Investigation of Observed Bias in Ozone Measurements at Clean Air Status and Trends Network Sites Collocated in Rocky Mountain National Park

Prepared by CASTNET-related personnel at:

U. S. Environmental Protection Agency

National Park Service

AMEC Environment & Infrastructure, Inc. (EPA Contractor)

Air Resource Specialists, Inc. (NPS Contractor)

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Background

The U. S. Environmental Protection Agency (EPA) and the National Park Service (NPS) jointly fund and operate the Clean Air Status and Trends Network (CASTNET) ambient air monitoring program. The field measurements portion of the program includes meteorological measurements, continuous ozone monitoring and week-long filter-pack samples which are laboratory analyzed for long-term documentation of sulfur and nitrogen deposition. More information on the CASTNET program can be found at http://epa.gov/castnet/javaweb/index.html (EPA, 2013).

Both the EPA and the NPS are responsible for operating a portion of the stations in the network and employ their own contractors to perform all field operations, maintenance, data collection, validation and reporting. Operations at all sites are documented by the CASTNET Quality Assurance Project Plan (AMEC, 2013). Performance audits are contracted separately by the EPA for all the stations on an annual basis. In some cases states or local agencies provide additional audits on a quarterly or yearly basis.

CASTNET was not originally designed or configured as a regulatory ozone network. The network transitioned to a regulatory network in 2011. Precision for regulatory ozone measurements is now calculated according to the requirements documented in Title 40, Part 58 of the Code of Federal Regulations. Precision for regulatory ozone measurements is not calculated using collocated stations.

Maintenance of high precision and low bias across the network is important to both the EPA and the NPS. In order to understand the precision of the CASTNET network, collocated stations have been operated at several sites over the history of the network. The data collected, including ozone data, were compared using standard statistics. The three sites collocated as of the end of 2012 are Mackville, Kentucky, Yosemite National Park, California, and Rocky Mountain National Park, Colorado. The primary Mackville site (MCK131) has monitored ozone since July 1990 and the collocated site (MCK231) since December 1992. The collocated Mackville stations are both operated and maintained by the EPA and their contractor AMEC. NPS and their contractor Air Resource Specialists, Inc. (ARS) operated and maintained collocated ozone systems at the Yosemite station from April 2012 through April 2013. The primary site at Rocky Mountain National Park (ROM406) became a CASTNET site in October 1994. The collocated site (ROM206) has measured ozone since July 2001. The two collocated stations at the Rocky Mountain National Park are independently operated by NPS (ROM406) and EPA (ROM206), along with their respective contractors ARS and AMEC.

Historically, precision data for ozone measurements from the Mackville site have met the established criterion with no apparent bias. Results from the Yosemite site were similar to Mackville. Data from the Rocky Mountain collocated sites have shown poorer precision while still meeting the criterion but showed a consistent bias. With few exceptions, the ROM206 ozone measurements were consistently 1-6 parts per billion (ppb) lower than ROM406 measurements. This difference between the two sites has been noted by other ambient air quality scientists.

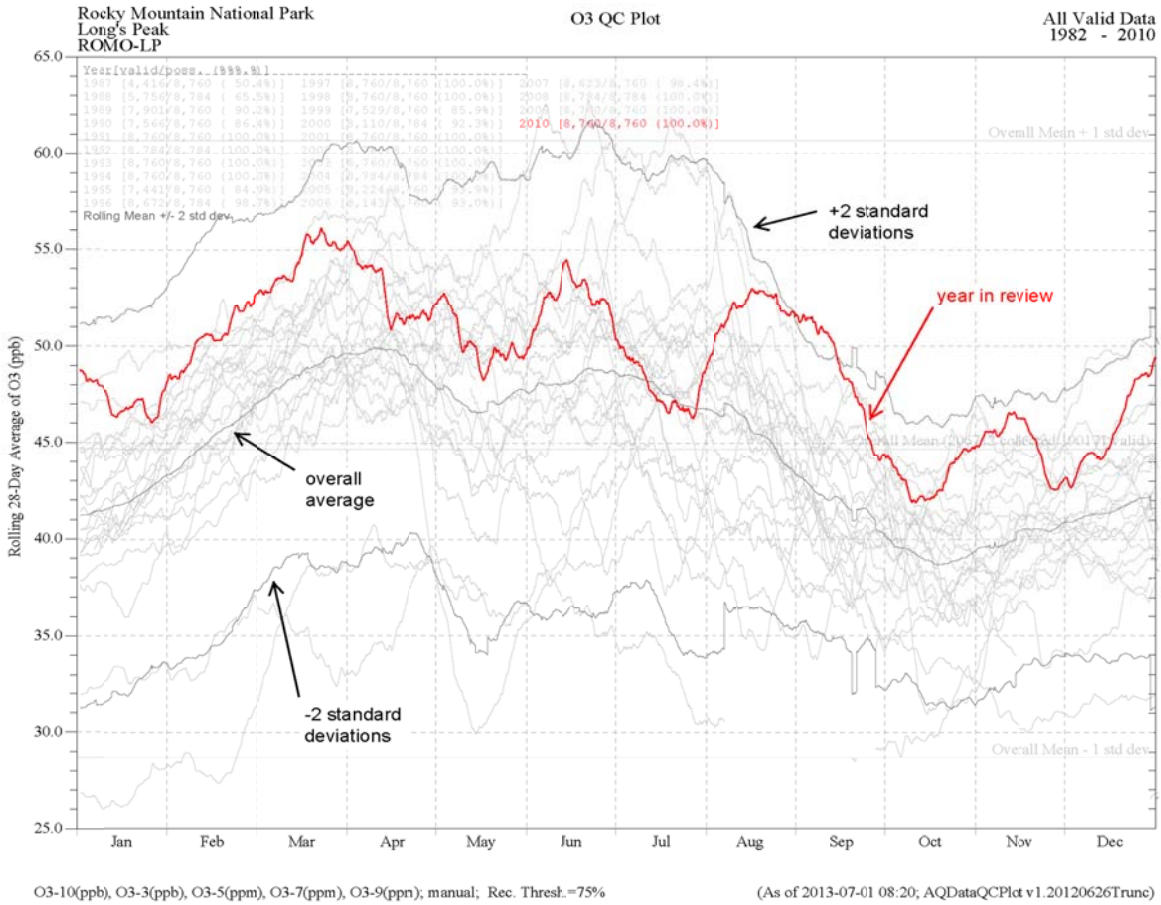
This difference, coupled with ongoing efforts by EPA and NPS to improve and enhance the network operations has caused the two agencies to take a closer look at these discrepancies in an attempt to understand their root causes. Since the two Rocky Mountain stations are operated independently of each other by two different contractors and EPA-sponsored CASTNET sites began reporting ozone data to EPA's Air Quality System (AQS) in 2011, CASTNET management decided to review the entire technical system in place within each agency in order to identify and reconcile inconsistencies. This document summarizes the technical systems review, which included data handling processes, on-site configurations and procedures, and changes in historical station configurations, and changes made to improve CASTNET data quality.

Data Handling Review

The first step in this process involved reviewing the data sets carefully to identify periods with the largest difference in ozone measurements. The historical data record does show a consistent offset between the two stations, but periods of larger differences have also occurred intermittently. Once these periods were identified, site records were scrutinized to see if maintenance that occurred at the stations could account for the differences. This data review revealed several periods of data that should have been identified as invalid made it through to the final data set. For example, some data had been invalidated but were inadvertently submitted as valid due to a combination of human and software errors. These data were only submitted to the database maintained by the EPA Clean Air Markets Division and were never present in AQS. Other periods of data were not invalidated because the review processes that were in place at the time were not sufficient to identify problems such as periods anomalously high or low compared to historical ranges.

In order to prevent these errors from going undetected in the future, AMEC has adopted a procedure developed and utilized by ARS as an additional step in the data review process. This additional data review occurs once all data have been validated for a calendar year. The procedure was first utilized by AMEC with ARS assistance to review historical data collected from 1990 through 2010. Subsequent years have also been reviewed. One step in the process is to review the data on an annual time series plot to help identify data that may have shifted or drifted throughout the year. The second step involves reviewing the year of ozone data compared to all previous years from the same station. A rolling average of all hourly data for the year and the overall standard deviation for each period of time are plotted. This plot helps to identify periods that fall outside of expected limits based on the site's history. After further investigation, these periods may be determined to be invalid. An example is shown in Figure 1.

Figure 1. Example Plot used during Annual Review



Note: Data set available for ROMO-LP predates inclusion of site in CASTNET.

On-Site Configuration and Procedures Review

In June 2011, AMEC's Field Operations Manager met with ARS's Field Operations Manager to perform an on-site configuration review of the two ozone systems and the measurement procedures in order to initiate an investigation into the potential sources of continued bias between the collocated ozone measurements. While differences in instruments and procedures were observed and noted, no one procedure stood out as the root cause of the bias. Where practical, differences found at this meeting were mitigated resulting in improved data quality.

The following differences were noted at the time of this visit:

- While AMEC used one minute averages for quality checks and five minute averages for calibrations, ARS used one minute averages for both.
- AMEC used Purafil as part of EPA site zero air systems and ARS did not (only charcoal).
- ARS uses a 15-30 minute warm up time for the traveling transfer standard while AMEC uses a 1-hour warm up.
- ARS uses PFA (perfluoroalkoxy) Teflon tubing while AMEC uses FEP (fluorinated ethylene propylene) Teflon tubing.

- Tubing inner diameters were different; 3mm (1/8 inch) inner diameter for AMEC, 3.96mm (5/32 inch) inner diameter for ARS.

- AMEC uses a knockout bottle at all sites, ARS does not use.

- During the June 2011 visit, AMEC audited both sets of analyzers and site transfer standards with its traveling transfer standard and found them to be within acceptance limits.

The June 2011 meeting also included an evaluation and discussion of each firm's air quality calibration laboratories and their procedures for preparing, adjusting, and maintaining both primary and transfer ozone standards as well as each firm's field operations procedures for ozone calibration and measurement. The current procedure for maintaining Level 3 site transfer standards at all CASTNET sites is described in the CASTNET Quality Assurance Project Plan (QAPP) 8.1 (Appendix 1, Section 4.B.3, Attachment B). The evaluation of these procedures revealed some differences:

- The ARS laboratory and traveling transfer standards at the time were Thermo Scientific (Thermo) 49C PS models. The laboratory transfer standards were sent to EPA Region 8 for verification every year. There is not a sample inlet to the 49C PS model instruments, therefore, ARS used a surrogate analyzer and audited the surrogate using the laboratory transfer standard adjusting the output of the traveling transfer until the surrogate matched the laboratory standard results. ARS has since adopted the AMEC procedure outlined below (Region 8 Standard Reference Photometer (SRP) is still used for verification).

- AMEC's 49C and 49i PS models are sent to Region 7 and 49i traveling transfers are sent to the National Institute of Standards and Technology (NIST). AMEC only uses model PS instruments for the laboratory transfer standards and is able to audit the calibration transfer standards directly. All traveling transfer standards are non-PS model 49i. All transfer standards maintain a level 2 authority.

- The correction procedure used by ARS is to adjust the calibration factors of the laboratory transfer standard when necessary and not perform mathematical adjustment of the output based on the SRP verification results. AMEC's procedure is to leave the calibration factors at 1 and 0 and mathematically adjust the transfer output using the slope and intercept results from the SRP verification.

In September 2011, state of Colorado representatives performed a PE at the site. Both analyzers passed audit criteria. Both ROM406 and ROM206 analyzers continued to pass audit criteria during regular visits by AMEC, ARS, and Environmental, Engineering & Measurement Services, Inc. (EEMS), the auditor contracted by the EPA to conduct annual performance evaluations for CASTNET. In an effort to further investigate the bias that was still evident in the measurements, CASTNET management directed AMEC and ARS to install duplicate analyzers at their respective sites to isolate differences responsible for the bias.

In July 2012, a duplicate ozone analyzer was installed at ROM406 for the comparison study. The duplicate analyzer, ROM406-b, was not adjusted in the field during installation using a PS-model traveling transfer standard. Later in July, ARS replaced the ROM406 primary ozone analyzer due to noted discrepancies with the ROM406-b analyzer. The replacement primary analyzer was also not adjusted in the field using a PS-model traveling transfer standard. After the replacement there was better agreement between both of the ARS operated analyzers and between ROM406 and ROM206.

Both contractors met at the site a second time, in August 2012, to review monitoring methodology and for AMEC to install a duplicate analyzer at ROM206. The purpose of this meeting was to

compare the ARS and AMEC transfer standards to one another and to the site analyzers. Further comparisons were made using the different transfer standards at different settings with calibration lines of different inner diameters and different venting locations.

Testing was conducted using PS model and non-PS model transfer standards since ARS had used a PS model transfer previous to July 2012. Results indicated that greater pressure in the calibration line results in a greater imbalance in the detector cells and affects the performance of a PS model. Because the PS model uses an internal vent for the reference air, the sample and reference measurements can be made at different pressures. This pressure difference can be the result of smaller inner diameter calibration tubing (e.g., 3 millimeter), longer calibration tubing, or increased gas flow rate. In the 49i-PS, a positive sample to reference pressure differential leads to a higher indicated ozone concentration than what is actually generated. Transfer standards incorporating an internal scrubber (such as a non-PS model 49i) scrub sample air to generate reference air; therefore, the sample and reference measurements are always made at the same pressure. The inner diameter and length of the sample and calibration gas tubing does not affect the performance of a transfer standard if it is not a PS model. As a result, PS models will only be used in the future as traveling transfer standards if specific guidelines are followed. These guidelines will be defined in a Standard Operating Procedure document.

Review of Station Configuration

When necessary, CASTNET makes changes to its network to modernize and upgrade equipment and to keep current with evolving techniques and procedures. Historical changes specific to either of the collocated stations are listed in Table 1 below.

Table 1. Changes to site configurations at the EPA and NPS sites at Rocky Mtn National Park

Site ID	Change Date	Parameter	Description of change	Comments
ROM206	11/19/08	Datalogger	CR3000 datalogger installed. Wiring standardized.	
ROM206	11/11/09	Ozone	Prototype regulatory ozone site installed using ozone generator as site transfer standard.	
ROM206	7/6/10	Ozone	40CFR Part 58 ozone site installed using independent site transfer standard.	Match ROM406 setup. Initially Level 4 standard.
ROM206	11/6/10	Ozone	Ozone tubing changed from 3/8 inch to 1/4 inch.	Match ROM406 setup. I.D. of 206 tubing= 3mm. I.D. of 406 tubing = 3.96
ROM206	5/3/11	Ozone	Ozone sample line filter removed from inside the shelter.	Match ROM406 setup.
ROM206	5/4/11	Ozone	Upgrade completed to Level 3 site transfer standard.	
ROM206	5/7/12	Ozone	Replacement pressure transducer installed in site analyzer.	
ROM206	5/7/12	Ozone	10 ft. exhaust tubing added to both analyzers.	Run outside of shelter Match ROM406 setup.
ROM206	5/7/12	Ozone	Knock out bottle removed	Match ROM406 setup.
ROM406	7/12/12	Ozone	Duplicate ozone analyzer (ROM406-b) added to site for comparison study.	Thermo 49i
ROM406	7/23/12	Ozone	ROM406- Primary ozone analyzer	Thermo 49i

Site ID	Change Date	Parameter	Description of change	Comments
			replaced due to discrepancies with ROM406-b.	
ROM206	8/16/12	Ozone	Duplicate ozone analyzer (ROM206-b) added to site for comparison study.	Thermo 49i
ROM406	7/12/12	Ozone	Upgrade completed to Level 3 site transfer standard.	Match ROM206 setup.
ROM206	11/30/12	Ozone	Knock out bottle reintroduced to sample train.	Based on comparisons with ROM406 and ROM206-b, it was determined that the presence of the knockout bottle in-line had no effect on ambient concentrations.

As discovered during this bias investigation review, NPS and EPA ozone systems still have differences in configuration and procedures. Suggested activities for future comparisons are listed in Table 2 below.

Table 2. Recommended system testing

Test/Check/Activity	Current Status
Compare use of PFA Teflon tubing versus FEP Teflon tubing and tubing inner diameter size	Referred to the network reconciliation committee to determine a standard policy for use when tubing is replaced at a site
Consider use of an oxidizing agent versus charcoal-only in the zero air system	ARS is adding Purafil to canisters in its zero air systems
Ongoing intranetwork transfer standard comparison.	Meet at an eastern site for comparison. Perform periodic AMEC transfer comparison at ARS's laboratory and vice versa

Results since July 2012 at ROM406/206 site

In support of investigations initiated in July of 2012, a second analyzer was installed at each site. The data from all four analyzers from the two sites have correlated well (Figure 2) since July 2012, and the comparison between the primary site analyzers has improved following the replacement of the primary ozone analyzer at ROM406 in July 2012 (Figure 3).

Figure 2. Comparison of Site Analyzers (July 12 through September 20, 2012)

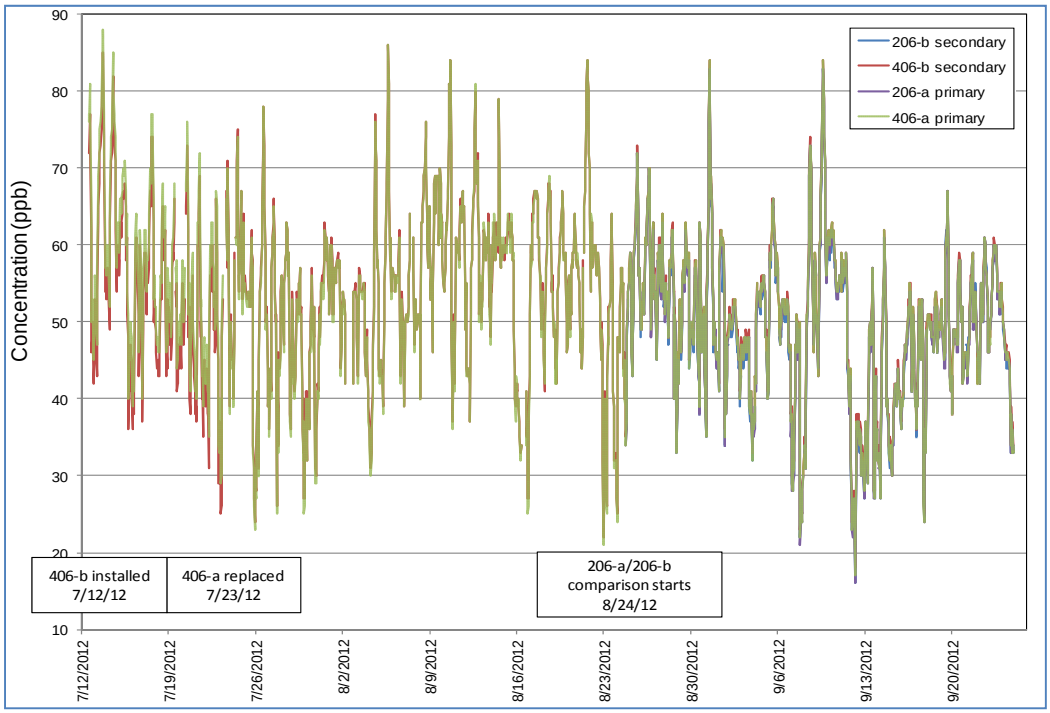
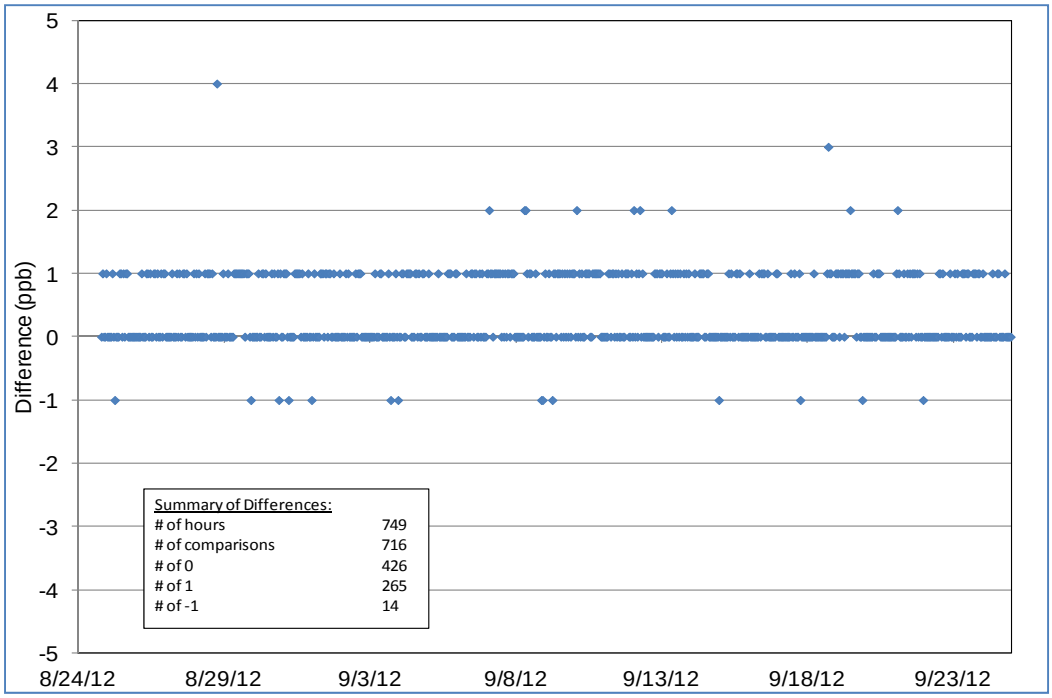


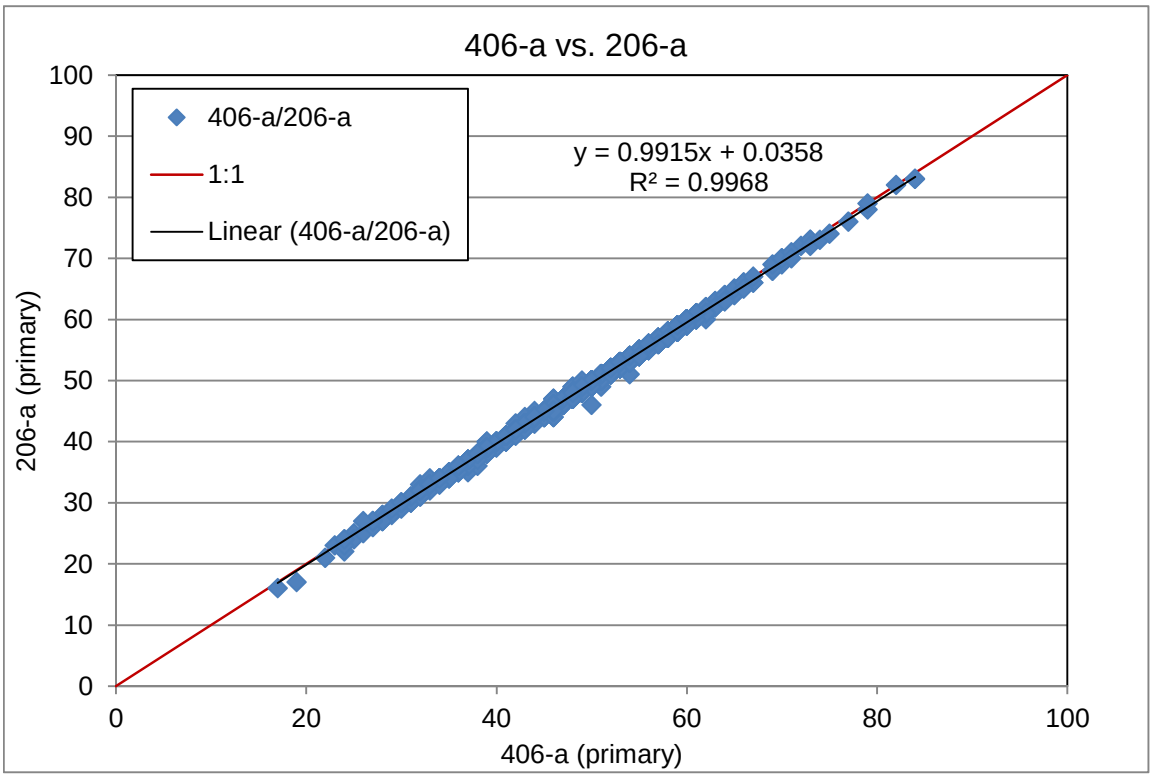
Figure 3. Difference (406-a minus 206-a) between Primary Analyzers



On-site changes were concluded by August of 2012. Prior to making these changes, the collocated stations disagreed on an hourly basis by 1-6 ppb with ROM406 consistently higher. Since these changes were put in place, the bias between the two ozone measurements has been approximately 0.5 ppb. Figure 4 presents a correlation between the two data sets since on-site consistency has been improved.

It should be noted that the differences in procedures that existed prior to July 2012 did not cause quality check failures based on the requirements described in the Code of Federal Regulations (CFR). Both sites passed their respective Performance Evaluations conducted by EEMS and the state of Colorado. ROM406 is considered the regulatory site for the designation of attainment. ROM206 is a special study (non-regulatory) site within AQS.

Figure 4. Correlation between primary analyzers for August 24, 2012 through September 24, 2012



Summary

Due to the historical bias in ozone measurements at the collocated Rocky Mountain National Park stations, a technical systems review was performed in an effort to understand and improve these differences. The data sets were reviewed in detail and periods that should have been invalidated were identified. To prevent validating periods of questionable data in the future, additional data validation steps have been adopted and applied to the data review process. This eliminated the largest discrepancies seen between the two sites, but it did not account for the nearly constant bias of 1-6 ppb. Further systems review included a comparison of on-site configurations and procedures. ARS and AMEC met at the site in 2011 and again in 2012 to perform these comparisons. Differences were identified and many have been resolved. Some inconsistencies still exist and future actions are recommended. However, ozone measurements have agreed well between the two stations since the summer of 2012, when numerous efforts were made to improve consistency and the technical systems review was concluded.

References

AMEC Environment & Infrastructure, Inc. (AMEC). 2013. Clean Air Status and Trends Network (CASTNET) Quality Assurance Project Plan (QAPP) Revision 8.1. Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, DC. Contract No. EP-W-09-028. Gainesville, FL. http://java.epa.gov/castnet/documents.do.

Environmental Protection Agency Clean Air Status and Trends Network Home Page. See http://epa.gov/castnet/javaweb/index.html (accessed October 2013).