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Environmental Technology Verification Report

Sunset Laboratory Model 4 OC-EC Field Analyzer

Prepared by

Battelle
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Under a cooperative agreement with

EPA **U.S. Environmental Protection Agency**

ETV ETV ETV

Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

Sunset Laboratory Model 4 OC-EC Field Analyzer

By

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Notice

Foreword

The EPA is charged by Congress with protecting the nation's air, water, and land resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development provides data and science support that can be used to solve environmental problems and to build the scientific knowledge base needed to manage our ecological resources wisely, to understand how pollutants affect our health, and to prevent or reduce environmental risks.

The Environmental Technology Verification (ETV) Program has been established by the EPA to verify the performance characteristics of innovative environmental technology across all media and to report this objective information to permitters, buyers, and users of the technology, thus substantially accelerating the entrance of new environmental technologies into the marketplace. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. ETV consists of six environmental technology centers. Information about each of these centers can be found on the Internet at http://www.epa.gov/etv/.

Effective verifications of monitoring technologies are needed to assess environmental quality and to supply cost and performance data to select the most appropriate technology for that assessment. Under a cooperative agreement, Battelle has received EPA funding to plan, coordinate, and conduct such verification tests for "Advanced Monitoring Systems for Air, Water, and Soil" and report the results to the community at large. Information concerning this specific environmental technology area can be found on the Internet at http://www.epa.gov/etv/centers/center1.html.

Acknowledgments

The authors wish to acknowledge the support of all those who helped plan and conduct the verification test, analyze the data, and prepare this report. Specifically the authors thank Andrea Polidori of the South Coast Air Quality Management District, Joann Rice of EPA Office of Air Quality Planning and Standards, and Zachary Willenberg, Battelle Quality Assurance Officer, for their review of this verification report.

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List of Abbreviations

AMS	Advanced Monitoring Systems Center
BC	black carbon
CO_2	carbon dioxide
csv	comma separated variable
CV	coefficient of variation
DL	detection limit
DQO	data quality objective
DRI	Desert Research Institute
EC	elemental carbon
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
FID	flame ionization detector
He	helium
IMPROVE	Interagency Monitoring of PROtected Visual Environments
KHP	potassium hydrogen phthalate
LAC	light absorbing carbon
LPM	liters per minute
MnO_2	mangenese oxide
$\mu g/m^3$	micrograms per cubic meter
μL	microliter
NDIR	non-dispersive infrared
NIST	National Institute of Science and Technology
OC	organic carbon
PE	performance evaluation
PM	particulate matter
ppm	parts per million
QA	quality assurance
QC	quality control
QMP	quality management plan
r^2	coefficient of determination
RISC	reduced instruction set computer
RPD	relative percent difference
TOR	thermal optical reflectance
TOT	thermal optical transmittance
TSA	technical systems audit

Chapter 1
Background

The U.S. Environmental Protection Agency (EPA) supports the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized testing organizations; with stakeholder groups consisting of buyers, vendor organizations, and permitters; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance and quality control (QA/QC) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The EPA's National Risk Management Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center recently evaluated the performance of the Sunset Laboratory Model 4 OC-EC Field Analyzer at an ambient air monitoring site in Columbus, Ohio. Black carbon (BC) monitors were identified as a priority technology category for verification through the AMS Center stakeholder process.

Chapter 2
Technology Description

The objective of the ETV AMS Center is to verify the performance characteristics of environmental monitoring technologies for air, water, and soil. This report provides results for the verification testing of the Sunset Laboratory Model 4 OC-EC Field Analyzer. The following is a description of the Model 4 OC-EC analyzer, based on information provided by the vendor. The information provided below was not verified in this test.

Sunset Laboratory's semi-continuous Model 4 OC-EC Field Analyzer has been developed as a field deployable alternative to integrated filter collection with subsequent laboratory analysis. This instrument can provide time-resolved analyses of organic carbon (OC) and elemental carbon (EC) in airborne particulate matter (PM) on a semi-continuous basis. A quartz filter disc is mounted in the oven within the instrument, and samples are collected for the desired time period. Once the collection is complete, the oven is purged with helium, and a stepped-temperature ramp based on the NIOSH 5040 reference method[1] increases the oven temperature to 840 °C, thermally desorbing organic compounds and pyrolysis products into a manganese dioxide (MnO_2) oxidizing oven. As the carbon fragments flow through the MnO_2 oven, they are quantitatively converted to carbon dioxide (CO_2) gas. The CO_2 is swept out of the oxidizing oven with the helium stream and measured directly by a self-contained non-dispersive infrared (NDIR) detector system. The analyzer oven is cooled to 550 °C then a second temperature ramp is initiated in an oxidizing (O_2 in helium) gas stream and any elemental carbon is oxidized off the filter and into the oxidizing oven and NDIR. The EC is then detected in the same manner as the OC.

The Sunset Laboratory thermal/optical/transmittance (TOT) method uses the high light absorbance characteristic of EC to correct for the pyrolysis-induced error. This is done by incorporating a tuned diode laser (red, 660 nm), focused through the sample chamber such that the laser beam passes through the mounted filter in the sample oven. Initial transmission of the modulated laser beam is recorded. As the oven ramp proceeds, the laser transmission is monitored continuously by the data system. Any charring of the OC results in a decrease in transmission of the laser. After the initial temperature ramp, when the helium carrier is switched to a He/O_2 mixture, all of the EC is oxidized off and the laser transmission returns to the background level. When the resulting NDIR data are reviewed with an overlay of the laser absorbance, the point in the temperature ramp at which the laser transmission equals the initial laser transmission is the split point. Any EC detected before this point was formed pyrolytically by charring of the OC. This carbon is subtracted from the EC area observed during the oxidizing phase of the analysis and is assigned as OC. The primary assumption for this correction is that the particulate bound EC and the pyrolytically formed EC either have the same absorption coefficient, or else the pyrolytically formed EC will oxidize earlier. Three characteristic components of the semi-continuous Model 4 OC-EC analyzer are important in the strength of the analysis. The first of these is the optical detection and correction for EC. Elemental carbon is naturally present in many of these samples from some combustion source such as a diesel exhaust. This black material is a very strong absorber of light, and almost always the only absorber in the red light region. In addition to this EC in the sample, EC can be formed from some charring of the OC fraction of the sample as it is pyrolyzed during the initial temperature ramp. This can begin occurring as low as 300 °C depending on the organic components on the filter. This charring of OC could result in an artificially low measurement of the OC and a higher than actual measurement for the original EC if no correction was made.

The second component of the Model 4 OC-EC analyzer is the use of a sensitive, linear detector for this measurement. Historically, this has been a flame ionization detector (FID). Recently Sunset Laboratory has introduced its own self-contained flow-through NDIR system. It is a RISC processor controlled pseudo-dual beam instrument with temperature stabilized source and a linearized signal output. The vendor indicates that calibrations can be used for up to a year. NDIR eliminates the requirement for air or hydrogen at the field site.

The third important component of the Model 4 OC-EC analyzer is the incorporation of a fixed volume loop used to inject an external standard at the end of every analysis. The resulting external standard data are incorporated into every data package and used along with the known carbon concentration in the loop to calculate the analytical results.

The Sunset Laboratory semi-continuous instruments monitor the sample deposition by measuring the change in laser transmittance over the sample period. This change in transmittance can be directly correlated to the deposition of elemental carbon. This optically derived elemental carbon or “OptEC” is computed using a proprietary equation to compensate for the non-linear effects of the highly scattering effects of the quartz filter. It is assumed that at the beginning of each sample collection period that there is no EC. The absorbance of the sample is determined from the transmittance where the initial laser is 100% T and the final laser/initial laser as the end of the sample collection is the final percent transmittance. Absorbance is then calculated from the %T.

$$\text{OptEC (ugEC/cm}^2\text{)} = \text{abs}^\wedge 2 * X_2 + \text{abs}* X_1 + X_0$$

Multiplication by the deposit area (cm^2) and division by the sample volume (M^3) yields the results in ugOptEC/M^3.

Figure 2-1. **Model 4 OC-EC field analyzer**

Chapter 3
Test Design and Procedures

3.1 Introduction

The ETV Program's AMS Center conducts third-party performance testing of commercially available technologies that detect or monitor natural species or contaminants in air, water, and soil. Stakeholder committees of buyers and users of such technologies recommend technology categories, and technologies within those categories, as priorities for testing. Among the technology categories recommended for testing are "black carbon" monitors. Because of the nature of BC, this technology category includes monitors for both BC and EC. Two stakeholders were selected to serve as peer reviewers for the quality assurance project plan (QAPP)[2] and this verification report. The responsibilities of verification test stakeholders/peer reviewers included:

- Participate in technical panel discussions (when available) to provide input to the test design;
- Review and provide input to the QAPP; and
- Review and provide input to the verification report/verification statement.

The QAPP and this verification report were reviewed by experts in the fields related to black carbon monitors. The following experts provided peer review:

- Andrea Polidori, South Coast Air Quality Management District
- Joann Rice, EPA.

The purpose of this verification test was to generate performance data on BC monitors so organizations and users interested in installing and operating these systems can make informed decisions about their use. Black carbon is a term that is commonly used to describe strongly light absorbing carbon (LAC), which is thought to play a significant role in global climate change through direct absorption of light, interaction with clouds, and by reducing the reflectivity of snow and ice. BC is formed from the incomplete combustion of fossil fuels, biofuels, and biomass and can be emitted from both anthropogenic and natural sources. It is a primary component of soot and has been linked to adverse health effects and visibility reduction. Consequently, there is a great deal of interest in monitoring BC in the atmosphere. However, differences in measurement techniques result in measurements that are operationally defined and characterize the particulate matter based on either its light absorbing properties (leading to determination of BC) or its refractory properties (leading to determination of EC), as illustrated in Figure 3-1. In this figure, the use of the subscript *a* denotes that the measurements are technique specific and result in estimations of BC or EC that are "apparent" based on the technique being used. The methods used to determine EC are termed thermal-optical in Figure 3-1 because they involve conversion of particulate carbon to gaseous form under varying temperatures and controlled atmospheres while the particulate sample is monitored by either transmission or reflection of light.

This verification test was conducted according to procedures specified in the peer-reviewed ETV *Quality Assurance Project Plan (QAPP) for Verification of Black Carbon Monitors.*[2] Deviations from this QAPP are described in Section 4.1 of this report.

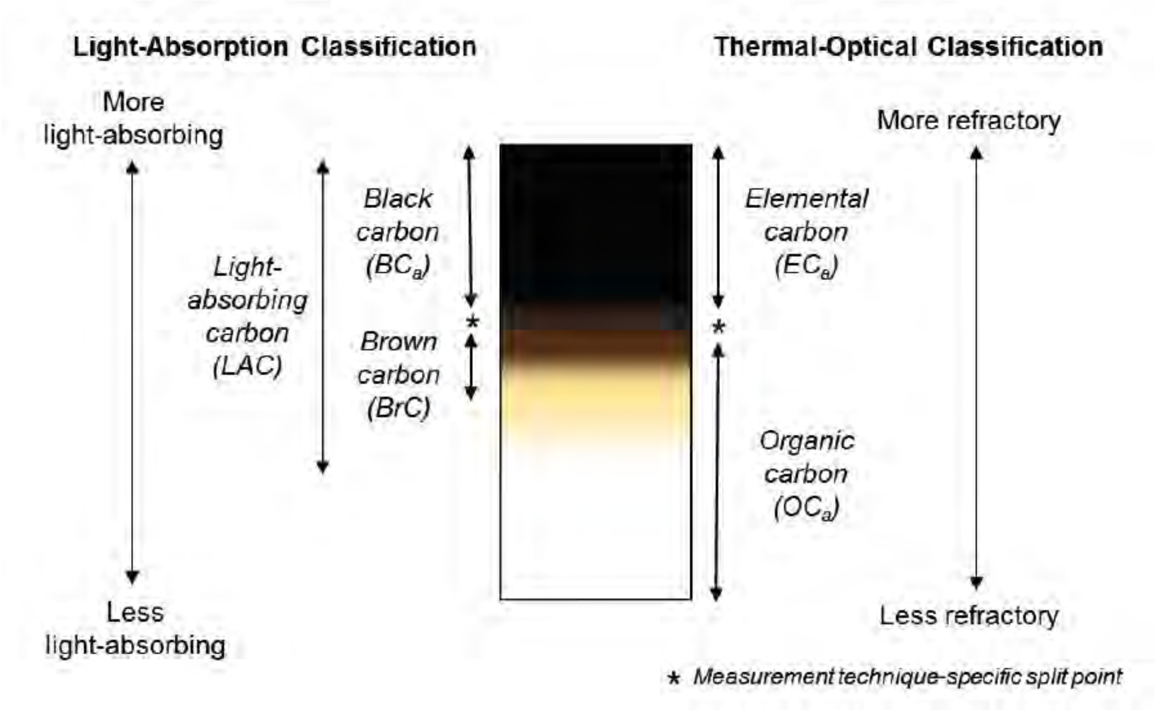

Figure 3-1. Illustration of measurements of carbonaceous particulate matter. (Source: U.S. EPA)[3]

The performance of the Model 4 OC-EC analyzer was verified by evaluating the following parameters:

- Comparability with collocated reference method results
- Correlation with collocated reference method results
- Precision between duplicate units
- Data completeness
- Operational factors such as ease of use, maintenance and data output needs, power and other consumables use, and operational costs.

3.2 Test Procedures

The test was conducted at the Battelle Columbus Operations Special Support Site (BCS3) located at 2555 International St., in Columbus, OH. For this test, duplicate Model 4 OC-EC monitors continuously sampled ambient air for approximately 33 days, during which period filter samples were collected on thirty days to use as a basis of comparison for the analyzers being tested. Specifically, during each test period duplicate integrated filter samples were collected over successive 12-hour periods each day (except as noted below) using commercially available air sampling equipment. The duplicate reference samples were collected from 7:00 am to approximately 6:50 pm and from 7:00 pm to approximately 6:50 am daily. From April 5 through April 25, a single four-channel Anderson Model RAAS-400 speciation sampler was used to collect the duplicate reference filter samples using separate channels of the sampler. Samples were not collected during one of the planned 12-hour sampling periods (beginning on the evening of April 16) because of adverse weather conditions. On April 25, a failure in the electronics of the RAAS sampler rendered it inoperable and the lack of replacement parts resulted in the RAAS being inoperable for the remainder of the test period. Duplicate BGI Model PQ200 samplers were immediately available and were used in replacement of the RAAS for the collection of the reference samples from April 26 to May 7.

The reference samples were collected on pre-cleaned quartz fiber filters at a nominal flow rate of 16.7 LPM with both the RAAS and BGI samplers. The change in samplers was not expected to result in any differences in the measured EC concentrations since the samples were collected at the sample flow rate and with similar $PM_{2.5}$ size selective inlets. Actual differences that may have been observed are likely the result of differences in the calibrated flow rates of the samplers. Over the 33-day field period, a total of 118 filter samples were successfully collected (i.e., duplicate samples during 59 of the 60 12-hour sampling periods).

The reference samples were analyzed for EC by Desert Research Institute (DRI) using the DRI Model 2001 EC-OC analyzers implementing the Interagency Monitoring of PROtected Visual Environments (IMPROVE) thermal/optical reflectance (TOR) method, which monitors the filter sample by means of optical reflectance.[4] DRI also reported EC results from the IMPROVE method with the filter monitored by thermal/optical transmission (TOT).[4] Results from the Model 4 OC-EC analyzers were compared to these filter sample results to assess the comparability of the Model 4 OC-EC analyzer results to the filter sample results.

The precision of the Model 4 OC-EC analyzers was determined from comparisons of paired data from the duplicate units. Other performance parameters such as data completeness, maintenance requirements, ease of use, and operational costs were assessed from observations by the Battelle field testing staff. This test was not intended to simulate long-term (e.g., multi-year) performance of BC monitors. As such, performance and maintenance issues associated with long-term use of the Model 4 OC-EC analyzers are not addressed in this report.

Note that in this report the filter samples will be referred to as “reference samples.” However, it should be noted that the IMPROVE method is not a true “Reference Method” in that it is not recognized as an absolute standard. Nonetheless, it is used within the IMPROVE network as the standard method for EC analysis. Thus the method was used in this test as an analytical technique used for comparison to the BC monitors. Other thermal/optical reference methods such as the NIOSH 5040 method may result in different results.

For the verification test, duplicate Model 4 OC-EC analyzers were installed inside an environmentally controlled instrument trailer at the BCS3 ambient air monitoring site in Columbus, OH. The two Model 4 OC-EC units were installed by the vendor and were operated continuously over the 33-day testing period. Trained Battelle testing staff performed periodic maintenance activities on the analyzers. These activities were documented and are reported in Section 6.5 of this report. The two analyzers collected ambient air through a common inlet protected by a rain guard. The RAAS-400 and the duplicate PQ200 samplers were installed on the platform such that each inlet was more than one meter from the inlet. The sample air flow passed through an organic vapor denuder, and then was split in two to pass through separate $PM_{2.5}$ cyclone separators before entering the analyzers. The analyzers were programmed on a two hour measurement cycle which included 108 minutes of sample collection and 12 minutes of thermal sample analysis using the NIOSH 5040 analysis profile. The cycles were timed to allow synchronization with the 12-hour reference method sampling periods. These two-hour cycle thermal measurements for OC and EC were reported by the two Model 4 OC-EC analyzers corrected to standard temperature and pressure (25 ºC and 1 atmosphere), along with minute-by-minute optical EC measurements made by the two analyzers.

3.3 Field Site

Figure 3-2 shows an aerial photograph of the BCS3 facility test site (red marker "A") and the surrounding area. The test site is located approximately ½ mile north of a rail yard and in the vicinity of multiple industrial and shipping facilities which result in frequent truck traffic past the site. The site also receives regionally transported air pollution due to its location on the western side of the Columbus metropolitan area. An environmentally controlled mobile laboratory was installed at the site to serve as a shelter for the Model 4 OC-EC analyzers and as work space for the testing staff. Figures 3-3 and 3-4 show the sampling trailer with RAAS sampler and BGI samplers, respectively, installed on a platform next to the trailer.

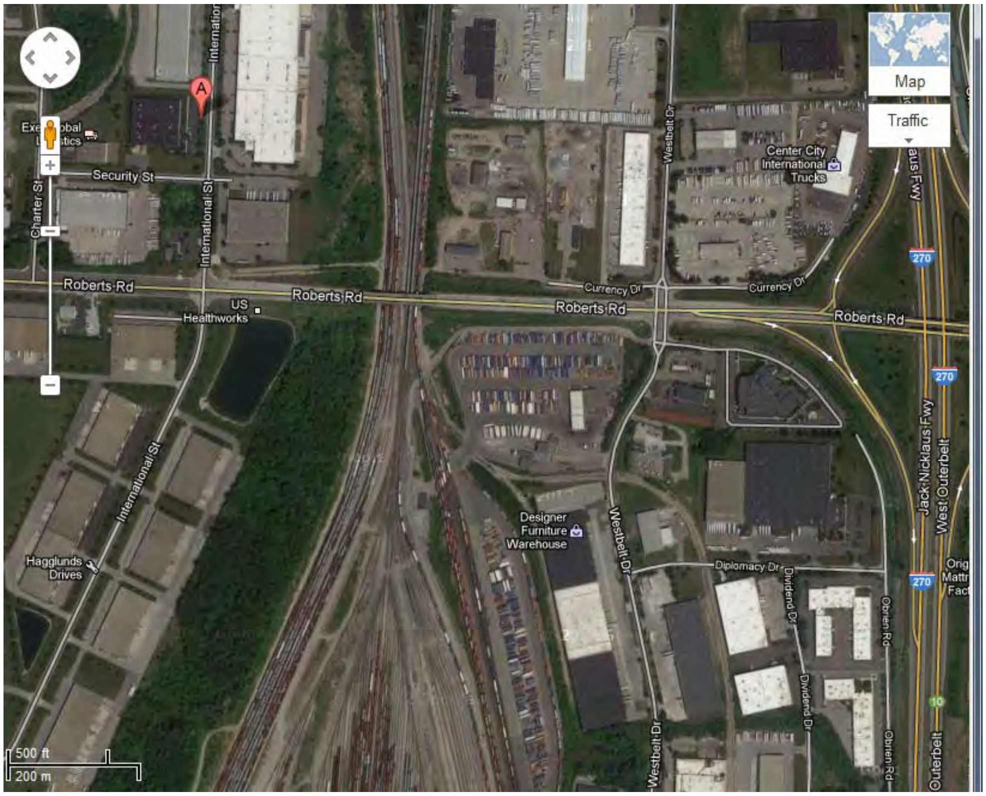

Figure 3-2. Aerial photograph of test site and surrounding area.

Figure 3-3. RAAS reference sampler installed at sampling site.

Figure 3-4. BGI PQ200 reference samplers installed at sampling site.

Chapter 4
Quality Assurance/Quality Control

QA/QC procedures and all verification testing were performed in accordance with the QAPP for this verification test[1] and the quality management plan (QMP) for the AMS Center[4] except where noted below. QA/QC procedures and results are described below. Other than an initial flow check during installation of the Model 4 OC-EC analyzers no additional QA/QC activities were performed on the Model 4 OC-EC analyzers. Maintenance activities performed on the Model 4 OC-EC analyzers is included in Section 6.5.1.

4.1 Amendments/Deviations

Two deviations to the test/QA plan were prepared, approved, and retained in the test documentation. The deviations established the following modification to the test/QA plan and the test procedures:

- The RAAS speciation sampler was replaced with duplicate BGI PQ200 samplers approximately half way through the sampling period because of a failure in the RAAS sampler. This change did not adversely affect the data quality since the new samplers functionally performed the same as the RAAS samplers. See Section 4.2.1 for a comparison of the results from the two sampler types.
- Routine flow checks were not performed as specified in the test plan for a portion of the test period. This deviation is not expected to adversely affect the results since subsequent leak checks met the acceptance criteria and no systemic bias was observed in the reference results.

4.2 Reference Method

The following sections describe the QA/QC procedures employed in the collection and analysis of reference samples. Only the results for the EC analyses are presented since OC results are not used to evaluate the performance of the Model 4 OC-EC Analyzers.

4.2.1 Reference Method Sampling

This verification test included a comparison of Model 4 OC-EC Analyzers results to those of the reference measurements described in Section 3.2. Figures 4-1 and 4-2, respectively, show the results of the TOR and TOT measurements of the duplicate reference samples collected during the testing period. In these figures, one of the two channels used in the RAAS for the collection of the reference samples was designated as the "primary sample" and the other channel was designated as the "collocated sample" to show potential biases between the two channels.

Similarly, one of the BGI samplers was designated as the "primary sample" and the other as the "collocated sample." Figures 4-3 and 4-4 show the corresponding differences between the primary and collocated reference sample measurements and indicate that there is no clear systematic bias observed in either the TOR or TOT results for either the RAAS sampler or the duplicate BGI samplers.

During the verification test the mean of the EC measurements for the duplicate reference samples ranged from <1.5 to 32.9 micrograms per filter (μg/filter) which corresponds to airborne concentrations ranging from <0.13 to 2.7 micrograms per cubic meter ($\mu g/m^3$) based on the sample volumes of ~12 m^3. According to DRI's documentation, at concentrations of greater than 10 times the method detection limit (10 x MDL ~1.5 μg/filter) the expected precision between duplicate samples is ~ 10%.[3] In general, the majority of the reference samples had EC concentrations that were below 10 times the MDL, consequently the percent difference between the duplicate samples was typically greater than 10%. Reference results that were reported as less than the MDL were assigned a value of ½ MDL for this report. Over all results with both reference sampler types, the calculated percent differences (i.e., the difference between the two duplicate results divided by their mean) ranged from -98% to 109%, with an average of 3%. The EC concentrations measured from the filters collected with the RAAS sampler ranged from <0.13 to 1.1 $\mu g/m^3$, with a mean concentration of 0.35 ± 0.28 $\mu g/m^3$. The average percent difference between the duplicate samples collected with the RAAS was 21% ± 71%. The EC concentrations measured from the filters collected with the BGI PQ200 samplers ranged from <0.13 to 2.7 $\mu g/m^3$, with a mean concentration of 0.64 ± 0.62 $\mu g/m^3$. The average percent difference between the duplicate samples collected with the BGI samplers was 1% ± 50%.

Figure 4-5 shows a scatter plot of the TOR results for the reference method samples indicating in which sampler type used to collect the filters (e.g., RAAS and BGI PQ200). Figure 4-6 presents a similar plot for the TOT analyses. These figures show that the TOT results exhibit a slope closer to 1.0, an intercept closer to zero, and a higher r^2 value, relative to the TOR results.

During testing a total of 12 reference method field blank samples were collected, representing 10% of the total reference method samples. The field blanks were installed in the filter cassettes and loaded into the reference method samplers without drawing air through the filters. Table 4-1 presents a summary of the field blank results including the results for the EC measurements for both the TOR and TOT analyses by the DRI Model 2001 analyzer. Table 4-1 shows that in all cases the measured EC on the reference method blank filters was below the detection limit of 1.5 μg/filter.

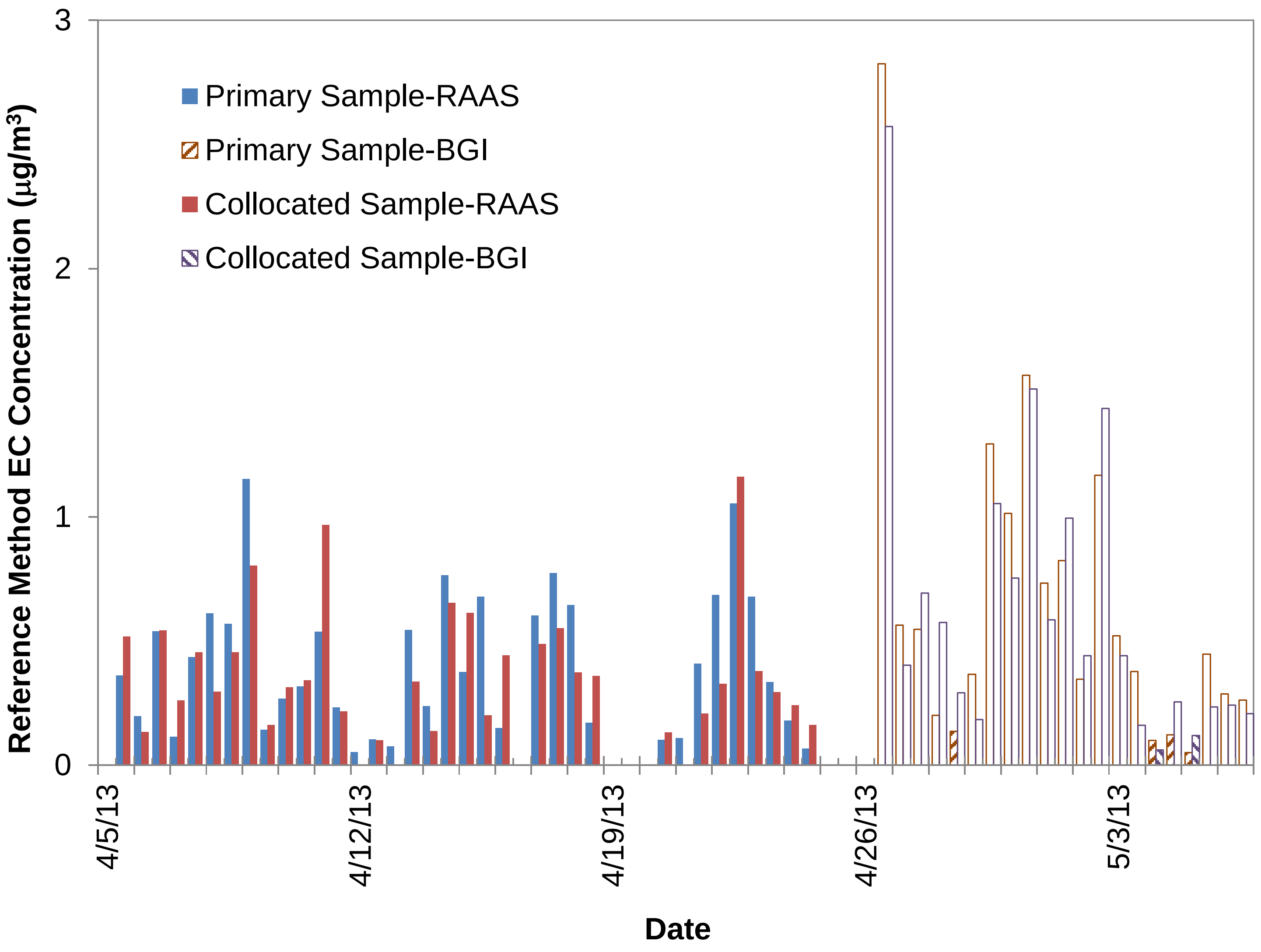

Figure 4-1. Duplicate Reference Method EC results from TOR analysis.

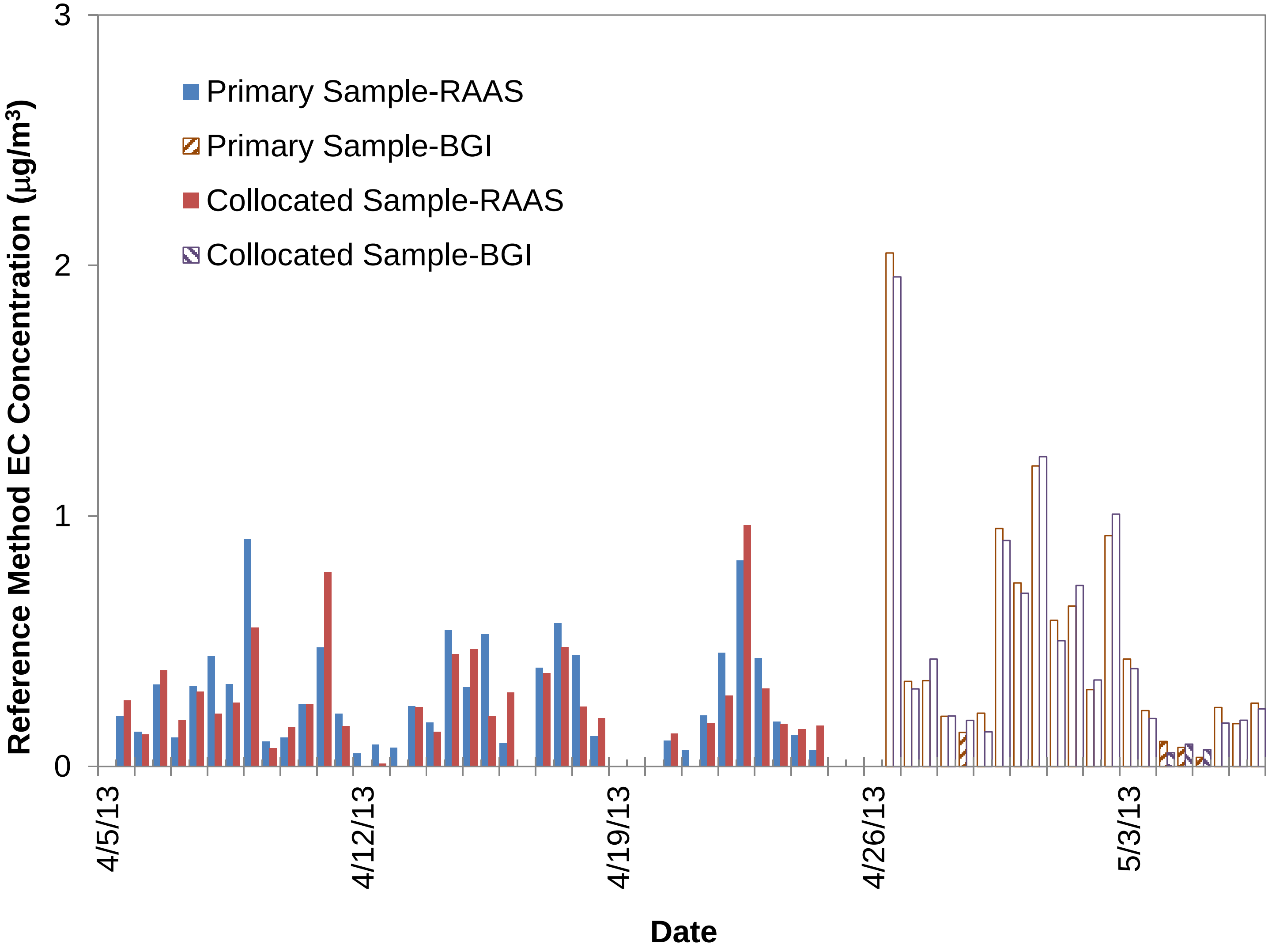

Figure 4-2. Duplicate Reference Method EC results from TOT analysis.

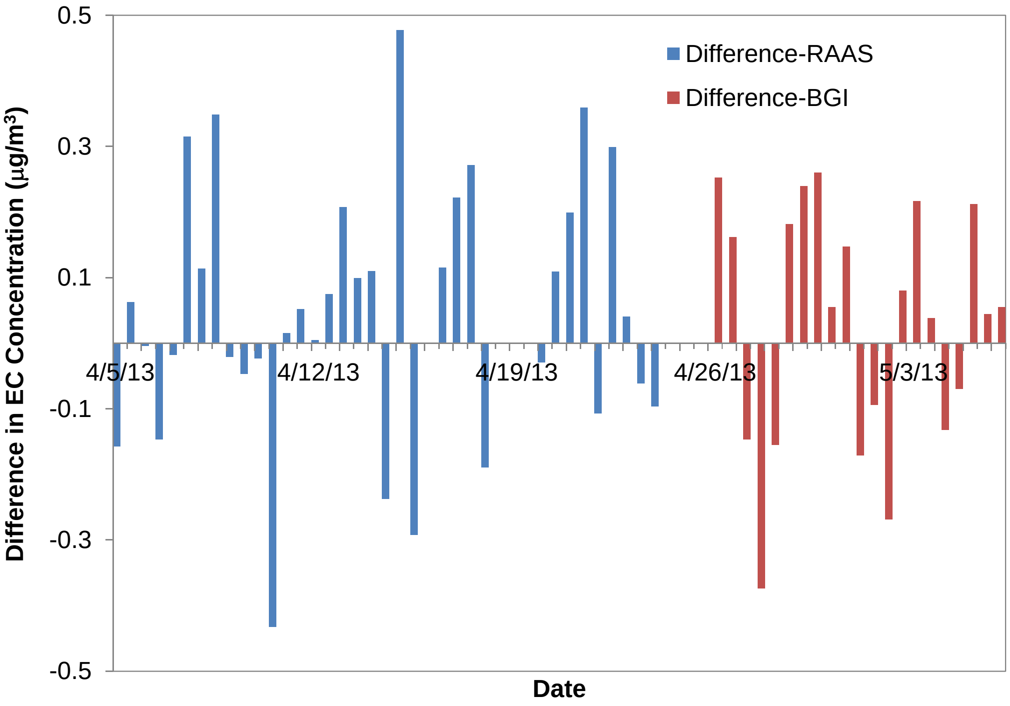

Figure 4-3. Differences between the duplicate reference method EC results from TOR analysis

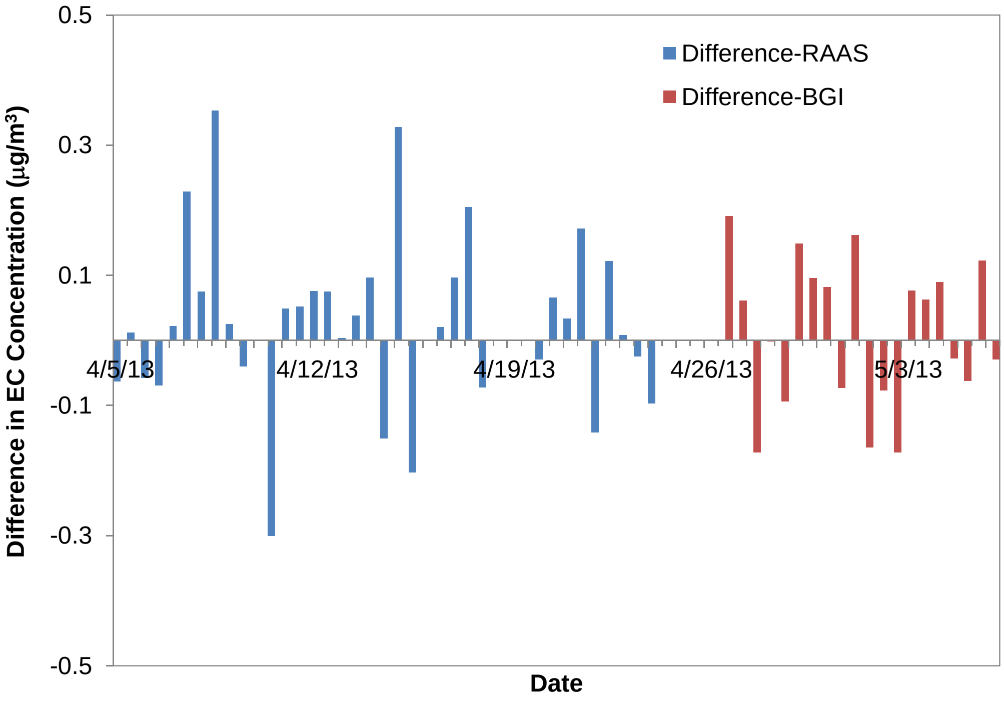

Figure 4-4. Differences between the duplicate reference method EC results from TOT analysis

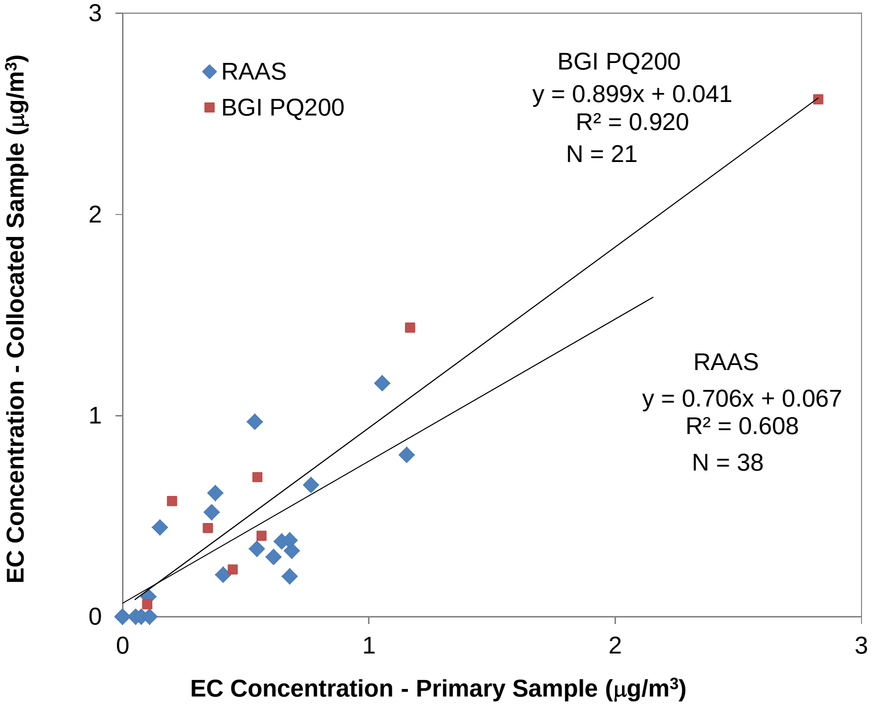

Figure 4-5. Regression of reference method results from TOR analysis by sampler type.

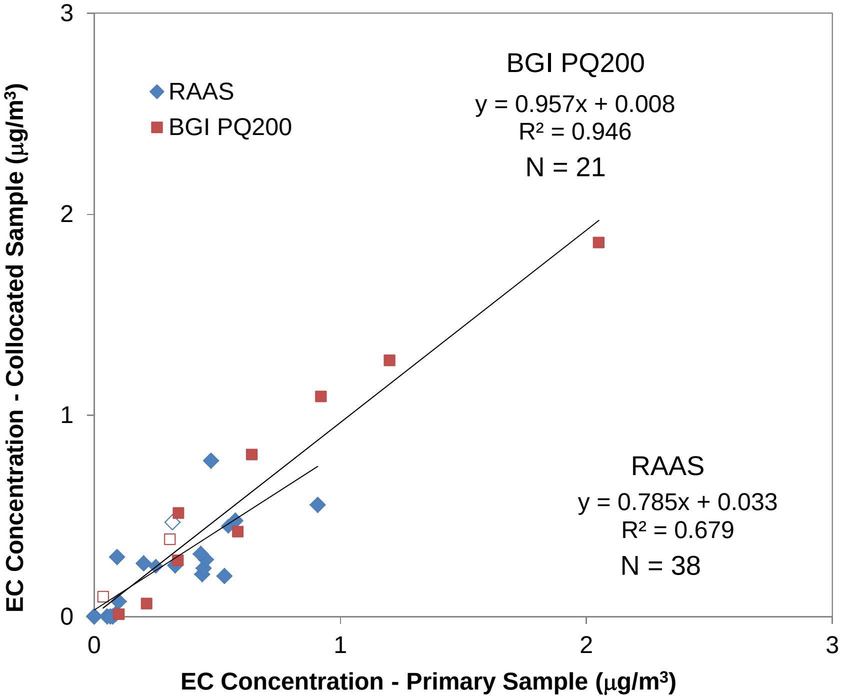

Figure 4-6. Scatter plot of reference method results from TOT analysis by sampler type.

Additionally, flow rate checks of the reference samplers were performed at least every three days during the sampling period to ensure that the reference samplers were operating within 5% of their nominal flow rate.

Table 4-1. Summary of Reference Method Field Blank Results

Filter ID	**EC (µg/filter)**	
	TOR	**TOT**
BTOQ001	0.00	0.00
BTOQ002	0.00	0.00
BTOQ011	0.05	0.00
BTOQ055	0.00	0.00
BTOQ072	0.00	0.00
BTOQ073	0.00	0.00
BTOQ074	0.00	0.00
BTOQ075	0.00	0.00
BTOQ090	0.00	0.00
BTOQ097	0.00	0.00
BTOQ109	0.00	0.00
BTOQ110	0.10	0.00

4.2.2 Reference Method Analysis

Routine calibrations of the DRI Model 2001 carbon analyzers used to analyze the reference samples were performed at the beginning and end of each day by injecting known volumes of either CH_4 or CO_2 with nominally the same amount of carbon (approximately 21.4 µg) and comparing the resulting OC3 and EC1 measurements[4]. The acceptable level is ±5% difference between peaks injected during the OC3 and EC1 temperature step. Table 4-2 presents a summary of these routine calibrations for each of the carbon analyzers (identified as uniquely numbered CA units below) and the calculated percent differences between carbon measurements from the OC3 and EC1 measurements for each calibration. Exceedences of the acceptance criterion require recalibration of the analyzer.

Table 4-2. Auto-Calibration Results of DRI EC/OC Analyzer.

	OC3 (µg)								
Date	**CA#6**	**CA#7**	**CA#8**	**CA#9**	**CA#10**	**CA#11**	**CA#12**	**CA#13**	**CA#16**
4/23/2013	21.80	20.90	22.35	20.22	21.67	21.08	21.06	22.59	17.67
5/17/2013			20.10	22.33		21.89	21.10		22.50
5/18/2013		22.75	20.31	22.37		21.87	21.17		22.37
5/20/2013			20.27	22.29			21.01		22.39
5/21/2013	19.46			22.24	21.15	21.85	21.00		22.41
	EC1 (µg)								
	CA#6	**CA#7**	**CA#8**	**CA#9**	**CA#10**	**CA#11**	**CA#12**	**CA#13**	**CA#16**
4/23/2013	21.11	20.53	22.02	20.78	21.29	20.91	20.94	21.40	19.48
5/17/2013			20.26	22.04		21.27	21.00		21.43
5/18/2013		22.31	20.09	22.00		21.17	20.82		21.40
5/20/2013			20.25	21.95			20.94		21.46
5/21/2013	20.10			22.00	21.70	21.24	20.92		21.52
	%Diff								
	CA#6	**CA#7**	**CA#8**	**CA#9**	**CA#10**	**CA#11**	**CA#12**	**CA#13**	**CA#16**
4/23/2013	3.3%	1.8%	1.5%	-2.7%	1.8%	0.8%	0.6%	5.6%	-9.3%
5/17/2013			-0.8%	1.3%		2.9%	0.5%		5.0%
5/18/2013		2.0%	1.1%	1.7%		3.3%	1.7%		4.6%
5/20/2013			0.1%	1.5%			0.3%		4.3%
5/21/2013	-3.2%			1.1%	-2.5%	2.9%	0.4%		4.1%

[*] CA#16 was taken offline on 4/23/2013 for FID and laser issues.

†Missing values indicate the instruments were offline during the day.

Full instrument calibrations are performed semiannually or after major maintenance or repairs and are used to establish the calibration slope used in converting CO_2 detector counts to µg of carbon. Four types of standards are used for full instrument calibration: 5% nominal methane (CH_4) in helium (He), 5% nominal CO_2 in He, potassium hydrogen phthalate (KHP), and sucrose. Instrument calibration involves spiking pre-fired quartz punches at four different levels from 5.0 to 20.0 microliters (µl) of the 1,800 parts per million (ppm) KHP and sucrose solutions and injecting CH_4 and CO_2 gases at four levels from 200 to 1,000 µL. The calibration slopes derived from the two gases and the KHP- and sucrose-spiked filter punches are averaged together to yield a single calibration slope for a given analyzer. This slope represents the response of the entire analyzer to generic carbon compounds and includes the efficiencies of the oxidation and methanator zones and the sensitivity of the FID. Table 4-3 presents a summary of the recent full calibrations of the analyzers used to analyze the reference samples. Note that the treatment of the calibration data ensures that the data passes through the origin, so no intercept is presented. The calculated slopes are compared to previous calibration results and should be with 10% of previous calibrations if no major changes to the instrument have been made. If the differences in the slope exceed 10%, the calibration must be repeated to verify the results.

Table 4-3. Full Calibration Results used for DRI Analyzers

Analyzer	Date	Slope	r^2
CA#6	4/3/2013	21.482	0.991
CA#7	5/7/2013	19.436	0.976
CA#7	4/26/2013	22.000	0.996
CA#7	10/11/2012	20.513	0.986
CA#8	5/13/2013	20.094	0.981
CA#8	12/7/2012	20.483	0.987
CA#9	4/18/2013	22.040	0.988
CA#10	5/21/2013	21.457	0.982
CA#10	5/4/2013	23.228	0.996
CA#10	3/29/2013	20.502	0.991
CA#11	3/14/2013	21.320	0.987
CA#12	4/1/2013	20.904	0.989
CA#13	11/19/2012	20.818	0.985
CA#16	3/10/2013	22.685	0.987

The instrument calibration was verified several times a week using sucrose and KHP standards near the midpoint of the calibration curve (18 μgC). Table 4-4 presents a summary of the calibration checks performed. In all cases the agreement between the measured and standard concentration was within the ±1 μgC acceptance criterion.

Table 4-4. Results of Periodic Calibration Checks

Date	CA#6	CA#8	CA#9	CA#10	CA#11	CA#12	CA#13	CA#16
4/23/2013	18.718	17.729	18.441	17.450	18.119	17.876	18.071	17.761
5/17/2013		17.433	17.783		18.149	17.688	17.749	18.104
5/20/2013		17.505	17.447		18.439	17.692		18.595
5/21/2013		17.739	17.523	17.223	17.332	17.402		18.147

†Missing values indicate the instruments were offline during the day.

Temperature calibrations are performed at least semiannually on all instruments to verify that the sample temperature is as accurate as possible. Quick-drying temperature-indicating liquids of different melting points, TempilaqºG (Tempil, Inc., South Plainfield, NJ, USA), were used as temperature indicators. Temperature indicators of 121, 184, 253, 510, 704, and 816 ºC were chosen for the IMPROVE_A protocol temperature calibration. The accuracy of TempilaqºG is certified within 1% of its designated temperature and is traceable to the National Institute of Standards and Technology (NIST). Table 4-5 shows the results of the most recent temperature calibrations of the analyzers used to analyze the reference samples. In all cases the linear relationship between the thermocouple and standard TempilaqºG values met the $r^2 > 0.99$ acceptance criterion.

Table 4-5. Temperature Calibration Results

	Date	Slope	Intercept	r^2
CA#6	11/26/2012	1.016	8.3	0.999
CA#6	5/16/2013	1.027	19.0	0.999
CA#7	4/29/2013	1.041	8.9	0.991
CA#7	6/3/2013	1.01	3.0	1.000
CA#8	12/7/2012	1.018	5.8	1.000
CA#8	5/13/2013	1.037	7.6	0.997
CA#9	4/5/2013	1.012	8.7	0.999
CA#9	4/22/2013	1.026	1.8	0.999
CA#10	2/19/2013	1.015	8.0	0.999
CA#11	3/15/2013	1.019	11.7	0.999
CA#12	2/25/2013	1.02	7.1	1.000
CA#13	11/19/2012	1.012	9.7	0.999
CA#13	5/21/2013	0.995	12.7	0.999
CA#16	3/11/2013	1.012	11.2	1.000

System blanks were performed once a week without filter punches in the analyzer to determine the instrument baseline. Calculated carbon concentrations from the system blank should not be more than 0.2 μg carbon. Table 4-6 presents a summary of the EC system blank results for the analyzers used to analyze the reference samples. Table 4-6 shows that the great majority of the EC system blanks showed no detectable carbon, and all EC blanks easily met the 0.2 μgC acceptance criterion.

Table 4-6. System Blank Results

	EC (μg)							
	CA#6	**CA#8**	**CA#9**	**CA#10**	**CA#11**	**CA#12**	**CA#13**	**CA#16**
4/28/2013	0.000	0.000	0.003		0.000	0.000	0.000	
5/5/2013	0.000	0.000	0.000		0.000		0.000	0.000
5/12/2013	0.002			0.068	0.000	0.000	0.000	0.000
5/19/2013		0.000	0.000		0.000	0.000		0.000
5/26/2013	0.004	0.000	0.000	0.000	0.000	0.000		

[*] System blanks on 5/12/2013 were high due to instruments being idle for the weekend and subsequent laboratory blank checks indicated normal conditions.

Laboratory blanks were performed daily to check for system contamination and evaluate laser response. If total carbon exceeded 0.2 μgC, values were voided and additional laboratory blanks were run after performing the oven bake procedure until the system is clean (i.e., OC < 0.2 μg C/cm^2 and no EC). Analyzers exceeding the limit for laser drift, reflectance, transmittance, total carbon, and calibration peak area after three laboratory blank runs must be taken offline for maintenance. Table 4-7 presents the results of the laboratory blanks for the analyzers used to analyze the reference samples. One of the analyzers (CA#7) repeatedly failed the blank check and was taken offline on 5/18/2013 for maintenance.

Table 4-7. Laboratory Blank Results

	EC (μg)								
	CA#6	**CA#7**	**CA#8**	**CA#9**	**CA#10**	**CA#11**	**CA#12**	**CA#13**	**CA#16**
4/23/13	0.000		0.000	0.000	0.000	0.000	0.000	0.000	0.000
5/17/13			0.000	0.000	0.000	0.000	0.000	0.000	0.000
5/18/13		0.017	0.000	0.000			0.000		0.000
5/20/13	0.063	0.005	0.000	0.000	0.000	0.000	0.003		0.000
5/21/13	0.000	0.000	0.011	0.000	0.012	0.000	0.021		0.005

CA#7 was taken offline for 5/18/2013.

Replicates of analyzed samples were performed at the rate of one per group of ten samples. The replicate was selected randomly and run immediately after each group of ten was completed. The random analyzer for the replicate was identified using a chart created in Microsoft Excel using the random number generator, which results in replicate analysis on the same and different analyzers. The μg/cm^2 values for EC were compared with the original run for both the TOR and TOT analysis. Precision was determined from replicate measurements as the average fractional difference between original and replicate analysis concentrations. Concentration uncertainty is the fractional precision times sample concentration. If sample concentration times fractional precision is zero, then the detection limit is used as concentration uncertainty. Table 4-8 shows the results of the replicate analyses. The results of the replicate analyses ranged from 0% to 52% for the TOR analysis and from 0% to 36% for the TOT analysis. In general, the percent difference exceeded the goal of 15% for the majority of the duplicate analyses indicating a lower degree of data quality than desired.

4.3 Audits

Three types of audits were performed during the verification test: a performance evaluation (PE) audit of the reference method sampling, a technical systems audit (TSA) of the verification test performance, and a data quality audit. Audit procedures are described further below.

4.3.1 Performance Evaluation Audit

A PE audit of the RAAS reference method sampler was performed by measuring the sample flow rate through the two channels used for collection of the reference samples. The flow rate through each channel was measured using a NIST-traceable flow transfer standard (BIOS DryCal, Serial No. 103777). After installation of the BGI PQ200 samplers, the flow rates of those samplers were audited using a BGI DeltaCal calibrator (Serial No. 001255). The results of those checks are summarized in Table 4-9, and indicate that the sampler flow rates were well within the target ±5% tolerance of the nominal 16.7 L/min flow rate.

Table 4-8. Replicate EC Analysis Results

	Run 1	
Filter ID	**TOR**	**TOT**
BTOQ037	6.97	4.55
BTOQ041	7.77	6.06
BTOQ107	2.55	1.89
BTOQ114	3.81	3.00
BTOQ133	4.37	2.43
BTOQ086	4.33	2.52
BTOQ055	0.00	0.00
BTOQ057	5.22	4.17
BTOQ081	8.21	6.09
BTOQ009	3.44	1.99
BTOQ078	4.76	3.30
BTOQ095	8.68	6.91
	Run 2	
BTOQ037	5.85	3.76
BTOQ041	6.40	5.21
BTOQ107	1.50	1.46
BTOQ114	4.38	3.93
BTOQ133	3.89	2.50
BTOQ086	3.47	1.76
BTOQ055	0.00	0.00
BTOQ057	3.96	3.23
BTOQ081	6.96	4.43
BTOQ009	3.27	2.03
BTOQ078	6.16	3.81
BTOQ095	7.50	6.08
	Percentage Diff.	
BTOQ037	17.5%	19.0%
BTOQ041	19.3%	15.1%
BTOQ107	52.1%	25.8%
BTOQ114	14.0%	26.9%
BTOQ133	11.8%	3.1%
BTOQ086	22.1%	35.5%
BTOQ055	0.0%	0.0%
BTOQ057	27.3%	25.3%
BTOQ081	16.5%	31.6%
BTOQ009	5.2%	2.1%
BTOQ078	25.6%	14.2%
BTOQ095	14.7%	12.7%

Table 4-9. Summary of Flow Rate PE Audit

Date	Reference Sampler	Measured Flow (L/min)	Difference from Nominal
4/5/13	RAAS – Channel 1	16.63	-0.6%
	RAAS – Channel 4	16.67	0.0%
4/26/13	BGI – Sampler 1	16.82	0.9%
	BGI – Sampler 2	16.83	1.0%

Additionally, the temperature and pressure sensors of the reference samplers were audited using NIST-traceable transfer standards. A summary of those audit results are shown in Table 4-10 and indicate that both the temperature and pressure sensors in the reference samplers were within the acceptance criteria for the verification test (i.e., ± 2ºC for temperature, and ± 5 mmHg for pressure).

Table 4-10. Summary of Temperature and Pressure PE Audit

Date	Reference Sampler	Sampler Temp. (ºC)	Audit Temp. (ºC)	Sampler Pressure (mmHg)	Audit Pressure (mmHg)
4/5/13	RAAS	15.3	15.6	--	--
4/8/13	RAAS	--	--	736	736
4/26/13	BGI – Sampler 1	12.6	12.1	749	749
	BGI – Sampler 2	13.0	12.8	748	749

4.3.2 Technical Systems Audit

A Battelle QA Officer performed one TSA as part of this verification test. The TSA was performed at the BCS3 site in Columbus, OH. The TSA focused on observation of the reference method sampling and field QA/QC procedures in preparation for the field test. The purpose of the audit was to ensure that the verification test was being performed in accordance with the AMS Center QMP, and the test/QA plan for this verification test. In the audit, the Battelle QA Officer observed the reference method sampling and sample recovery, compared the actual test procedures being performed to those specified or referenced the test/QA plan, reviewed data acquisition and handling procedures, inspected documentation of reference sample chain of custody, performance of flow, pressure, and temperature PE audits, and reviewed test record books. One finding and five observations were noted requiring two deviations. The first deviation pertained to leak checks not occurring at the recommended frequency after each flow check. The VTC started performing leak checks after each flow check. It is not expected that the failure to conduct the leak checks had a substantial impact on the results since subsequent leak checks passed the acceptance criteria and there were no systemic biases between the reference results prior to conducting regular leak checks. The second deviation was to address the change from the Anderson RAAS to the two BGI PQ 200 samplers. While not a finding, this deviation was necessary to document the change in samplers and did not impact the quality of results. The remaining observations noted were minor and did not impact the quality of results.

4.3.3 Data Quality Audit

At least 10% of the data acquired during the verification test were audited. Battelle's Quality Manager traced the data from the acquisition, through reduction and statistical analysis, to final reporting, to ensure the integrity of the reported results. All calculations performed on the data undergoing the audit were checked and QC results verified. Corrections from the other vendor report were made to the Magee data prior to QA review, resulting in minor comments. A few data issues were noted in the data quality audit, with minimal to no effect on the overall quality of the verification results.

4.4 QA/QC Reporting

Each audit was documented in accordance with Sections 3.3.4 and 3.3.5 of the QMP for the ETV AMS Center.[6] The results of the audits were submitted to the EPA.

4.5 Data Review

All data received from DRI for the reference measurements underwent 100% review and validation by Battelle technical staff before being used for any statistical calculations. This review included a review of the data files containing the measured EC values from the individual thermal steps for each filter and tracing of the calculated total EC measurements for both the TOR and TOT methods. The Model 4 OC-EC Analyzer data were reviewed to ensure that the minute by minute data were appropriately averaged into hourly and 24-hour values. Based on review of Model 4 OC-EC Analyzer data files and operator logs, a small number of 2 hour measurements were missing because of instrument maintenance activities. Those data are detailed in Section 6.5.1. All reference data were found to be valid and were included in the data analysis.

Records generated in the verification test received a one-over-one review (e.g., review by staff not involved in the generation of the record, but with at least the same technical expertise as the person generating the record) before these records were used to calculate, evaluate, or report verification results. Data were reviewed by a Battelle technical staff member involved in the verification test. The person performing the review added his/her initials and the date to a hard copy of the record being reviewed.

Chapter 5
Statistical Methods

The statistical methods used to evaluate the quantitative performance factors listed in Section 3.1 are presented in this chapter.

5.1 Comparability

The Model 4 OC-EC analyzers were evaluated for comparability in two ways. Firstly, comparability was determined from a linear least squares regression analysis of the measured EC concentrations from the Model 4 analyzers against the corresponding mean EC results from the duplicate reference samples. Separate analyses were performed for the thermal EC and optical EC results of the Model 4 analyzers. For comparison to the reference results, average concentrations from each of the analyzers were determined separately for each of the 12-hour sampling periods, by averaging the monitor's individual 2-hour results over the corresponding sampling period. The analyzers that were tested were set such that the measurement times were synchronized with the reference measurements to the extent possible. The 12-hour EC averages from the two Model 4 OC-EC analyzers were plotted against the mean of the corresponding duplicate reference method EC measurements. The slope and intercept of these plots were determined from a linear regression analysis and reported independently for each of the monitors.

Additionally, comparability was determined in terms of the relative percent difference (RPD) between the mean value of the reference measurements and the results from each Model 4 OC-EC analyzer tested. The RPD was calculated using Equation 1:

$$RPD = \frac{1}{n}\sum_{i=1}^{n}\frac{C_i - \overline{C(ref)_i}}{C(ref)_i}\cdot 100 \qquad (1)$$

where: C_i is the average EC concentration measured by the analyzer during the i^{th} reference sampling period, and

$\overline{C(ref)}_i$ is the mean of the duplicate reference method EC concentrations for the i^{th} reference sampling period.

5.2 Correlation

The degree of correlation of the results from each Model 4 OC-EC analyzer to the reference method results was determined based on the coefficient of determination (r^2) of the linear regression performed to assess comparability (Section 5.1). Correlation was determined separately for each unit of each analyzer undergoing testing, and relative to the results from the reference method.

5.3 Precision

Precision (P) was determined based on a comparison of paired measurements from the duplicate analyzers being tested. For this assessment of precision, the P between the paired measurements from the duplicate analyzers was calculated using Equation 2:

$$P = \frac{1}{n}\sum_{i=1}^{n} \frac{\left|C(1)_i - C(2)_i\right|}{[C(1)_i + C(2)_i]/2} \tag{2}$$

where $C(1)_i$ and $C(2)_i$ are the EC concentrations measured by the first and second of the two duplicate analyzers. Precision was calculated for the duplicate analyzers for each reference sampling period, and the overall mean precision was also calculated. For this calculation, measurement data below the vendor's stated instrumental detection limit was excluded from the analysis.

5.4 Data Completeness

Data completeness was assessed in two ways, based on the overall data return achieved by each analyzer during the testing period. First, for each of the analyzers data completeness was calculated as the total hours of apparently valid data reported by the monitor divided by the maximum total possible hours of monitoring data in the entire field period. Also, for each analyzer data completeness was calculated as the percentage of 12-hour reference method sampling periods in which the analyzer provided at least 9 hours of valid data (75%). The causes of any substantial incompleteness of data return were established from operator observations or vendor records, and noted in the discussion of data completeness results.

5.5 Operational Factors

Operational factors such as maintenance needs, data output, consumables used, ease of use, repair requirements, etc., were evaluated based on observations recorded by Battelle staff, and explained by the vendor as needed. A laboratory record book was maintained at the test site, and was used to enter daily observations on these factors. Examples of information recorded in the record book include the daily status of units, maintenance performed, and observations recorded during the installation and removal of the units.

Chapter 6
Test Results

Figure 6-1 shows the results of the 2-hour thermal EC measurements from the duplicate Model 4 OC-EC analyzers for the verification testing period. Investigation of the raw data files indicated that beginning on 4/28/13 at 15:00 (indicated by the vertical dashed line) and continuing through the end of the test period, an anomalous spike in the optical reference signal occurred in the raw data for one of the two duplicate analyzers being tested (RT3219). This spike occurred consistently in the time segment between 238 and 258 seconds of the thermal analysis. This reference signal is measured at a wavelength where no CO_2 absorption occurs and serves as a baseline for correction of the measurement channel signal. The recurring spike in the reference channel resulted in a positive bias in the measured thermal EC concentrations for that analyzer only, which can be observed in Figure 6-1 as a divergence of the traces from the two analyzers over the last 9 days of the test.

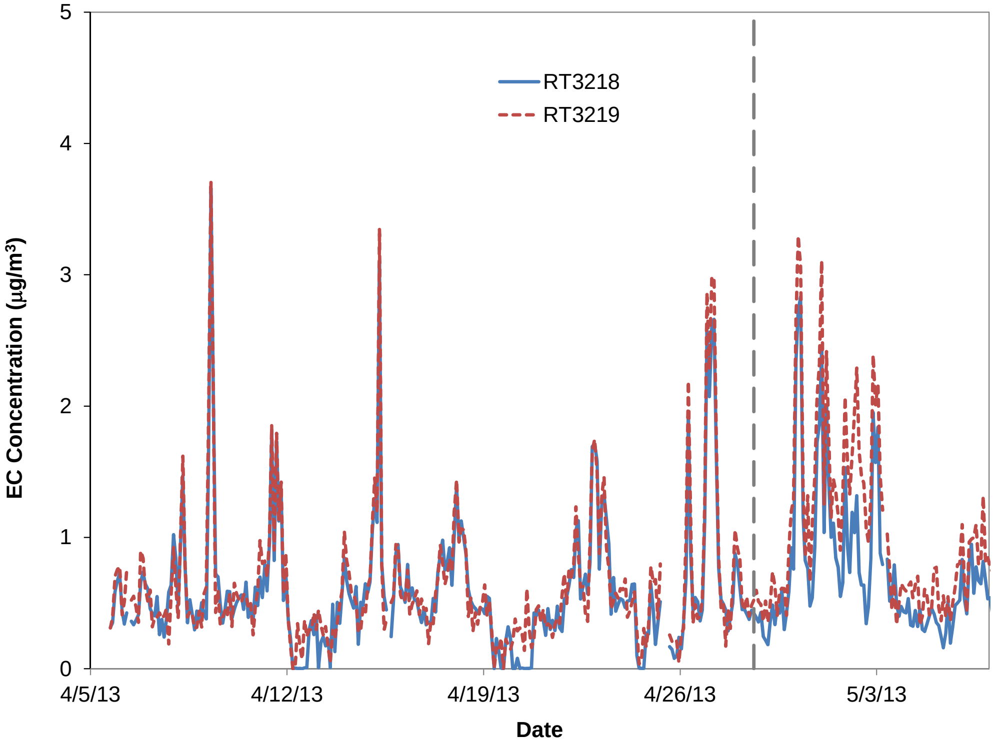

Figure 6-1. Measured 2-hour average thermal EC concentration from the duplicate Model 4 OC-EC analyzers during testing.

Prior to that time period, the 2-hour EC results from the two analyzers were more closely in agreement.

The cause of this anomaly in the RT3219 reference signal could not be identified or reproduced once the analyzers were returned to the vendor facility. To correct this anomaly, the vendor replaced the values in the raw reference channel data file with the average of the values recorded from 234 to 237 seconds (i.e., just prior to the spike) in the same file. This correction was done only for the one analyzer that exhibited the anomaly (RT3219). Both the raw and corrected values for the thermal EC measurements are presented in this report along with the optical EC measurements recorded by the analyzer. Figures 6-2 and 6-3 show the corrected thermal EC data and the optical EC data for the two analyzers. Figure 6-2 shows that the correction applied to the RT3219 analyzer results in improved agreement of the 2-hr thermal EC traces from the two analyzers for the last 9 days of the testing period.

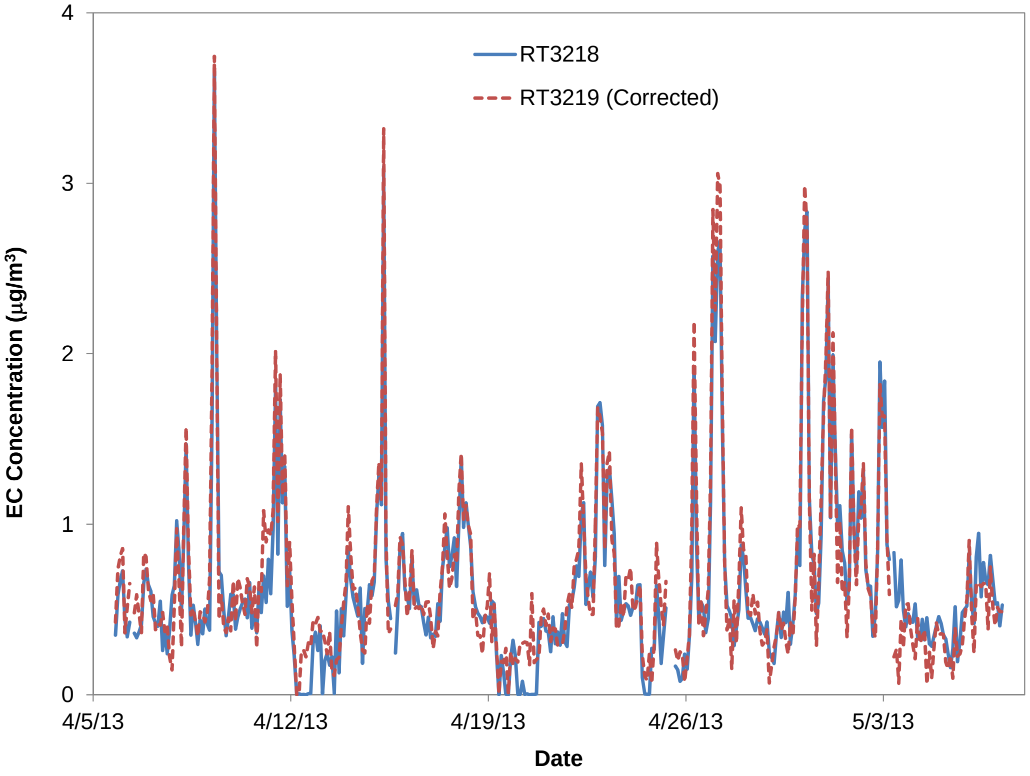

Figure 6-2. Measured 2-hour average corrected thermal EC concentration from the duplicate Model 4 OC-EC analyzers during testing.

The calculated differences (expressed in terms of RT3218 – RT3219) are presented in Figure 6-4, for both the raw and the corrected data. The raw data show a sharp divergence between the two analyzers after 4/28/13.

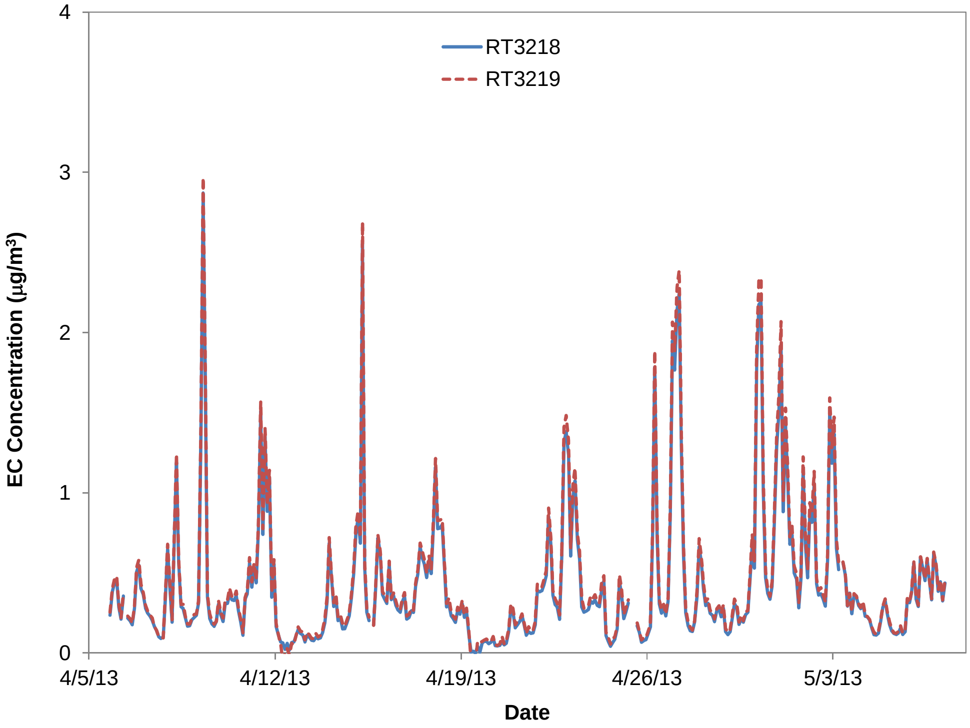

Figure 6-3. Measured 2-hour average optical EC concentration from the duplicate Model 4 OC-EC analyzers during testing.

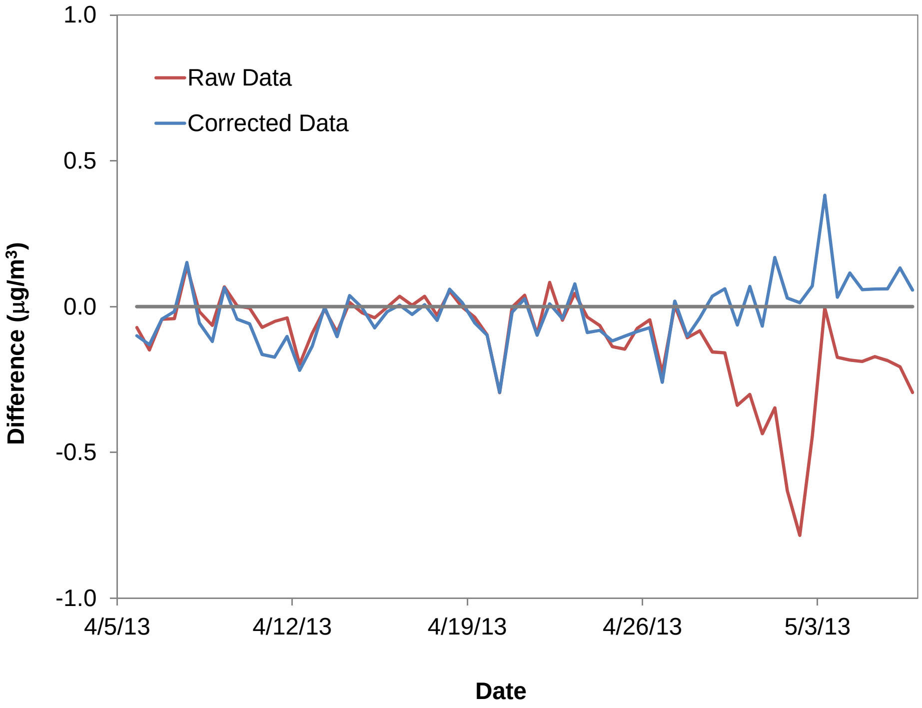

Figure 6-4. Calculated differences between the hourly average EC concentration from the duplicate Model Model 4 OC-EC analyzers during testing (Difference = SN 3218-3219 - SN 90) .

6.1 Comparability

The comparability of the Model 4 OC-EC analyzers with the reference method was determined in two ways. Firstly, comparability was determined from a linear least squares regression analysis of the EC concentrations measured by the Model 4 OC-EC units and by the reference methods as described in Section 5.1.1. Also, comparability was determined from the RPD of the Model 4 OC-EC data and the mean of the reference method data for each sampling period, as described in Section 5.1.2. For these calculations, the 12-hour results for the Model 4 analyzers were calculated as the averages of the 2-hour readings collected during the respective reference method periods. Comparability was determined independently for both the raw thermal data and the corrected thermal data from the Model 4 OC-EC analyzers as well as for the optical EC measurements of the Model 4 OC-EC analyzers. In each case the comparability was calculated with respect to both the TOR and TOT reference method results. The results of these analyses are presented below.

Figures 6-5 shows a time series plots of the mean TOR reference method EC results and the corresponding 12-hour average uncorrected Model 4 OC-EC thermal EC results. Figure 6-6 shows the same time series plot, but using the corrected thermal EC data from the Model 4 unit RT3219. Similarly, Figures 6-7 and 6-8 show the time series plots of the mean TOT reference method results with the corresponding 12-hour average uncorrected and the corrected Model 4 OC-EC thermal EC results. Figures 6-9 and 6-10 show time series plots of the TOR and TOT reference method results with the corresponding 12-hour average Model 4 OC-EC optical EC results. The dates shown correspond to the start of the respective sampling periods, with the first sampling period beginning on April 5 at 7:00 pm and ending on April 6 at 6:50 am.

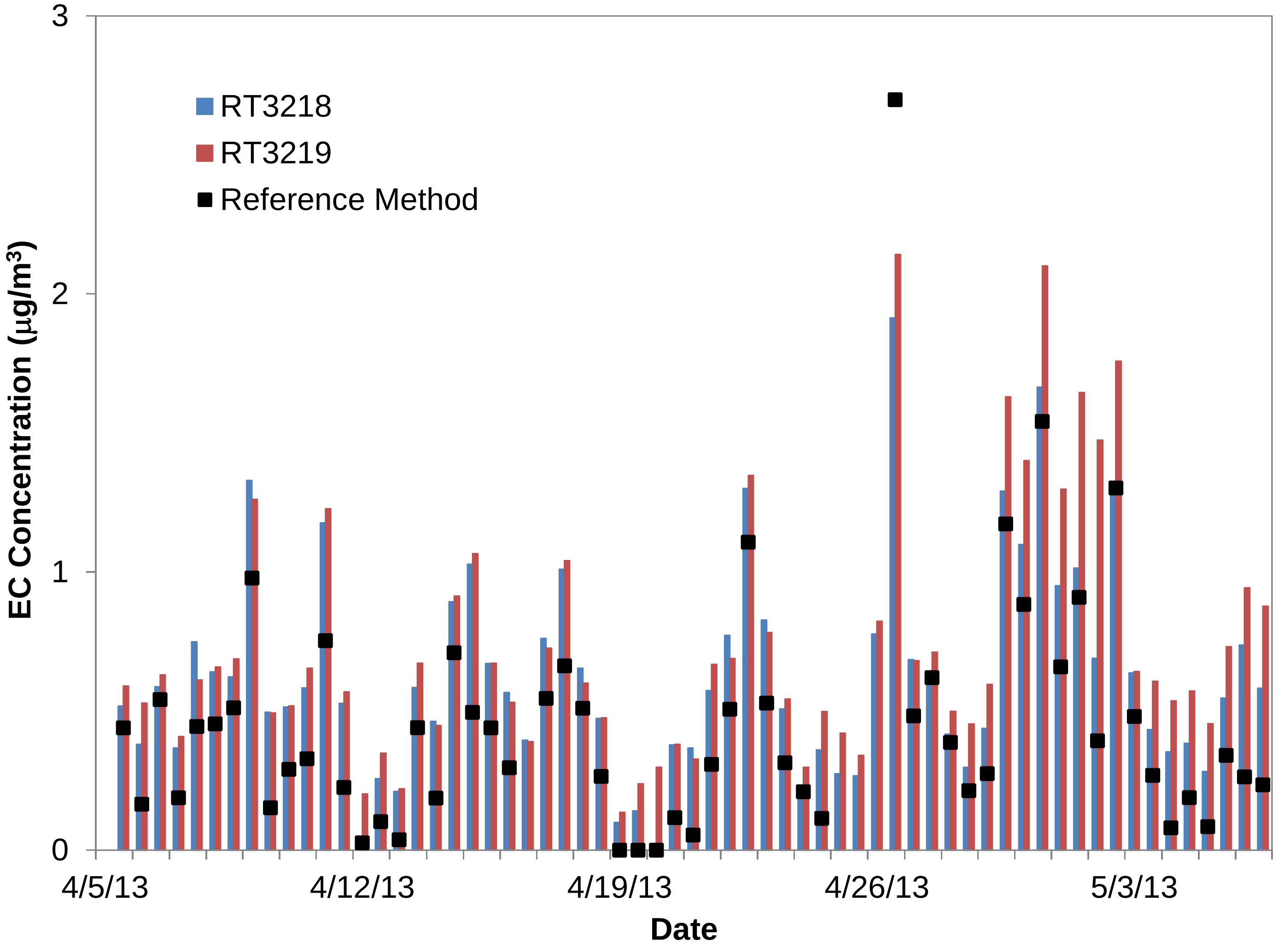

Figure 6-5. Comparison of uncorrected thermal EC results from the Model 4 OC-EC analyzers and the mean reference method TOR EC concentrations.

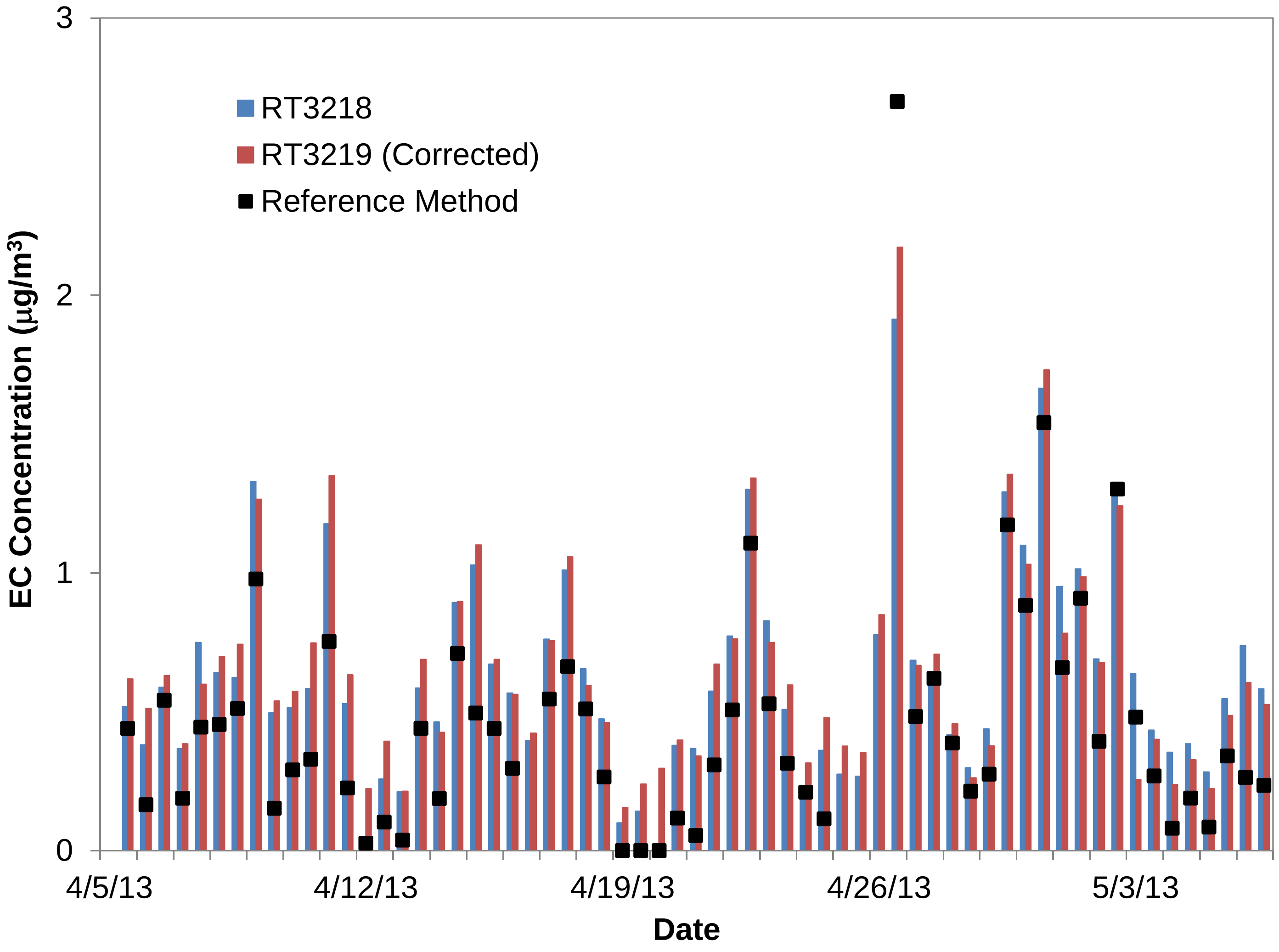

Figure 6-6. Comparison of corrected thermal EC results from the Model 4 OC-EC analyzers and the mean reference method TOR EC concentrations.

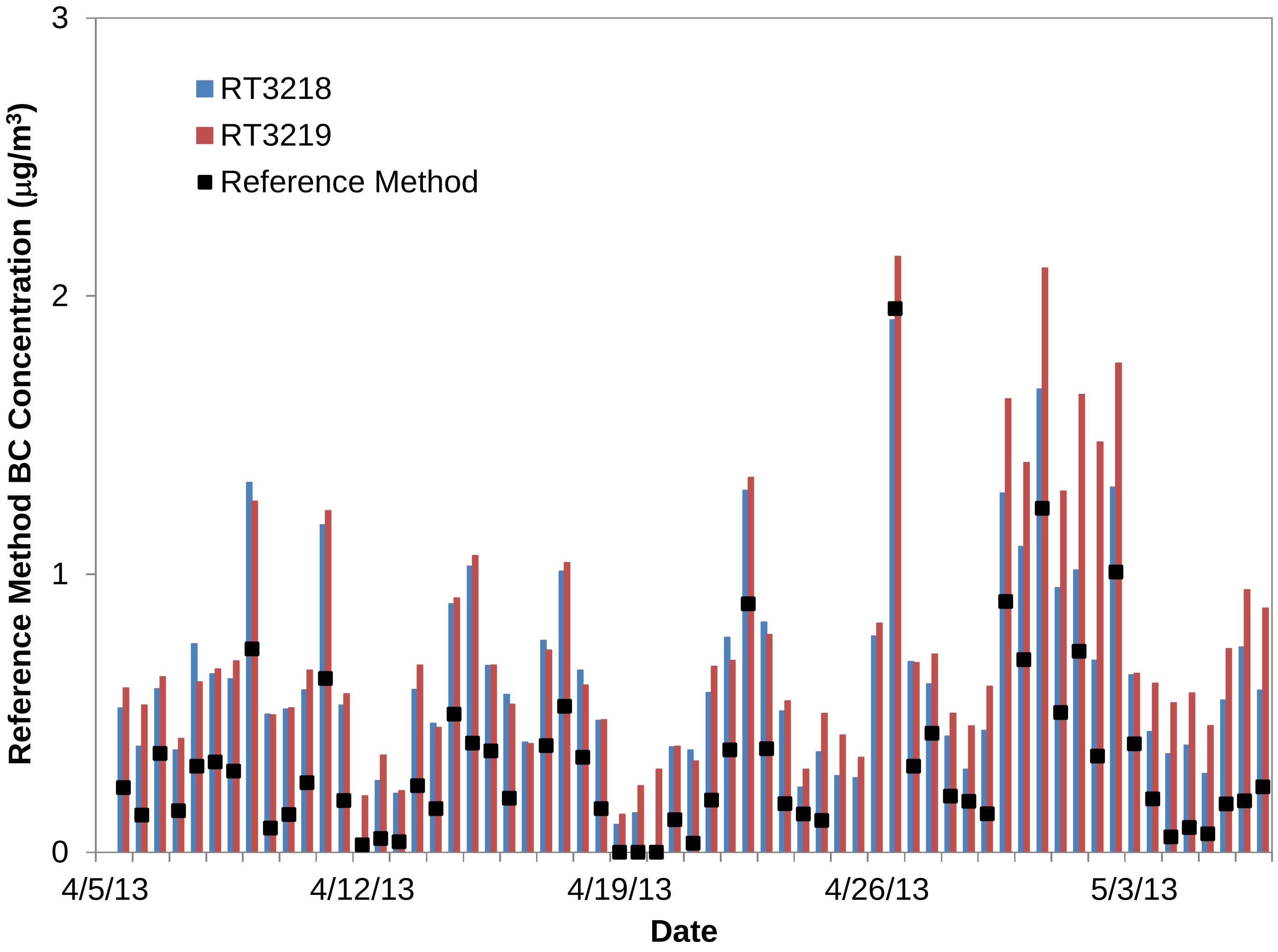

Figure 6-7. Comparison of uncorrected thermal EC results from the Model 4 OC-EC analyzers and the mean reference method TOT EC concentrations.

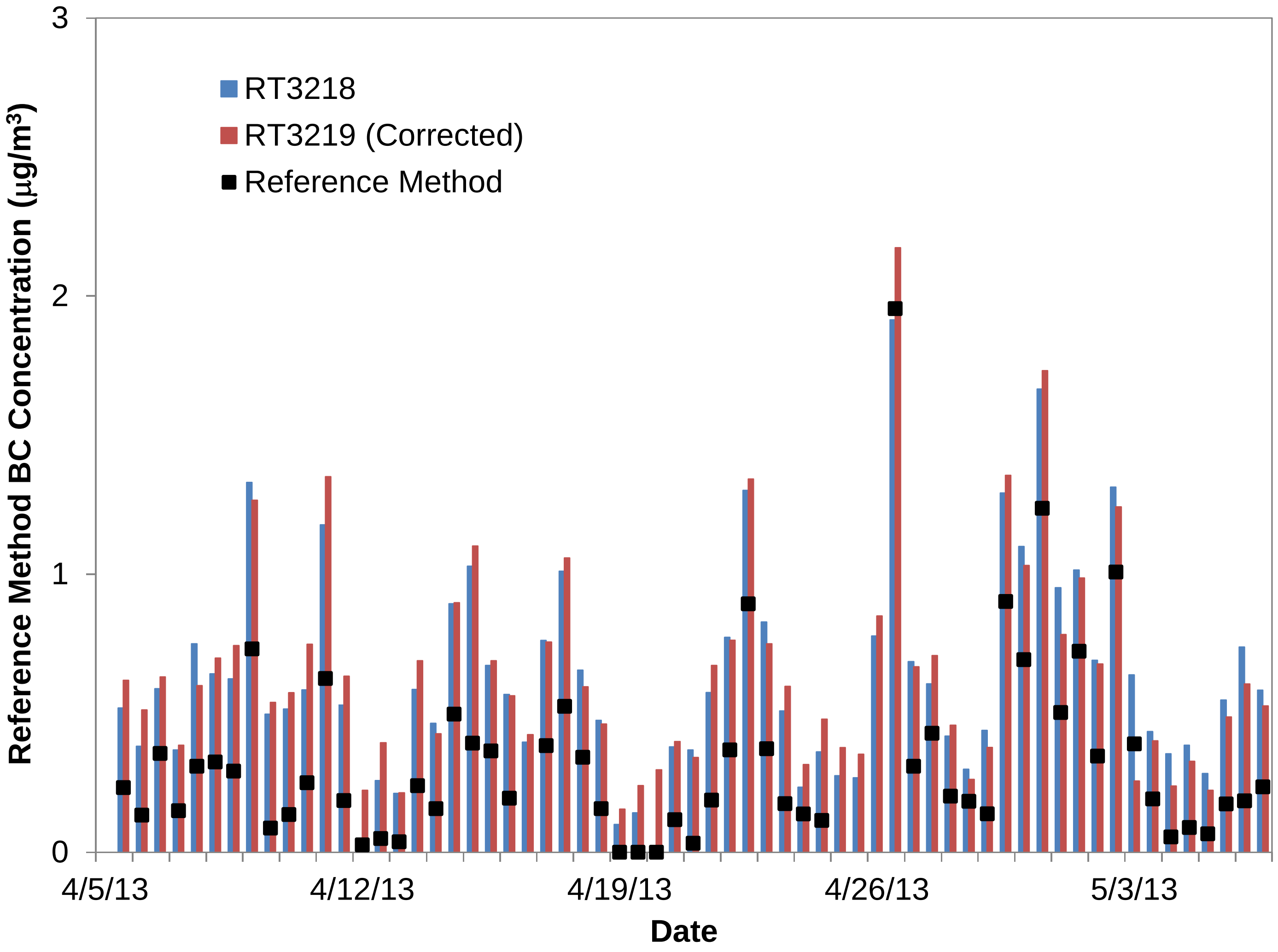

Figure 6-8. Comparison of corrected thermal EC results from the Model 4 OC-EC analyzers and the mean reference method TOT EC concentrations.

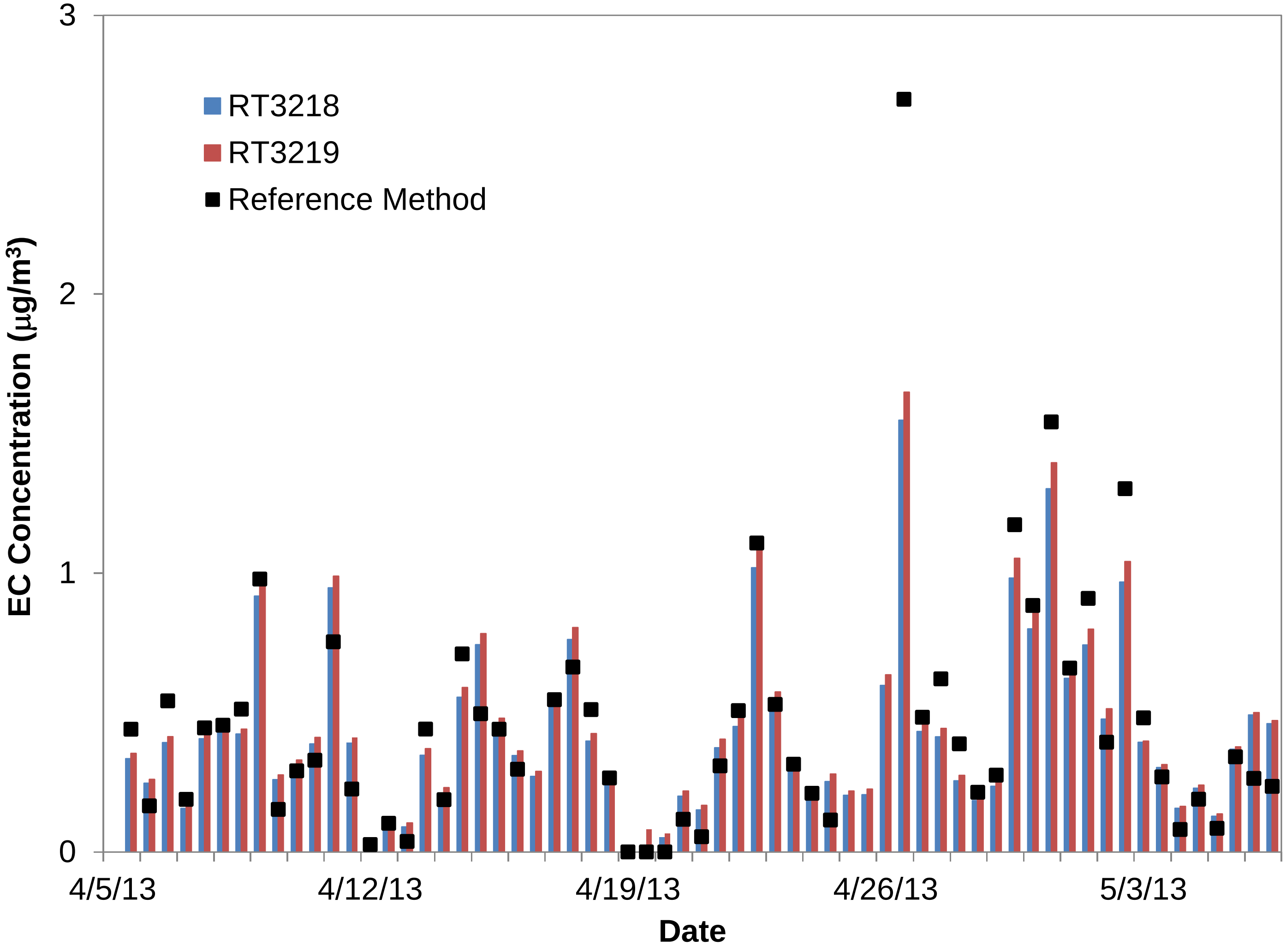

Figure 6-9. Comparison of optical EC results from the Model 4 OC-EC analyzers and the mean reference method TOR EC concentrations.

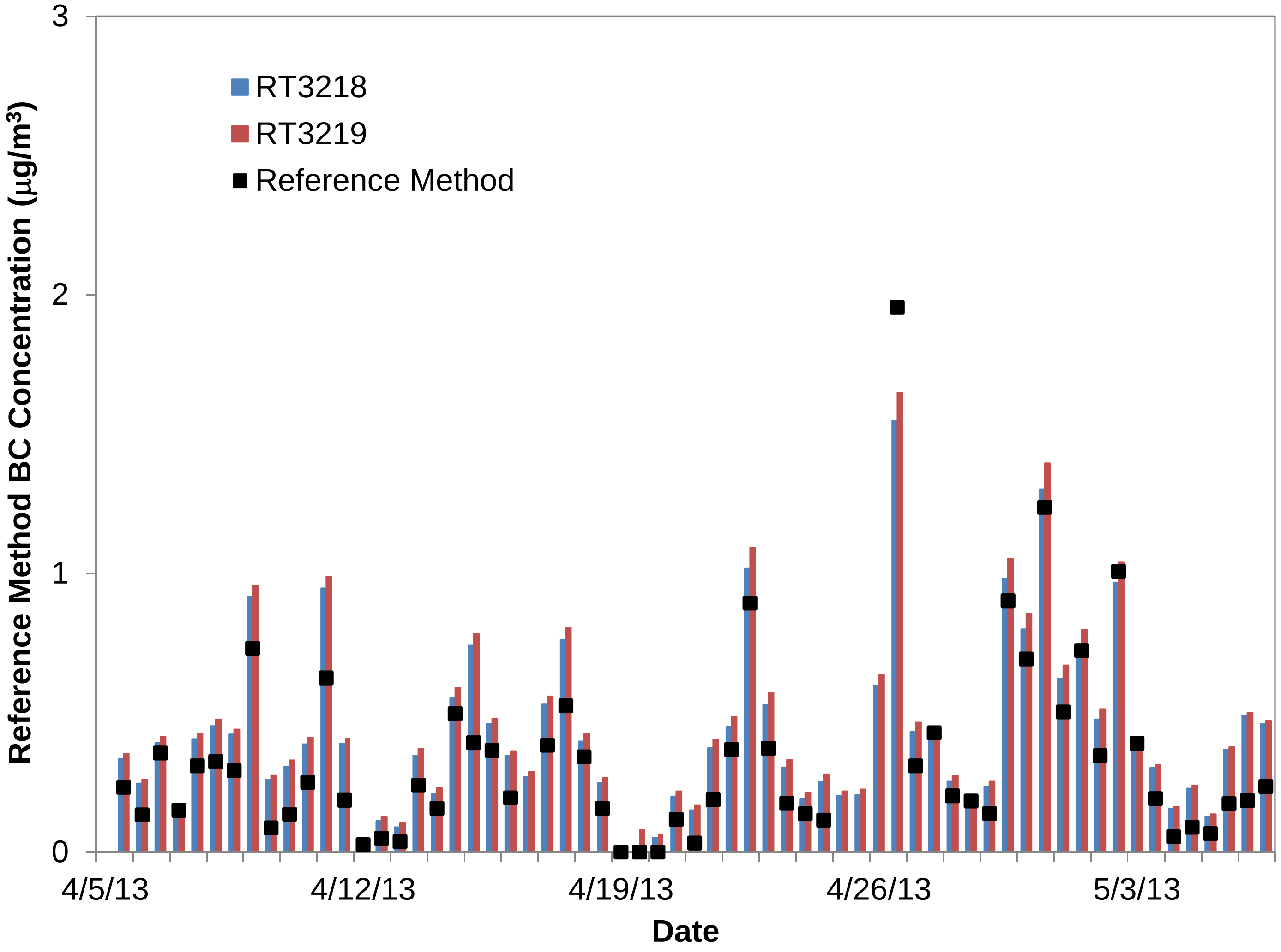

Figure 6-10. Comparison of optical EC results from the Model 4 OC-EC analyzers and the mean reference method TOT EC concentrations.

6.1.1 Regression Analysis

Figures 6-11 and 6-12 show linear regressions of the corrected and uncorrected Model 4 OC-EC 12-hour thermal EC averages, respectively, with the corresponding TOR reference method results. These figures show that there is a negative bias (i.e., slope < 1) of the Model 4 OC-EC results relative to the reference method TOR results, as well as a positive intercept of ~0.3 µg/m^3 for each of the regression lines. Comparison of the regression analyses shows that use of the corrected data (Figure 6-11) substantially changes the slope and intercept of the RT3219 data. Also indicated in Figure 6-11 is a data point that appears to be an outlier from the rest of the data. These data resulted from measurements on April 26, 2013, and can be seen in Figures 6-5 to 6-10. This data point is clearly apparent in each of the regression plots (Figures 6-11 through 6-16) and consistently falls below the regression lines in each plot. A linear relationship appears to exist below 1.5 µg/m^3 and that additional measurements at higher concentrations are needed to confirm a linear relationship at higher concentrations.

Figures 6-13 and 6-14 show linear regressions of the corrected and uncorrected Model 4 OC-EC 12-hour averages, respectively, with the corresponding TOT reference method results. The slopes of the regression lines in these figures are greater than unity indicating positive bias of the Model 4 OC-EC results relative to the TOT reference results. As with the TOR results, the intercepts of the regression lines are ~0.3 µg/m^3.

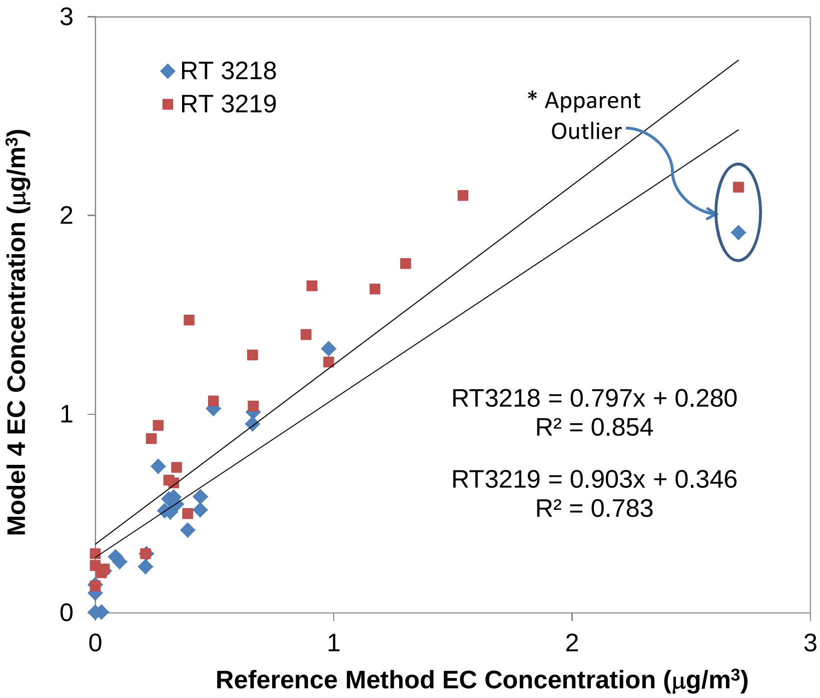

Figure 6-11. Scatter plot of uncorrected Model 4 EC 12-hour thermal averages against mean reference method TOR results.

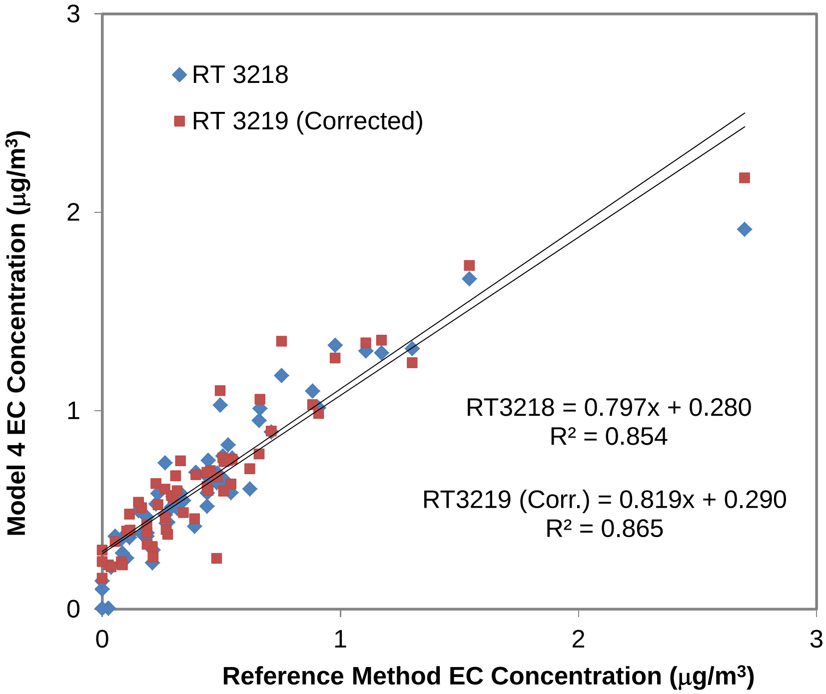

Figure 6-12. Scatter plot of corrected Model 4 EC 12-hour thermal averages against mean reference method TOR results.

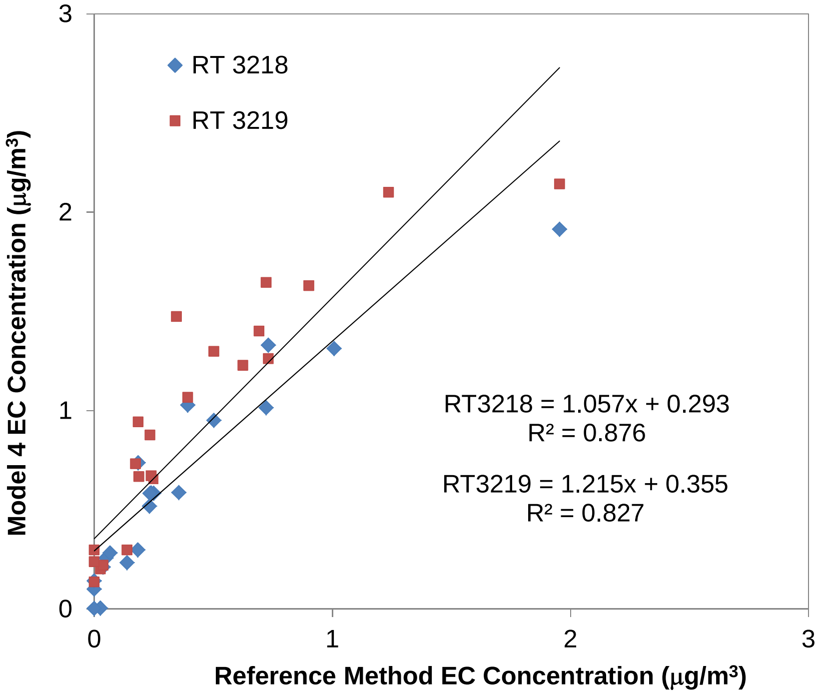

Figure 6-13. Scatter plot of uncorrected Model 4 EC 12-hour thermal averages against mean reference method TOT results.

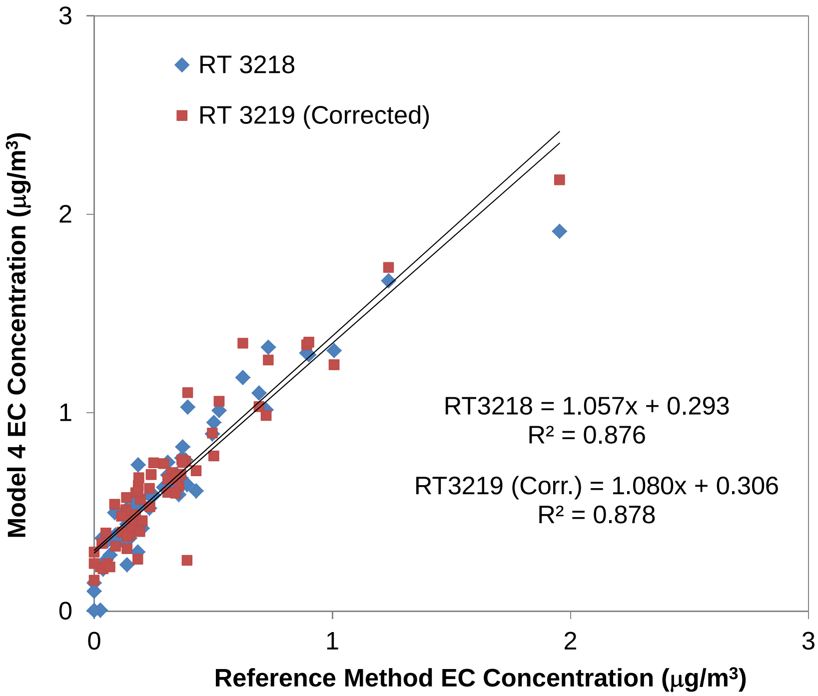

Figure 6-14. Scatter plot of corrected Model 4 EC 12-hour thermal averages against mean reference method TOT results.

Figures 6-15 and 6-16 show linear regressions of the optical Model 4 OC-EC 12-hour averages with the corresponding TOR and TOT reference method results, respectively. The slopes of the regression lines in these figures are less than unity indicating negative bias of the Model 4 OC-EC optical results relative to the reference results. The intercepts of the regression lines are ~0.1 µg/m^3.

Table 6-1 presents a summary of the regression results for the corrected and uncorrected thermal EC results, and the optical results from the Model 4 OC-EC analyzers relative to both the TOR and the TOT reference method EC results. The uncertainties (one standard deviation) of the calculated slopes and intercepts are included parenthetically. These regression results include the apparent outlier data points noted above at the highest observed concentration with each Model 4 analyzer. Table 6-2 presents revised regression results excluding those data points. In both Table 6-1 and 6-2, bolded entries indicate slopes or intercepts whose 95% confidence interval does not include 1.0 or 0.0, respectively.

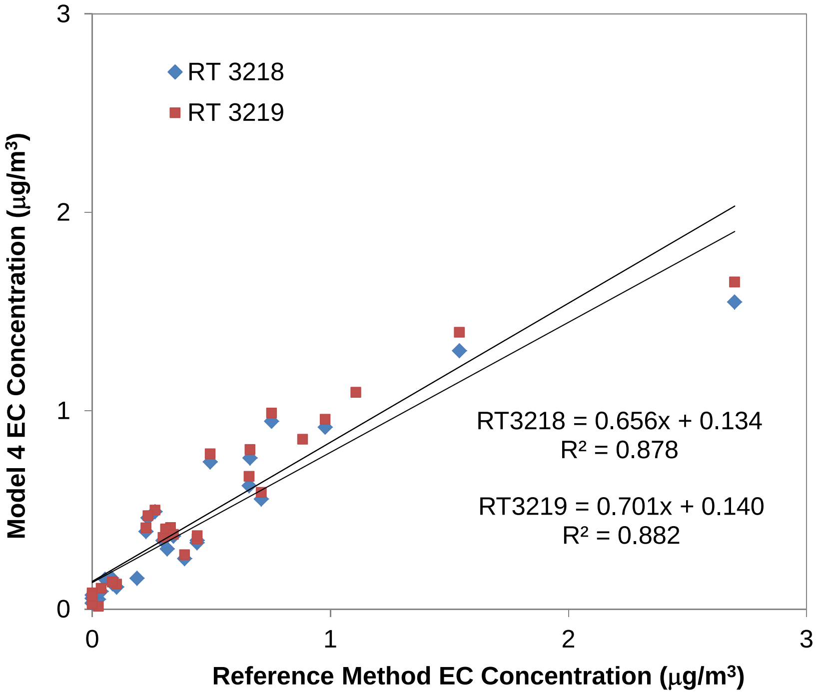

Figure 6-15. Scatter plot of Model 4 EC 12-hour optical averages against mean reference method TOR results.

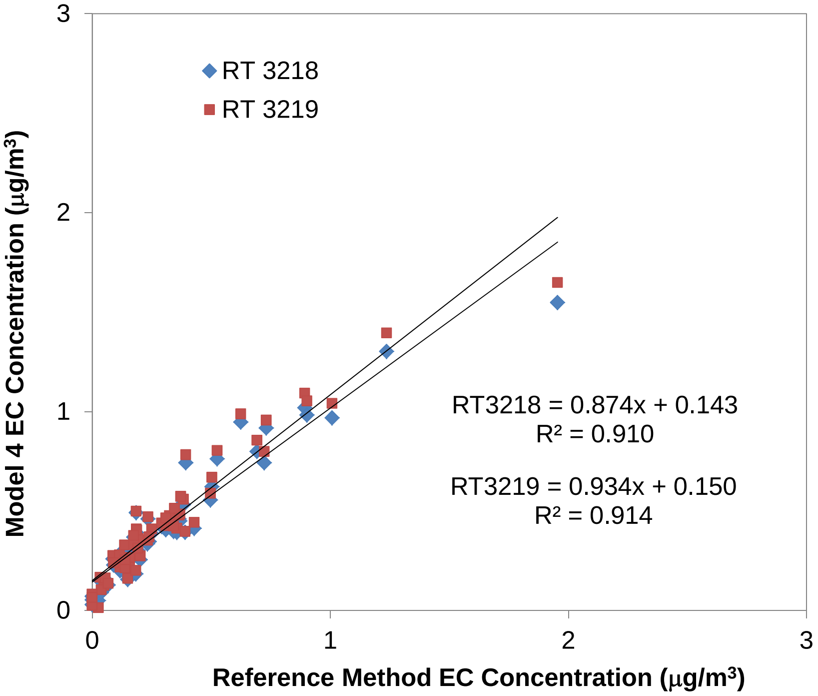

Figure 6-16. Scatter plot of corrected Model 4 EC 12-hour optical averages against mean reference method TOT EC results.

Table 6-1. Summary regression results of the Model 4 OC-EC analyzers and the reference method

Analyzer - Mode	TOR		TOT	
	Slope	Intercept ($\mu g/m^3$)	Slope	Intercept ($\mu g/m^3$)
RT3218 - Thermal	**0.797 (0.044)**	**0.280 (0.028)**	1.057 (0.053)	**0.293 (0.025)**
RT3219 – Thermal	0.903 (0.063)	**0.346 (0.040)**	**1.215 (0.073)**	**0.355 (0.035)**
RT3219 (Corrected) - Thermal	**0.819 (0.043)**	**0.290 (0.027)**	1.080 (0.053)	**0.306 (0.025)**
RT3218 - Optical	**0.656 (0.034)**	**0.134 (0.021)**	**0.874 (0.036)**	**0.143 (0.017)**
RT3219 - Optical	**0.701 (0.034)**	**0.140 (0.022)**	0.934 (0.038)	**0.150 (0.018)**

Table 6-2. Summary of Regression Results of the Model 4 OC-EC Analyzers and the Reference Method, Excluding Apparent Outlier Data Points

Analyzer - Mode	TOR		TOT	
	Slope	Intercept ($\mu g/m^3$)	Slope	Intercept ($\mu g/m^3$)
RT3218 - Thermal	0.982 (0.046)	**0.211 (0.025)**	**1.239 (0.057)**	**0.245 (0.023)**
RT3219 – Thermal	1.131 (0.072)	**0.261 (0.038)**	**1.455 (0.081)**	**0.292 (0.033)**
RT3219 (Corrected) - Thermal	0.936 (0.053)	**0.247 (0.028)**	**1.180 (0.066)**	**0.280 (0.027)**
RT3218 - Optical	**0.783 (0.036)**	**0.087 (0.019)**	0.999 (0.039)	**0.111 (0.016)**
RT3219 - Optical	**0.838 (0.037)**	**0.090 (0.020)**	1.068 (0.040)	**0.115 (0.016)**

Table 6-1 shows that with the outlier data points included, the regression slopes for both the thermal (corrected) and optical EC from the Model 4 analyzers were closer to 1.0 in comparison to the TOT data than in comparison to the TOR data. The regression intercepts were closely similar in the TOR and TOT regressions. Table 6-2 shows that the same was true of the Model 4 optical data when the outlier data points were excluded. However, the regression slopes for the Model 4 thermal (corrected) EC data were closer to 1.0 with the TOR data when the outlier data were excluded.

6.1.2 Relative Percent Difference Analysis

Table 6-3 presents a summary of the calculated RPD between the 12-hour averages for the corrected and uncorrected thermal EC, and the optical EC results from the Model 4 OC-EC analyzers relative to the TOR and the TOT reference method results, respectively. For these calculations, reference method results below twice the method detection limit (i.e., below 0.26 $\mu g/m^3$) were excluded. For perfect agreement between the Aethalometers and the reference method results, the RPD would be zero. Table 6-3 shows that the thermal EC data from the two Model 4 OC-EC analyzers exhibited similar RPD values relative to the reference data, when the RT3219 corrected data were considered. The RPD values were lower in comparison to the TOR data than to the TOT data. The Model 4 optical EC data showed a strong trend in the opposite direction, exhibiting RPD values of less than 4% relative to the TOR data and approximately 20 to 30% relative to the TOT data. In general, the thermal EC measurements from the Model 4 OC-EC analyzers were greater than those from the reference method resulting in positive RPD values. It should be noted that only about two thirds of the TOR reference method results and fewer than half the TOT reference method results were above twice the detection limit.

Table 6-3. Summary of Relative Percent Difference between the Model 4 OC-EC Analyzers and the TOR and TOT Reference Method Results

Analyzer - Mode	**RPD**	
	TOR	**TOT**
RT3218 – Thermal (All)	45.3%	80.6%
RT3218 – Thermal (RAAS)	51.6%	98.4%
RT3218 – Thermal (BGI)	36.6%	56.4%
RT3219 – Thermal (All)	66.2%	101.4%
RT3219 – Thermal (RAAS)	54.2%	95.7%
RT3219 – Thermal (BGI)	83.4%	109.2%
RT3219 (Corrected) – Thermal (All)	45.7%	77.6%
RT3219 (Corrected) – Thermal (RAAS)	60.1%	100.7%
RT3219 (Corrected) – Thermal (BGI)	25.0%	46.1%
RT3218 – Optical (All)	-3.8%	23.6%
RT3218 – Optical (RAAS)	-1.1%	33.8%
RT3218 – Optical (BGI)	-7.3%	9.6%
RT3219 – Optical (All)	2.0%	31.1%
RT3219 – Optical (RAAS)	4.9%	41.4%
RT3219 – Optical (BGI)	-2.0%	17.2%

6.2 Correlation

Table 6-4 presents a summary of the coefficient of determination (r^2) values for the corrected and uncorrected thermal, and the optical results from the Model 4 OC-EC analyzers relative to both the TOR and the TOT reference method results. The correlation results were calculated including all of the data and also with the apparent outliers shown in Figure 6-10 removed.

Table 6-4 shows that r^2 values for both the thermal EC and optical EC were always slightly higher relative to the reference TOT data than to the corresponding reference TOR data. In addition, the r^2 values observed with the optical EC data were always higher than those for the thermal EC data in comparison to the same TOR or TOT data. Finally, the exclusion of the outlying data increased the r^2 values in the comparisons listed in Table 6-4 in all but one case: the corrected data from Model 4 unit RT3219 showed lower r^2 values when the outlier data were excluded than when those data were included.

Table 6-4. Summary of regression results of the Model 4 OC-EC analyzers and the reference method

	r^2 (All data)		**r^2 (Outlier removed)**	
Analyzer/Mode	**TOR**	**TOT**	**TOR**	**TOT**
RT3218 - Thermal	0.854	0.876	0.890	0.896
RT3219 – Thermal	0.783	0.827	0.816	0.852
RT3219 (Corrected) - Thermal	0.865	0.878	0.847	0.850
RT3218 - Optical	0.878	0.910	0.896	0.920
RT3219 - Optical	0.882	0.914	0.902	0.926

6.3 Precision

Table 6-5 presents a summary of the calculated unit-to-unit precision results for the corrected and uncorrected thermal EC, and the optical EC results from the duplicate Model 4 OC-EC analyzers. For this calculation, measurement data below the vendor’s stated instrumental detection limit of 0.5 $\mu g/m^3$ was excluded. The total number of paired measurements in which the readings from both analyzers exceeded the detection limit is included parenthetically for each calculation.

Table 6-5 shows that correction of the Model 4 unit RT3219 data as described in the introduction to this chapter resulted in a substantial improvement in the calculated inter-unit precision of the two Model 4 analyzers. Precision values for the corrected thermal EC results were 12.4% for the 2-hr data and 9.7% for the 12-hr data. The precision of the optical EC results was better than for the thermal EC results, with both the 2-hr and 12-hr data showing precision better than 7%.

Table 6-5. Summary of Calculated Precision Results of the Model 4 OC-EC Analyzers

	Thermal		**Optical**	
	2-hour	**12-hour**	**2-hour**	**12-hour**
Uncorrected	19.9% (N=168)	14.3% (N=38)	5.7% (N=91)	6.3% (N=16)
Corrected	12.4% (N=157)	9.7% (N=36)	--	--

Figures 6-16 through 6-18 show regressions of the 2-hour data for the corrected and uncorrected thermal EC measurements and the 2-hour optical measurements for the duplicate Model 4 analyzers, and Figures 6-19 through 6-21 show scatter plots of the corresponding

12-hour averages. Table 6-6 summarizes the regression statistics from the Model 4 unit-to-unit comparison plots shown in Figures 6-16 through 6-21. The slope, intercept, and r^2 values for the Model 4 thermal EC comparisons for both the 2-hr and 12-hr data were all improved by correction of the unit RT3219 data. The regressions using the corrected data show slopes at or near 1.0, intercepts below 0.04 µg/m^3, and r^2 values exceeding 0.91. The regressions of the Model 4 optical EC data show slopes slightly above 1.0, near-zero intercepts, and r^2 values of 0.999, substantially higher than the r^2 values of the thermal EC comparisons.

Table 6-6. Summary of Unit-to-Unit Regression Results of the Model 4 OC-EC Analyzers

Mode	2-hour			12-hour		
	Slope	Intercept (µg/m^3)	r^2	Slope	Intercept (µg/m^3)	r^2
Thermal	1.075 (0.021)	0.064 (0.017)	0.880	1.104 (0.055)	0.044 (0.040)	0.872
Thermal - Corrected	1.000 (0.016)	0.024 (0.013)	0.912	0.980 (0.036)	0.035 (0.027)	0.925
Optical	1.057 (0.002)	0.002 (0.001)	0.999	1.065 (0.004)	-0.001 (0.002)	0.999

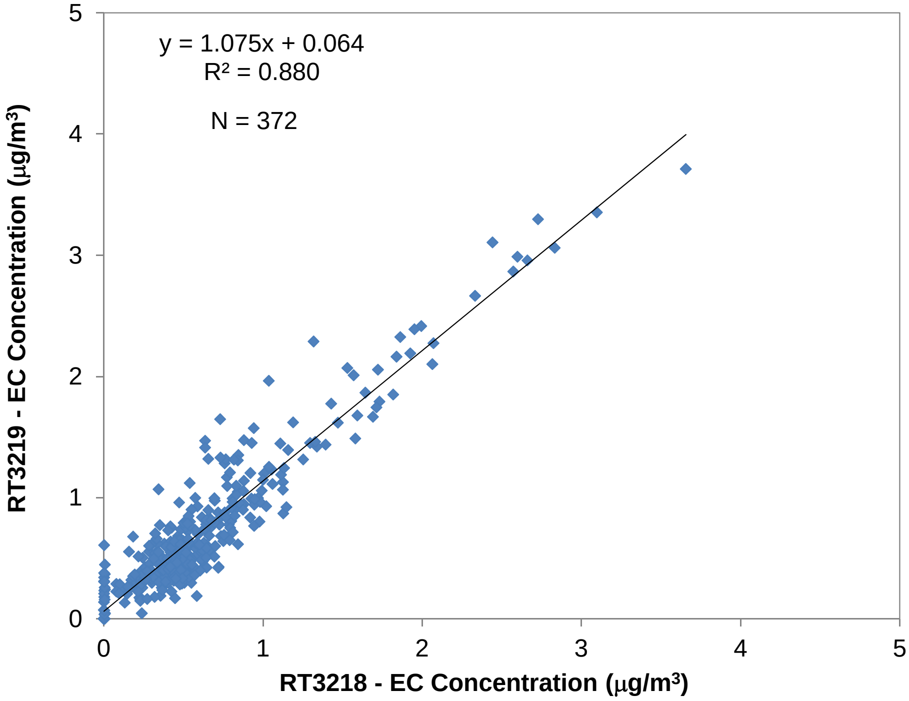

Figure 6-16. Regression of uncorrected Model 4 2-hour thermal EC measurements.

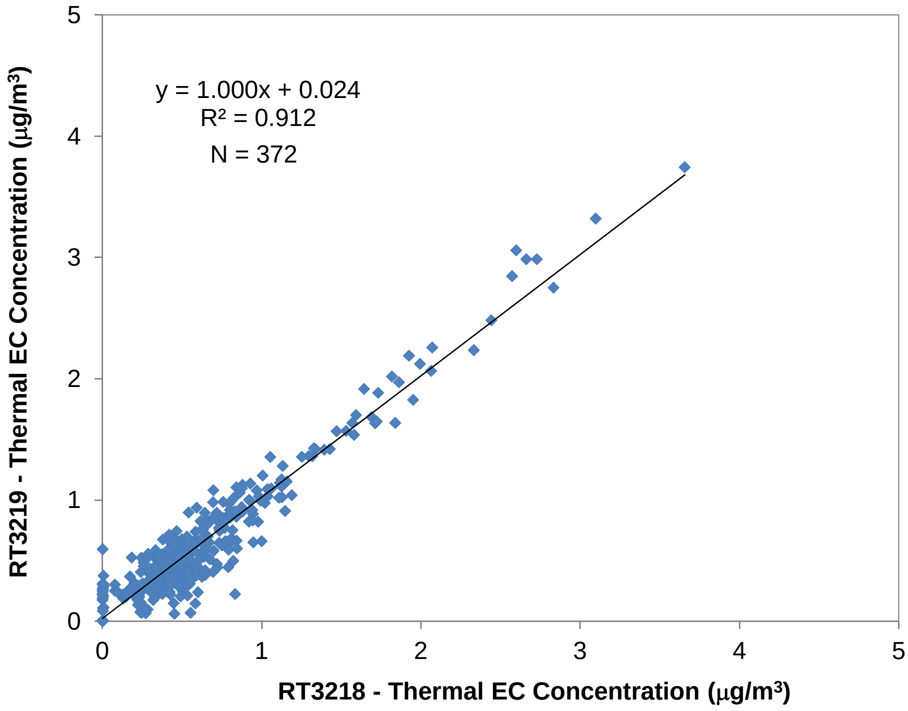

Figure 6-17. Regression of corrected Model 4 2-hour thermal EC measurements.

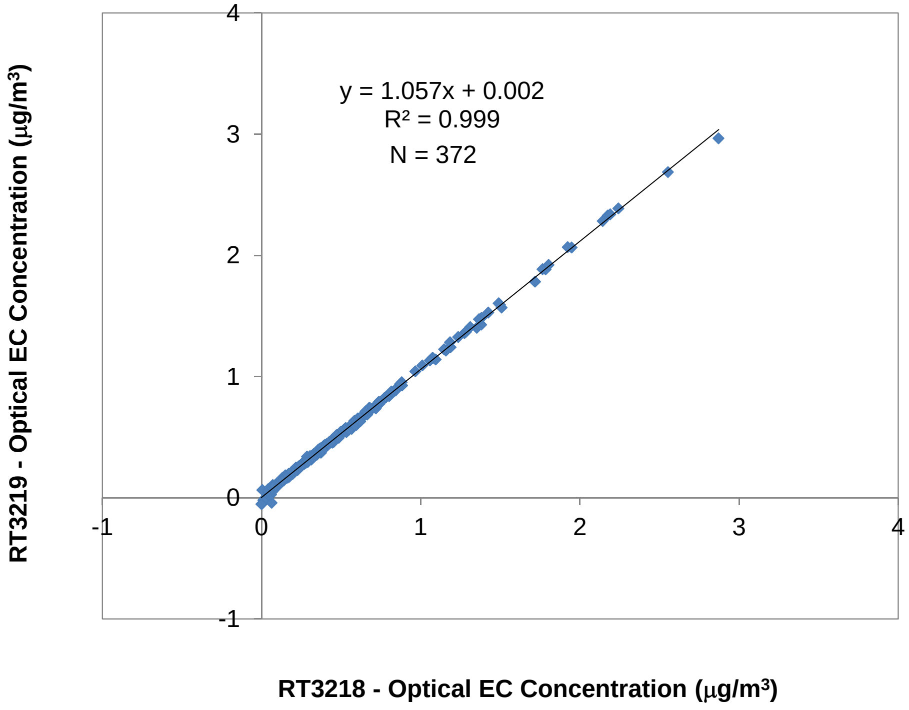

Figure 6-18. Regression of Model 4 2-hour optical EC measurements.

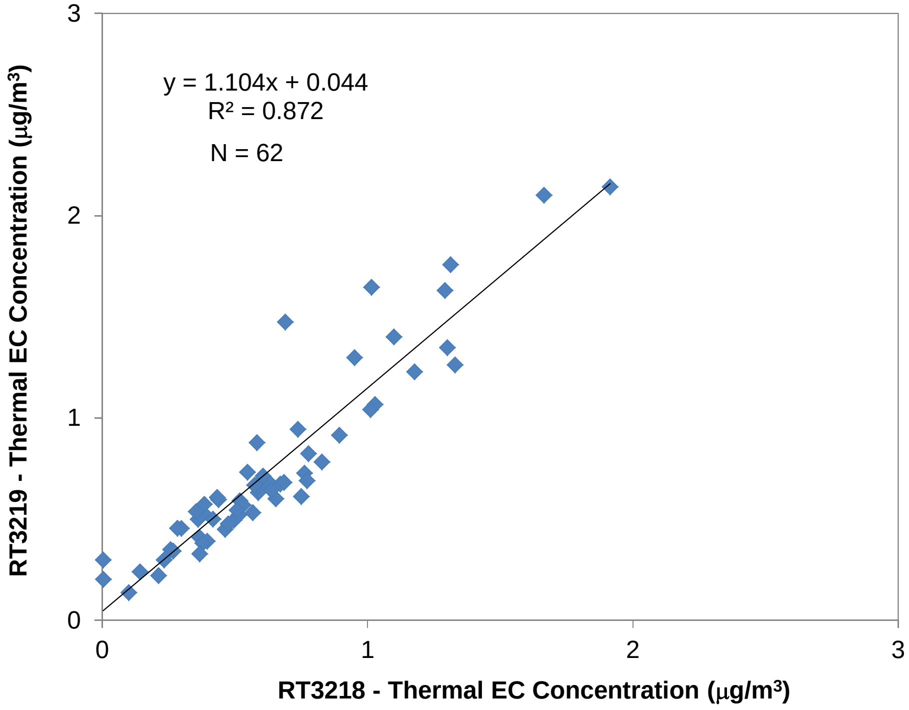

Figure 6-19. Regression of uncorrected Model 4 12-hour thermal EC averages.

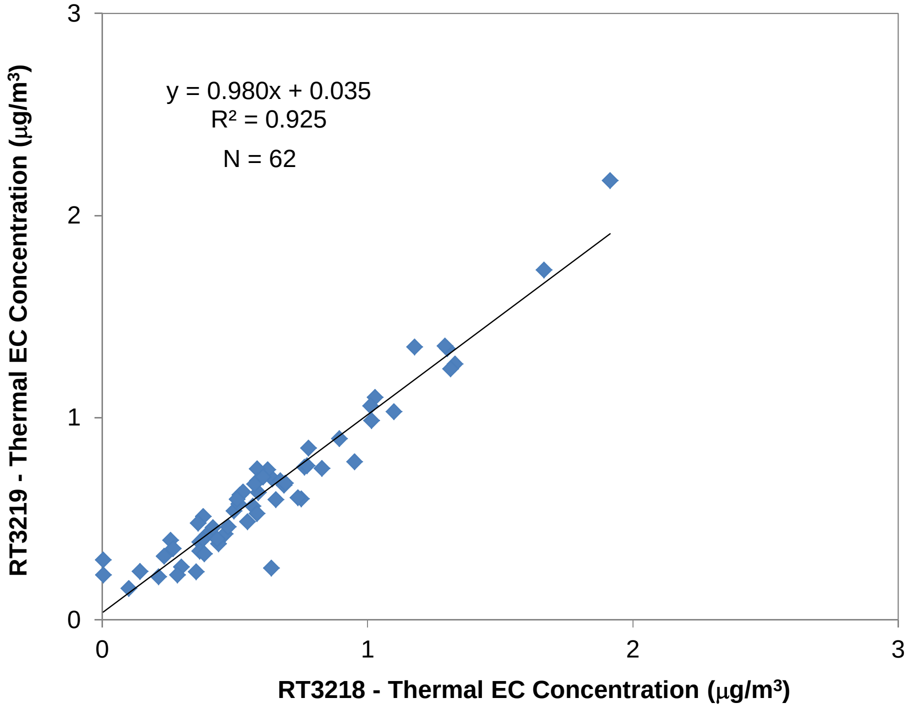

Figure 6-20. Regression of corrected Model 4 12-hour thermal EC averages.

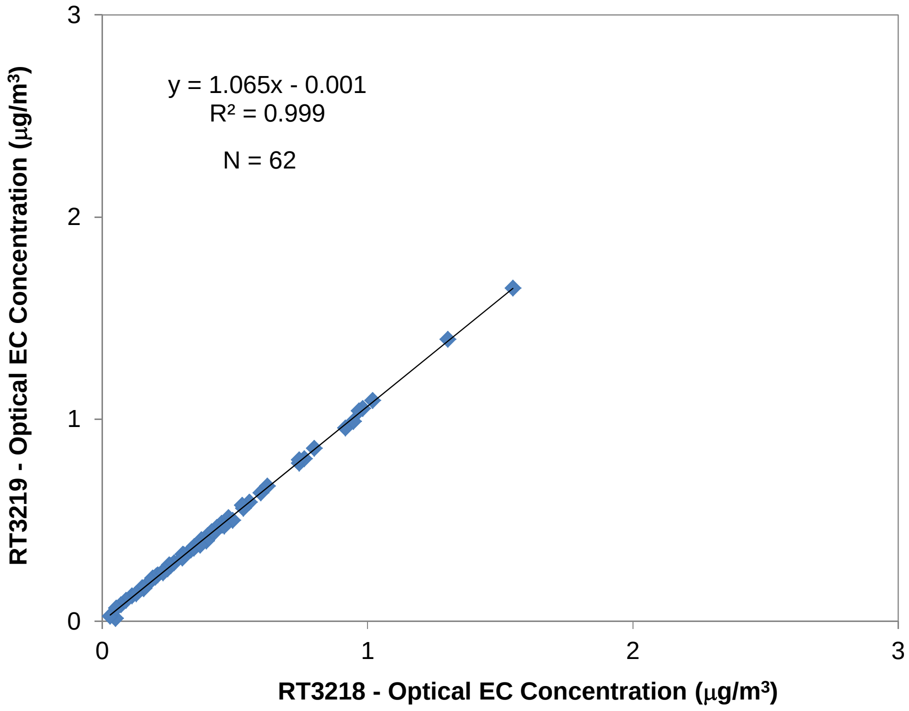

Figure 6-21. Regression of Model 4 12-hour optical EC averages.

6.4 Data Completeness

Table 6-7 presents a summary of the data completeness for the duplicate Model 4 analyzers during the testing period. Each of the analyzers recorded a total of 372 valid measurements out of 378 measurement periods during the verification test. The six periods of missing data were all associated with periods when the analyzers were off line to conduct routine maintenance as indicated in Section 6.5.1. The single missing 12-hour average for each of the analyzers was also the result of the analyzers being off line for maintenance.

Table 6-7. Summary of data completeness for the Model 4 OC-EC analyzers

Analyzer	2-hour			12-hour		
	Total Periods	Valid Measure ments	% Complete	Total Periods	Valid Measure ments	% Complete
RT3218	378	372	98%	63	62	98%
RT3219	378	372	98%	63	62	98%

6.5 Operational Factors

This section addresses the maintenance, consumables, waste generation, ease of use, and other factors relevant to automated field operation of the Model 4 OC-EC analyzer.

6.5.1 Routine Maintenance

Table 6-8 shows the maintenance activities that were performed on the two Model 4 OC-EC analyzers during the verification test.

Table 6-8. Summary of maintenance performed on Model 4 OC-EC analyzers

Date	Maintenance	Approximate time	Data loss
4/3/13 [a]	Filters changed – both analyzers	~15 minutes	2 hours (one measurement cycle)
4/15/13	Filters changed – both analyzers	~15 minutes	2 hours (one measurement cycle)
4/25/13	Filters changed – both analyzers	~15 minutes	6 hours (three measurement cycles)[b]
5/3/13	Filters changed – both analyzers	~15 minutes	2 hours (one measurement cycle)

[a] Filter change occurred after installation of the Model 4 analyzers but before reference sampling began.

[b] The analyzers were remotely stopped, but the filters were not changed until ~4 hours later.

6.5.2 Consumables/Waste Generation

During the verification test, the Model 4 OC-EC analyzers required the use of various compressed gases including ultra-high purity helium, 5% CH_4 in helium, and 10% oxygen (O_2) in helium. These gases were supplied to the analyzers from individual cylinders (size AQ) that were returned to the supplier with a substantial amount of the gases remaining. The Model 4 OC-EC analyzers also required the replacement of quartz fiber filters (two punches per analyzer) approximately weekly.

6.5.3 Ease of Use

Installation of two Model 4 units with inlets was completed in approximately 4 hours. After installation, the units were allowed to operate overnight and were calibrated the following morning using sucrose standard solutions. The calibration of both units was completed in approximately 3 to 4 hours. Routine operation required no effort other than brief daily instrument checks and approximately weekly data downloads. The data was processed using the vendor software to generate comma separated variable (csv) data files.

Chapter 7
Performance Summary

Table 7-1 presents a summary of the results of the verification of the Model 4 OC-EC analyzers during this verification test.

Table 7-1. Summary of Verification Test Results for the Model 4 OC-EC

		TOR		TOT	
	Analyzer/Mode	**Slope**	**Intercept**	**Slope**	**Intercept**
Comparability- Regression analysis comparison to reference samples	RT3218 Thermal	0.797 (0.044)	0.280 (0.028)	1.057 (0.053)	0.293 (0.025)
	RT3219 Thermal	0.903 (0.063)	0.346 (0.040)	1.215 (0.073)	0.355 (0.035)
	RT3219 Corrected Thermal	0.819 (0.043)	0.290 (0.027)	1.080 (0.053)	0.306 (0.025)
	RT3218 Optical	0.656 (0.034)	0.134 (0.021)	0.874 (0.036)	0.143 (0.017)
	RT3219 Optical	0.701 (0.034)	0.140 (0.022)	0.934 (0.038)	0.150 (0.018)

	Analyzer/Mode	**RPD**	
		TOR	**TOT**
Comparability- Calculation of RPD between Model 4 OC-EC results and reference method results	RT3218 Thermal	45.4%	80.6%
	RT3219 Thermal	66.2%	101.4%
	RT3219 Corrected Thermal	45.7%	77.6%
	RT3218 Optical	-3.7%	23.6%
	RT3219 Optical	2.1%	31.2%

	Analyzer/Mode	**r^2**	
		TOR	**TOT**
Correlation - Regression analysis comparison to reference samples	RT3218 Thermal	0.854	0.876
	RT3219 Thermal	0.783	0.827
	RT3219 Corrected Thermal	0.865	0.878
	RT3218 Optical	0.878	0.910
	RT3219 Optical	0.882	0.914

		RPD (# of Observations)			
		Thermal		**Optical**	
		2-hour	**12-hour**	**2-hour**	**12-hour**
Precision - Comparison of results from duplicate Model 4 OC-EC Analyzers	Uncorrected	19.9% (N=168)	14.3% (N=38)	5.7% (N=91)	6.3% (N=16)
	Corrected	12.4% (N=157)	9.7% (N=36)	--	--

Table 7-1 (continued). Summary of Verification Test Results for the Model 4 OC-EC

	Mode	**Period**	**Slope**	**Intercept**	**r^2**
Precision – Regression analysis of results from duplicate monitoring systems	Thermal Uncorrected	2-hour	1.075 (0.021)	0.064 (0.017)	0.880
		12-hour	1.104 (0.055)	0.044 (0.040)	0.872
	Thermal Corrected	2-hour	1.000 (0.016)	0.024 (0.013)	0.912
		12-hour	0.980 (0.036)	0.035 (0.027)	0.925
	Optical	2-hour	1.057 (0.002)	0.002 (0.001)	0.999
		12-hour	1.065 (0.004)	-0.001 (0.002)	0.999
Data Completeness	**Analyzer**	**Period**	**Total Periods**	**Valid Measurements**	**% Complete**
	RT3218	2-hour	378	372	98%
		12-hour	63	62	98%
	RT3219	2-hour	378	372	98%
		12-hour	63	62	98%
Maintenance	• Routine maintenance consisted of replacing filters approximately weekly.				
Consumables/waste generated	• Three different compressed gas cylinders required to operate the units • Internal filters replaced weekly.				
Ease of use	• Installation of two Model 4 units with inlets completed in ~4 hours. • Calibration of units completed in ~3-4 hours, after allowing the units to operate overnight. • Routine operation required no effort other than brief daily instrument checks and approximately weekly data downloads. • Data processed using vendor software to generate csv data files.				

Chapter 8
References

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