canada
NILU = Norwegian Institute for Air Research
SA = Shepard Analytical
SP1, etc. = blind reference sample numbers

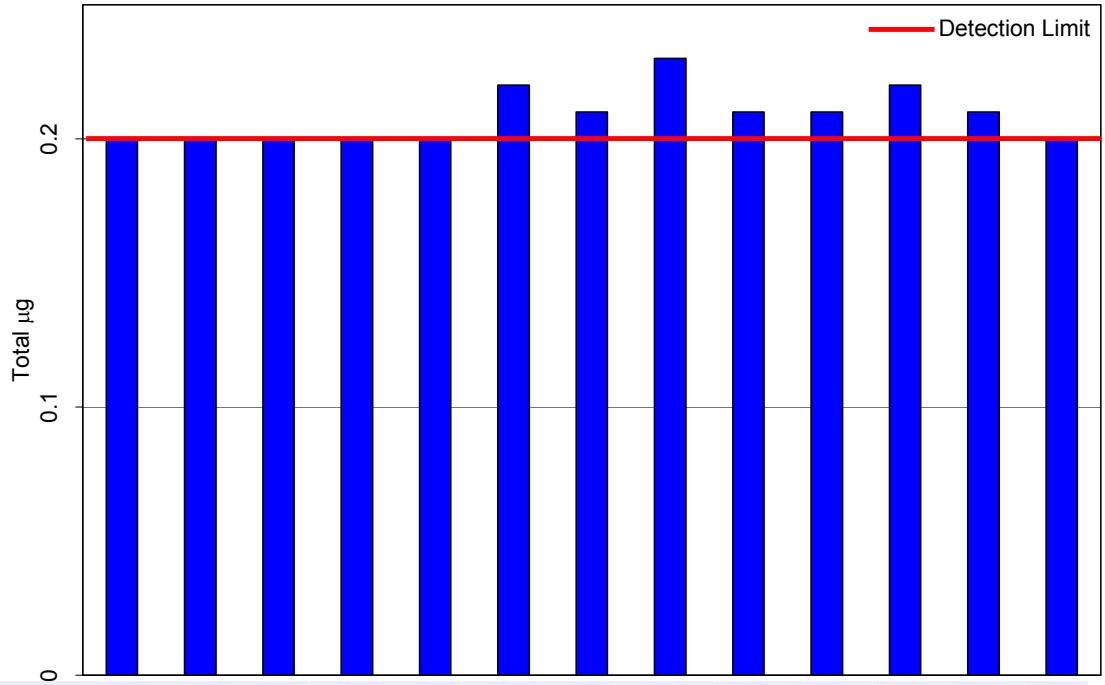
* 2002 results were only available for MACTEC (denoted as ESE). Results for 2002 for other participating laboratories were not available prior to publication of this report.

Figure 6-10. Results of Analysis for NO_3^- on Trip Blanks 1990 – 2002



Collection Year	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002
Average Concentration	0.21	0.21	0.21	0.22	0.21	0.22	0.21	0.22	0.22	0.21	0.22	0.21	0.20
> Detection Limit	66	24	108	160	52	99	25	45	30	21	45	24	19
Maximum Concentration	0.46	0.36	0.6	0.81	0.78	0.88	0.84	0.74	0.78	0.63	0.97	0.53	0.50
Standard Deviation	0.03	0.03	0.04	0.06	0.05	0.07	0.06	0.07	0.06	0.035	0.08	0.04	0.02
Detection Limit	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Count	659	136	136	777	563	490	194	267	188	304	306	316	331

Figure 6-11. Results of Analysis for NO_3^- on Laboratory Blanks 1990 – 2002



Collection Year	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002
Average Concentration	0.2	0.2	0.2	0.2	0.2	0.22	0.21	0.23	0.21	0.21	0.22	0.21	0.20
> Detection Limit	3	6	3	5	6	14	9	15	12	6	21	11	1
Maximum Concentration	0.32	0.35	0.22	0.3	0.26	0.6	0.45	1.51	0.34	0.45	0.44	0.61	0.27
Standard Deviation	0.02	0.02	0.00	0.01	0.01	0.06	0.05	0.15	0.03	0.03	0.04	0.05	0.01
Detection Limit	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Count	63	74	91	84	95	92	91	100	82	82	104	104	106