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National Water Quality Laboratory
P.O. Box 25585
Denver, CO 80225-0585

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Subject: Validation of high-temperature catalytic oxidation carbon analyzers for analysis of organic carbon in water samples

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Authors: Heather Miller, Analytical Services, NWQL, hmillier@usgs.gov, 303-236-3189
Julie Ray, Analytical Services, NWQL, jlawrenc@usgs.gov, 303-236-3247
Cecilia O'Connor, Analytical Services, NWQL, coconnor@usgs.gov, 303-236-3142

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1 PURPOSE

This memorandum provides method validation data for determination of dissolved organic carbon in filtered water samples and total organic carbon in unfiltered water samples using new high temperature catalytic oxidation carbon analyzers. The validation data support a change in method, new lab codes, and method codes for dissolved organic carbon. The instrumentation for total organic carbon is also updated, but no changes in coding are necessary. Results from a paired sample study are provided to allow data users the ability to compare results from the new instruments with historical results. The new instruments for total and dissolved organic carbon analyses and analyte information for dissolved organic carbon were implemented October 1, 2017.

2 BACKGROUND AND SUMMARY

In late 2016, the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) purchased new Shimadzu TOC-L instruments for analysis of dissolved organic carbon (DOC) and total organic carbon (TOC). These instruments replace Tekmar Phoenix and Apollo carbon analyzers previously in use at the NWQL. The new Shimadzu TOC-L instruments (herein referred to as "TOC-L 1" and "TOC-L 2") utilize high-temperature catalytic oxidation (HTCO) to convert organic carbon to carbon dioxide, which is then measured by non-dispersive infrared spectroscopy. The HTCO instrumentation represents a method change for DOC, and a description of the method is provided in Clesceri and others (1998). DOC was previously analyzed on the Tekmar Phoenix instrument (herein referred to as "Phoenix"), which utilizes low temperature ultra violet (UV)-persulfate wet chemical oxidation (WCO) to convert organic carbon to carbon dioxide (CO₂), which is then measured by non-dispersive infrared

spectroscopy. No method change occurred for TOC samples because the previous Tekmar Apollo instrument (herein referred to as “Apollo”) also utilizes HTOC. Table 1 describes the old and new instrument platforms.

Table 1. New and old instrument information for the analysis of DOC and TOC at the NWQL.

[NWQL, National Water Quality Lab; DOC, dissolved organic carbon; TOC, total organic carbon; WCO, wet chemical oxidation; HTOC, high temperature combustion oxidation; LC, laboratory code]

Instrument manufacturer	Instrument model	Instrument name	Constituents analyzed	Dates in use at NWQL	Method used
Tekmar	Phoenix	Phoenix	DOC LC 2612/2613	From 10/1/99 to 9/30/17	WCO
Tekmar	Apollo	Apollo	TOC LC 3211	From 10/1/09 to 9/30/17	HTCO
Shimadzu	TOC-L	TOC-L 1	DOC LC 2629/2630	Starting 10/1/17	HTCO
Shimadzu	TOC-L	TOC-L 2	DOC LC 2629/2630 & TOC LC 3211	Starting 10/1/17	HTCO

As described in table 2, the source method, NWQL laboratory codes (LC) and National Water Information System (NWIS) method codes will change for DOC because of this method change. NWIS parameter codes will remain the same. The detection limits (DLs), reporting limits (RLs) and analytical ranges will remain the same for both DOC and TOC.

Several studies have compared DOC method recoveries between types of analytical instruments. Studies that focused on comparisons of oxidation efficiencies of UV-persulfate instruments and HTOC instruments found that HTOC instruments were observed to have higher oxidation efficiency for complex organic molecules, such as humic acids, than WCO instruments (Raczyk and others, 2003). HTOC instrumentation is generally preferred for analysis of seawater due to high levels of chloride, which can interfere with accurate measurement of DOC using the WCO approach (Aiken, 1992). Samples that contain DOC primarily in the form of hydrophobic compounds may demonstrate lower recovery on HTOC instruments than on WCO instruments (Kaplan, 2000). This is because samples are acidified and sparged to remove inorganic carbon (IC); during this step, a pH-dependent precipitation of hydrophobic DOC can occur and a portion of the non-purgeable DOC may not be dissolved in solution. In the WCO approach, oxidant is added directly to the vessel where this precipitation occurs, so the lost fraction is oxidized and recovered prior to detection. HTOC instruments transfer an aliquot of the sparged sample from the syringe where IC removal occurs, to the combustion tube for oxidation and analysis, and the lost fraction of DOC is not recovered. Based on these studies, a difference in DOC concentration is expected for comparison samples analyzed on both the old Phoenix analyzer and the new TOC-L analyzers.

In summary, the data presented in this memo demonstrate that results for DOC analyses from samples analyzed on the TOC-L, beginning October 1, 2017 are expected to be low biased by approximately 10.76 +/- 1.80 percent compared to historical results obtained on the Phoenix instrument, for most samples. This is because the Phoenix instrument has a slightly high bias relative to standards with known concentrations, and the TOC-L results may be low-biased for samples containing hydrophobic DOC.

Paired comparison data suggests that customers will experience little to no change in analytical results for TOC analyses with the new TOC-L instruments compared to historical results obtained on the Apollo instrumentation. Data presented here indicate that when samples contain high levels of suspended solids, accuracy and precision of TOC measurements degrade across both old and new instrument platforms.

Table 2. Method and analyte parameter codes, detection and reporting limits, and holding times for previously used Tekmar Phoenix and Apollo carbon analyzers and new Shimadzu TOC-L instruments.

[NWIS, National Water Information System; P Code, parameter code; M Code, method code; DL, detection limit; RL, reporting limit; RL Code, reporting limit code; mg/L, milligrams per liter; μm ; micron; DLBLK, detection limit report code in NWIS set with blank data]

Analyte	Field Filtration	Preservation	New Source Method ¹	Previous Source Method ²	New Lab Code	Previous Lab Code	NWIS P Code	New NWIS M Code	Previous NWIS M Code	DL ³ (mg/L)	RL ⁴ (mg/L)	NWIS RL Code	Holding time
Dissolved Organic Carbon	Field filtered through 0.45 μm capsule filters	Preserved to pH < 2 with sulfuric acid, chilled	SM 5310B	O-1122-92	2629	2612	00681	CMB15	OX006	0.23	0.46	DLBLK	28 days
Dissolved Organic Carbon	Field filtered through burned and pre-rinsed glass fiber filters with a nominal pore size of 0.7 μm	Preserved to pH < 2 with sulfuric acid, chilled	SM 5310B	O-1122-92	2630	2613	00681	CMB16	OX008	0.23	0.46	DLBLK	28 days
Total Organic Carbon	none	chilled	SM 5310B	SM 5310B	3211	3211	00680	COMB9	COMB9	0.7	1.4	DLBLK	14 days

¹ Clesceri and others, 1998;

² Brenton and others, 1993

³The DL concentration is reported as the “less than” value to NWIS when an analyte either is not detected or is detected at a concentration below the DL based on the reporting convention (USGS Office of Water Quality Technical Memorandum 2010.07).

⁴The RL concentration reported is two times the DL concentration.

2.1 Anticipated analytical requirements

During a typical water year (October 1 to September 30 of the following year), approximately 4,100 – 4,200 samples are analyzed for LC 2612 and 1,250 to 1,300 samples are analyzed for LC 2613. Concentrations of DOC in 2015 and 2016 ranged from <0.23 milligrams per liter (mg/L) to 633 mg/L, and approximately 90 percent of values were between 0.23 mg/L and 10.0 mg/L.

During a typical water year, approximately 1,650 - 1,700 samples are analyzed for LC 3211. Concentrations of TOC in 2015 and 2016 ranged from <0.7 mg/L to 96.0 mg/L, and approximately 90 percent of values were between 0.7 mg/L and 25.0 mg/L.

2.2 Instrument overview

As described in table 1, the previous analytical instruments for organic carbon were Tekmar Phoenix WCO carbon analyzers for DOC and Tekmar Apollo HTCO carbon analyzer for TOC. The replacement systems for both DOC and TOC are Shimadzu TOC-L HTCO carbon analyzers. Both the previous systems and the new systems analyze directly for non-purgeable organic carbon (NPOC), which is advantageous over the indirect measure of total carbon (TC) minus inorganic carbon (IC) ($TC - IC = OC$) for samples with levels of organic carbon <5 mg/L. NPOC minimizes uncertainty in the organic carbon value because of the intrinsic uncertainty associated with taking two larger measurements to find a smaller difference in the $TC - IC = OC$ method. The new systems oxidize organic carbon to CO_2 by HTCO, and both the old and new systems use a similar non-dispersive infrared (NDIR) detector. All systems utilize vander-supplied stock solutions of potassium biphthalate (KHP) for calibration standards. Calibration standards used for the TOC-L systems during this study were 0.20, 0.50, 1.00, 5.00, 10.0, and 30.0 mg/L C for DOC and 0.5, 1.0, 5.0, 10.0, and 30.0 mg/L C for TOC.

An autosampler is used for all platforms for carbon analysis. The TOC-L autosampler is capable of performing dilutions automatically and this feature is used to dilute calibration standards, quality-control (QC) standards and environmental samples as needed. Samples were diluted manually for the old Phoenix and Apollo systems.

The autosampler removes an aliquot of sample from the vial and then transfers the aliquot to a sparging syringe where it is acidified and purged with carbon-free air to remove residual IC that may still exist in the sample after acidification in the field (for DOC) or in the lab (for TOC). The old Phoenix and Apollo systems used phosphoric acid and the new TOC-L systems use hydrochloric acid to remove residual IC. Sparging also removes purgeable organic carbon; some hydrophobic forms of non-purgeable organic carbon may precipitate onto the walls of the sparge vessel in this step (Kaplan, 2000). An IC check sample containing 250 mg/L IC is analyzed at the beginning and end of each analytical batch. If IC is effectively removed, the expected organic carbon concentration in this check is less than the DL. If it is not, associated samples are reanalyzed or data is qualified that IC removal efficiency is poor and sample DOC/TOC concentration may be biased high.

Once IC is removed, the remaining organic carbon in the sample is oxidized to CO_2 prior to detection by the NDIR detector. The Phoenix platform for DOC analysis utilized low-temperature UV-persulfate wet chemical oxidation, during which the chemical oxidant is added directly to the vessel where IC removal occurred. The Apollo and TOC-L systems utilize high temperature catalytic oxidation, which is accomplished by transferring an aliquot of the sample from the IC removal vessel to the combustion tube. For the Apollo and TOC-L systems, a fraction of hydrophobic DOC may precipitate on to the walls of the IC sparge vessel, and this fraction is not included in the aliquot of sample that is transferred to the combustion tube for oxidation. The TOC-L is equipped with a high sensitivity platinum catalyst, which is packed into a combustion tube in a furnace at a temperature of 680°C. An aliquot of sample is introduced onto the catalyst and organic carbon is oxidized to CO_2 , which is detected by the NDIR detector. This is repeated at least three times but up to five times for each sample, until three replicate results meet the precision requirements of a standard deviation (SD) of <0.1 mg/L or a coefficient of variation (CV) of 5 percent or less. The average of the three reps that meet the precision criteria is reported for the result from the TOC-

L. The Phoenix instrument analyzed two replicate readings for each sample and the average reading was reported. The Apollo analyzed three replicate readings for each sample and the average was reported.

DOC calibration standards, blanks and QC samples analyzed on the new TOC-L systems are prepared similarly to environmental samples by adding sulfuric acid during preparation of the standards in low-carbon reagent water. This differs from the Phoenix calibration standards, blank, and QC standards that were prepared in low-carbon reagent water with no added acid.

TOC calibration standards, blanks and QC samples analyzed on the old Apollo and new TOC-L systems are prepared similarly to environmental samples in low-carbon reagent water with no added acid. Acid is added manually to the vial of each environmental sample, calibration standard, blank and QC standard analyzed on the Apollo and TOC-L systems, immediately preceding analysis. This acid addition aids in IC removal since TOC samples are not acidified the field.

3 VALIDATION STUDY

Initial data collection for the DOC validation study was conducted over a 2-week period in March 2017 and was performed on two TOC-L systems (TOC-L 1 and TOC-L 2). A second set of data was collected over a 3 week period in June 2017 on TOC-L 1, which will be used for routine DOC analyses. Bias and variability were determined using replicate measurements of QC samples, blanks, blank spikes, surface and groundwater samples, and matrix spikes. QC samples were analyzed interspersed with environmental samples over the course of thirteen analytical batches. The DOC concentration of 160 environmental samples was determined on both the old and new platforms (see attachment 1 for a list of samples and analytical results). Environmental samples were randomly selected from available samples logged in at the NWQL for DOC analysis, and are representative of the matrices and concentrations usually analyzed on an annual basis. Samples were analyzed on both instruments on the same day.

Data collection for the TOC validation study was conducted between May 2017 and August 2017 and was performed on TOC-L 2. Bias and variability were determined using replicate measurements of QC samples, blanks, spikes, and surface and groundwater samples. QC samples were analyzed interspersed with environmental samples over the course of ten analytical runs. The TOC concentration of 46 environmental samples was determined on both the old and new platforms (see attachment 2 for a list of samples and analytical results). Environmental samples were randomly selected from available samples logged in at the NWQL for TOC analysis, and are representative of the matrices and concentrations usually analyzed on an annual basis.

The current NWQL DLs for DOC (0.23 mg/L) and TOC (0.7 mg/L) were verified on the new instruments using several procedures. U.S. Environmental Protection Agency (EPA) method detection limit (MDL) calculations (U.S. EPA, 2014) were performed with repeated measurements of a solution with a concentration of 0.50 mg/L for DOC and 1.0 mg/L for TOC. Additionally, blank results from throughout the validation were pooled and analyzed to determine blank-limited DLs using the procedures outlined in NWQL Technical Memorandum 15.02 (Williams and others, 2015). In 2015, the NWQL implemented the use of an American Society for Testing and Materials (ASTM) software program called DQCALC to determine and verify detection limits (Williams and others, 2015). The DQCALC software algorithm (ASTM, 2010) was utilized to determine a DOC DL based on calibration standards run on both instruments in March 2017.

An assessment of bias and variability for a reference material made from glucose purchased from Environmental Resource Associates (ERA, Golden, CO) was conducted. The certified DOC concentration of this standard was 12.4 mg/L (ERA 12.4). A similar standard was used during the TOC validation with a concentration of 8.7 mg/L (ERA 8.7). Third-party check (TPC) solutions made from salts at the NWQL, at concentrations of 1.0, 5.0 and 20.0 mg/L DOC were made from sodium benzoate and were also analyzed for bias and variability. For the second part of the DOC validation study, and the whole of the TOC validation study, a National Institute of Standards and Technology (NIST)-certified premade stock solution of sodium benzoate was purchased (TPC ERA) to verify the accuracy of the TPC stock made from salts at the NWQL.

Groundwater (WG) and surface-water (WS) samples were collected to determine the variability of DOC and to calculate bias with respect to spike recovery. The raw WG and WS were filtered through 0.7 micron (μm) glass

fiber filters, acidified with sulfuric acid in accordance with field procedures, and stored at <6°C. Groundwater was collected from a private well near Elizabeth, CO and was analyzed for DOC both unspiked and spiked with 5.00 mg/L DOC and 20.0 mg/L DOC using the sodium benzoate TPC solution made at the NWQL. Surface-water was collected from the South Platte River between Waterton Canyon and Chatfield Reservoir near Littleton, CO and was analyzed unspiked and spiked with 5.00 mg/L DOC and 20.0 mg/L DOC using the sodium benzoate TPC solution. Eight to ten measurements of each water source and spiked sample were taken on each TOC-L instrument over the course of the 2-week validation study that occurred in March 2017.

WG and WS samples were collected to determine the variability of TOC and to calculate bias with respect to spike recovery. The raw WG and WS samples for TOC were stored at <6°C. WG was collected from the USGS well on the Denver Federal Center near Building 95 and was analyzed unspiked and spiked with 5.00 mg/L DOC and 20.0 mg/L DOC using the sodium benzoate TPC ERA solution. WS was collected from the Clear Creek Canyon near Golden, CO and was analyzed unspiked and spiked with 5.00 mg/L DOC and 20.0 mg/L DOC using the sodium benzoate TPC ERA solution. Seven to eight measurements of each water source and spiked sample were taken on TOC-2.

An additional environmental sample from each validation run was chosen for duplicate, 5.00 mg/L spike, and spike duplicate sample measurements. At least one set of matrix duplicate, spike, and spike duplicate was analyzed per analytical run for DOC and TOC.

The environmental samples selected for spiking were spiked with a 100 mg/L carbon solution. For spikes of 5.00 mg/L, 9.50 mL of parent sample was mixed with 0.50 mL spiking solution, which resulted in the parent sample being diluted by 5 percent. For spikes of 20.0 mg/L, 8.00 mL of parent sample was mixed with 2.00 mL spiking solution, which resulted in the parent sample being diluted by 20 percent. A correction factor was calculated into the spike percent recoveries:

$$\% \text{ recovery for } 5 \frac{\text{mg}}{\text{L}} \text{ spike} = \frac{\left(\text{spike result} \left(\frac{\text{mg}}{\text{L}} \right) - \text{parent concentration} \left(\frac{\text{mg}}{\text{L}} \right) \times 0.95 \right)}{5 \frac{\text{mg}}{\text{L}}} \times 100\%$$

$$\% \text{ recovery for } 20 \frac{\text{mg}}{\text{L}} \text{ spike} = \frac{\left(\text{spike result} \left(\frac{\text{mg}}{\text{L}} \right) - \text{parent concentration} \left(\frac{\text{mg}}{\text{L}} \right) \times 0.80 \right)}{20 \frac{\text{mg}}{\text{L}}} \times 100\%$$

Note that spike and parent concentration values were not altered in the results, discussion and tables, where they are represented as the concentration reported by the instrument. The corrections were used only for calculations of spike percent recoveries.

Additional DOC QC samples were analyzed on the Phoenix and TOC-L instruments in order to measure the difference between environmental samples that were analyzed on both platforms. These samples were from the Branch of Quality Systems (BQS) organic blind sample project (OBSP) and performance testing (PT) samples from Environment Canada (EC), analyzed by the NWQL in June and July 2017. BQS OBSP samples are prepared from KHP in reagent water and were submitted to the lab blindly with both sample origin and concentration unknown to the analyst. EC PT samples contain major ions, nutrients, and organic carbon in the same sample. EC PT samples are submitted to the lab annually and the target concentrations are unknown to the analyst until after data are reported.

A certified reference material (CRM) purchased from ERA (catalog number 542) for TOC was analyzed with each TOC validation batch on the TOC-L and each analytical batch on the Apollo. The CRM is a dried soil purchased from ERA, which is then mixed with reagent water before TOC analysis to assess the precision and accuracy for samples with high levels of suspended solids.

Field personnel collected environmental TOC samples as described in the USGS field manual. At the request of the NWQL, they also collected a split, which was acidified in the field with sulfuric acid in an attempt to match the holding time and acid preservation of DOC samples. The results of this field preservation demonstrated a large difference between preserved and unpreserved samples and a change in preservation protocol will not be implemented at this time. It is likely that acidification of these samples led to precipitation of hydrophobic organic carbon. In order to implement an acidic preservation of TOC samples in the future, other types and amounts of acid would need to be considered.

4 RESULTS AND DISCUSSION

4.1 Detection limit study for DOC and TOC

The current NWQL detection limit of 0.23 mg/L for DOC was confirmed on the new instruments using several different methods as described in section 3 and table 3. An EPA-style spike-based detection limit calculation (U.S. EPA, 2014) using replicate analyses of a solution of 0.50 mg/L DOC, resulted in a calculated DL of 0.09 mg/L. A DQCALC algorithm multi-concentration DL (ASTM, 2010) was determined using 14 replicate reagent water spikes at each of five concentration levels, which resulted in a calculated DL of 0.14 mg/L. The highest DL determination resulted from a blank-based determination using the 2nd highest blank value, 0.21 mg/L. The NWQL will not lower the DL at this time and will reevaluate DL with one year of data. The NWQL has assigned a DL of 0.23 mg/L for DOC, which represents no change from the previous DOC method.

The current NWQL detection limit of 0.7 mg/L for TOC was confirmed on the new instrument using several different methods as described in section 3 and table 3. An EPA-style spike-based detection limit calculation (U. S. EPA, 2014) using replicate analyses of a solution of 1.0 mg/L resulted in a calculated DL of 0.1 mg/L. The highest DL determination, 0.2, resulted from a blank-based determination. The NWQL will not lower the DL at this time and will reevaluate DL with one year of data. The NWQL has assigned a DL of 0.7 mg/L for TOC, which represents no change from the previous TOC instrument platform.

Table 3. Detection-limit determination for DOC and TOC using new Shimadzu TOC-L instruments

[DL, detection limit; DOC, dissolved organic carbon; TOC, total organic carbon; EPA, Environmental Protection Agency; s, standard deviation; t, student's t value for n-1 at confidence interval of 99%; s x t, standard deviation times t value; DQCALC, software used for ASTM standard practice for performing detection and quantitation estimation and data assessment; NWQL, National Water Quality Laboratory; DL, detection limit; n, number of replicates analyzed; mg/L, milligrams per liter; n/a, not applicable]

DL determination method	Constituent	n	average result (mg/L)	standard deviation (mg/L)	Calculated DL (mg/L)
EPA spike-based s x t determination using 0.50 mg/L solution	DOC	47 (t = 2.687)	0.52	0.03	0.09
Blank-limited determination, s x t	DOC	93 (t = 2.6303)	0.07	0.06	0.15
Blank-limited determination, 2nd highest blank value	DOC	93	n/a	n/a	0.21
DQCALC determination	DOC	14 replicates at each concentration	n/a	n/a	0.14
NWQL assigned	DOC	n/a	n/a	n/a	0.23
EPA spike-based s x t determination using 1.0 mg/L solution	TOC	26 (t = 2.787)	1.0	0.0	0.1
Blank-limited determination, s x t	TOC	33 (t = 2.7385)	0.1	0.1	0.2
Blank-limited determination, 2nd highest blank value	TOC	33	n/a	n/a	0.2
NWQL assigned	TOC	n/a	n/a	n/a	0.7

The NWQL assesses DLs on an annual basis. After one year of analytical data during production, the DLs for both DOC and TOC will be reexamined and may be changed depending on method performance.

4.2 Bias and variability of repeated DOC and TOC measurements of standards and reference samples

Bias and variability in DOC and TOC analyses using the new instruments were assessed for several third-party check (TPC) standards, see table 4. Sodium benzoate TPC standards made at the NWQL demonstrate a low bias of 4-5 percent. The NIST-certified sodium benzoate solution purchased from ERA (TPC ERA) for the second portion of the DOC study and the entire TOC study demonstrated minimal bias with average recoveries within 2 percent of the expected value. This indicates that the TPC made at the NWQL was slightly lower in concentration than expected. NIST-certified standards made from glucose (ERA 12.4 and ERA 8.7) demonstrated minimal bias and variability, see table 4.

Bias and variability of NIST-certified standards purchased as pre-made stock solutions show improvement over the observed bias and variability of TPC standards made by the NWQL. The NWQL began to purchase all calibration stocks, TPCs and spike solutions as NIST-certified pre-made stock solutions during production analyses beginning October 1, 2017 because of this observation.

Table 4. Precision and bias of DOC and TOC standards in reagent water

[DOC, dissolved organic carbon; TOC, total organic carbon; TPC, third party check; ERA, Environmental Resource Associates is a vendor for organic carbon standards and reference materials; %, percent; RSD, relative standard deviation; DL, detection limit; n, number of replicates analyzed; mg/L, milligrams per liter]

Constituent	Standard Name	Standard expected carbon value (mg/L)	carbon source	n	Calculated mean (mg/L)	standard deviation (mg/L)	% RSD	Mean % recovery
DOC	TPC 1 ¹	1.00	sodium benzoate	20	0.96	0.05	4.86	96.0
DOC	TPC 5 ¹	5.00	sodium benzoate	29	4.76	0.30	6.39	95.2
DOC	TPC ERA ²	5.00	sodium benzoate	8	5.08	0.22	4.24	102
DOC	TPC 20 ¹	20.0	sodium benzoate	16	19.1	0.46	2.39	95.5
DOC	ERA 12.4 ¹	12.4	glucose	15	12.4	0.14	1.10	100
TOC	TPC ERA 1 ³	1.0	sodium benzoate	8	1.0	0.1	5.1	100
TOC	TPC ERA 5 ³	5.0	sodium benzoate	26	5.0	0.3	5.8	100
TOC	TPC ERA 20 ³	20.0	sodium benzoate	8	19.6	0.3	1.3	98.0
TOC	ERA 8.7 ³	8.7	glucose	3	8.8	0.1	0.9	101

¹ data collected on TOC-L 1 and TOC-L 2; ² data collected on TOC-L 1 only; ³ data collected on TOC-L 2 only

4.3 Variability of repeated DOC and TOC measurements of groundwater and surface water and recovery of matrix spikes

Variability of DOC analyses using the new instruments were assessed for surface water and groundwater replicate analyses and recovery and variability of matrix spikes of these water matrices were assessed at two concentrations as described in section 3 and table 5. The NWQL recognizes that by using the TPC standard made in-house, the values reported here for DOC spike recovery may be biased low. When compared to similar spikes in reagent water (TPC 5, section 4.2, tables 4 and 5), DOC recoveries in natural water samples near 5 mg/L carbon demonstrate approximately 2 to 5 percent negative bias. DOC recoveries in natural water samples near 20 mg/L carbon demonstrate similar recoveries to spikes in reagent water (TPC 20, section 4.2, tables 4 and 5).

TOC analyses of WG and WS spiked with TPC ERA that were analyzed on instrument TOC-L 2 exhibited minimal bias, which ranged from negative 1.6 to negative 3.4 percent across both matrices and all concentration levels (table 5). Variability was highest at lower concentrations, ranging from 4.0 to 5.2 percent RSD for WG and WS samples near 1.5 mg/L. Above 5 mg/L, variability decreased to 1.1 to 2.5 percent RSD. When compared to similar spikes in reagent water (TPC ERA 5, section 4.2, tables 3 and 4), TOC recoveries in natural water samples near 5 mg/L demonstrate 1.7 to 3.4 percent negative bias. TOC recoveries in natural water samples near 20 mg/L carbon demonstrate similar recoveries to spikes in reagent water (TPC ERA 20, section 4.2, tables 3 and 4).

Table 5. Precision and bias of DOC and TOC in surface water and ground water

[DOC, dissolved organic carbon; TOC, total organic carbon; %, percent; RSD, relative standard deviation; n, number of replicates analyzed; mg/L, milligrams per liter; n/a, not applicable]

Constituent	Sample matrix	Spiked carbon value (mg/L)	carbon source	n	Calculated mean concentration (mg/L)	standard deviation (mg/L)	% RSD	Mean % recovery ¹
DOC	Groundwater	n/a	n/a	17	1.61	0.07	4.14	n/a
DOC	Groundwater	5.00	sodium benzoate	18	6.12	0.22	3.57	91.9
DOC	Groundwater	20.0	sodium benzoate	18	20.4	0.51	2.49	95.8
DOC	Surface water	n/a	n/a	18	2.41	0.12	5.09	n/a
DOC	Surface water	5.00	sodium benzoate	17	6.94	0.24	3.51	93.2
DOC	Surface water	20.0	sodium benzoate	18	20.9	0.89	4.25	95.0
TOC	Groundwater	n/a	n/a	7	1.6	0.1	4.0	n/a
TOC	Groundwater	5.0	sodium benzoate	7	6.4	0.2	2.5	98.3
TOC	Groundwater	20.0	sodium benzoate	8	20.9	0.3	1.5	98.1
TOC	Surface water	n/a	n/a	8	1.5	0.1	5.2	n/a
TOC	Surface water	5.0	sodium benzoate	8	6.3	0.1	1.6	96.6
TOC	Surface water	20.0	sodium benzoate	8	20.9	0.2	1.1	98.4

¹ mean % recovery calculations corrected for dilution of parent sample due to significant volume added during spike procedure, see section 3 for a description of the corrections used.

During the DOC validation study, one environmental comparison sample was chosen for each run to be the parent sample for further sample specific QC samples including duplicate, spike, and spike duplicate analyses. Samples varied in matrix and native carbon concentration, and spike and spike duplicates were spiked with 5.00 mg/L organic carbon. In the first part of the study, the TPC solution made in-house by the NWQL was used to spike. In the second part of the study, which took place in June, the NIST-certified TPC ERA solution was used to spike. The

median spike recovery with the in-house TPC solution was 94.3 percent and the median spike recovery with the NIST-certified TPC ERA solution was 97.9 percent. These results support the observation that spike data collected using the in-house TPC solution may be artificially low biased. Duplicate samples for DOC had a median relative percent difference (RPD) of 3.98 percent and spike duplicates had a median RPD of 1.57 percent.

During the TOC validation study, the NIST-certified TPC ERA solution was used for all matrix spikes and the median spike recovery for TOC was 97.8 percent. Duplicate samples for TOC had a median RPD of 1.4 percent and spike duplicates had a median RPD of 0.6 percent.

4.4 Comparison data from paired environmental samples

One hundred and forty-nine environmental DOC samples were analyzed on the Phoenix and paired with samples analyzed on at least one of the TOC-L instruments. The environmental data from TOC-L 1 and TOC-L 2 were deemed statistically equivalent using a dependent sample t-test for means at a significance level of 0.01, therefore data from TOC-L 2 is not presented here. Data reported here are the 121 samples that were analyzed on the Phoenix and TOC-L 1, the primary instrument for DOC analysis (attachment 1, figure 1, and figure 2). Environmental surface water and groundwater samples filtered through 0.45 µm capsule filters and 0.7 µm glass fiber filters demonstrated similar comparability between the Phoenix and TOC-L instruments, so the data is presented together.

For environmental samples with low DOC concentrations (defined as within approximately four times the detection limit – below 0.89 mg/L on the Phoenix and 0.95 mg/L on TOC-L 1), the comparison data suggest that the results from the Phoenix and the results from the TOC-L are statistically equivalent. To determine this, a two-sample dependent t-test was used on the difference of means, which indicated no significant difference at a significance level of 0.01. Based on this analysis, it is likely that any observed differences in concentrations in this low concentration range are due to the inherent variability of the sample concentrations and random error near the instrument sensitivity threshold and detection limit.

For environmental comparison of samples with DOC concentrations above four times the detection limit (ranging from 0.92 mg/L to 21.1 mg/L on the Phoenix and 0.82 mg/L and 17.2 mg/L on TOC-L 1) the comparison data suggest that the results from the Phoenix and the results from the TOC-L are statistically different at a significance level of 0.01. The population mean was assessed using a one-sample dependent t-test for means. The average relative percent different between the TOC-L and the Phoenix is -10.76 +/- 1.80 percent, using a 99 percent confidence interval. This is an indication of the average difference expected between the two instruments, and a correction factor for the data is not recommended. Samples with results below the DL on the Phoenix instrument were not included in figures 1 and 2, but the data for every sample analyzed during this study are presented in attachment 1.

Forty-six environmental TOC samples were analyzed on the Apollo and TOC-L 2, the primary TOC-L instrument for TOC analyses (attachment 2, figure 3, and figure 4). The mean percent difference between platforms for data above 0.7 mg/L on the Apollo was positive 0.9 percent. Data between 0.7 mg/L and 18.2 mg/L on the Apollo and between 1.24 and 19.3 mg/L on the TOC-L were assessed using a dependent samples t-test for means and the instruments were determined to be statistically equivalent for the defined concentration range, at a significance level of 0.01. Two data points above the detection limit (42.8 mg/L and 43.2 mg/L on the Apollo and 46.3 mg/L and 44.7 mg/L on the TOC-L) was excluded from this analysis due to an insufficient number of data points between this concentration level and the next highest concentration level present in the sample group. Samples with results below the DL on the Apollo instrument were not included in figures 3 and 4, but the data for every sample analyzed during this study are presented in attachment 2.

Figure 1. Dissolved organic carbon (DOC) measurements from environmental samples on the existing Phoenix instrument and the replacement TOC-L 1 instrument in milligrams per liter carbon (mg/L C). Data are plotted next to a 1:1 reference line.

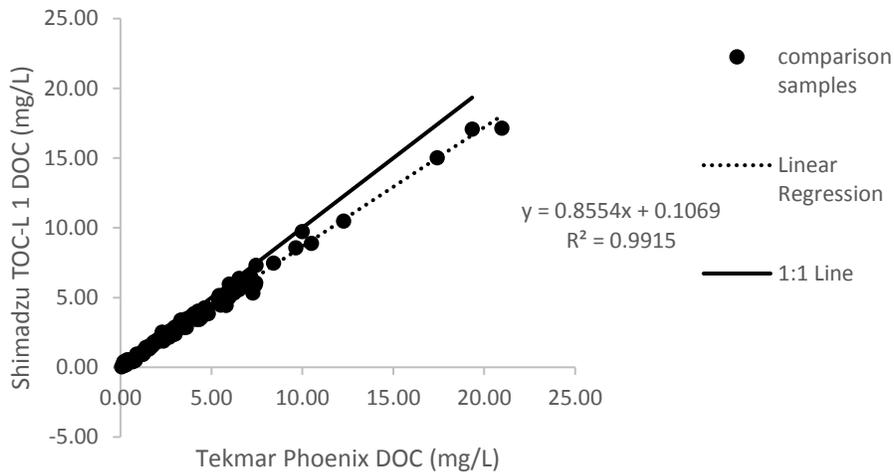


Figure 2. Percent difference of dissolved organic carbon (DOC) measurements from environmental samples on the existing Phoenix instrument and the replacement TOC-L 1 instrument versus the DOC measured on the Phoenix, in milligrams per liter carbon (mg/L C).

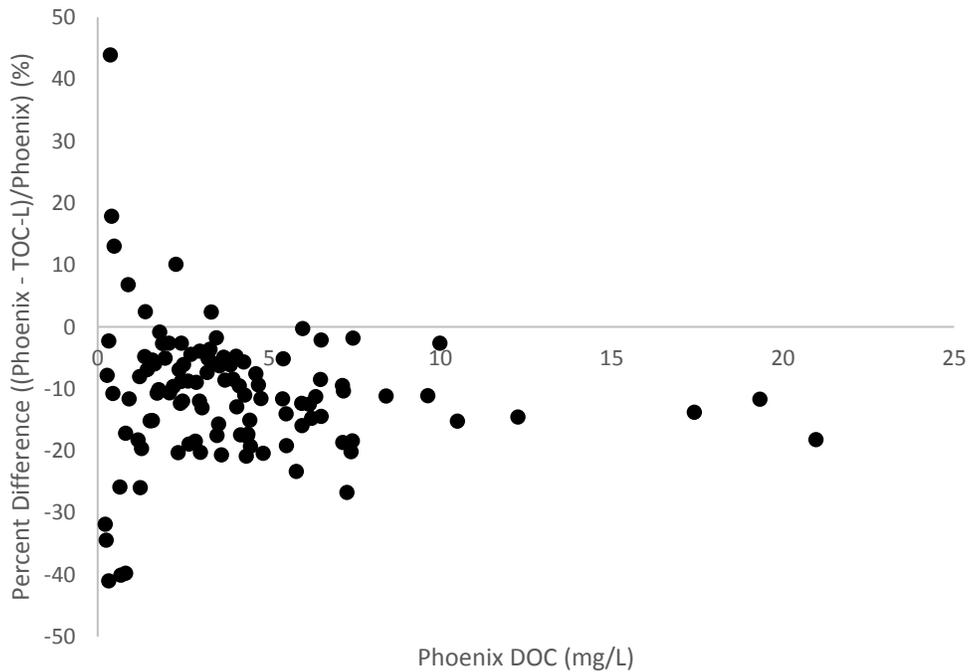


Figure 3. Total organic carbon (TOC) measurements from environmental samples on the existing Apollo instrument and the replacement TOC-L 2 instrument, in milligrams per liter carbon (mg/L C). Data are plotted next to a 1:1 reference line.

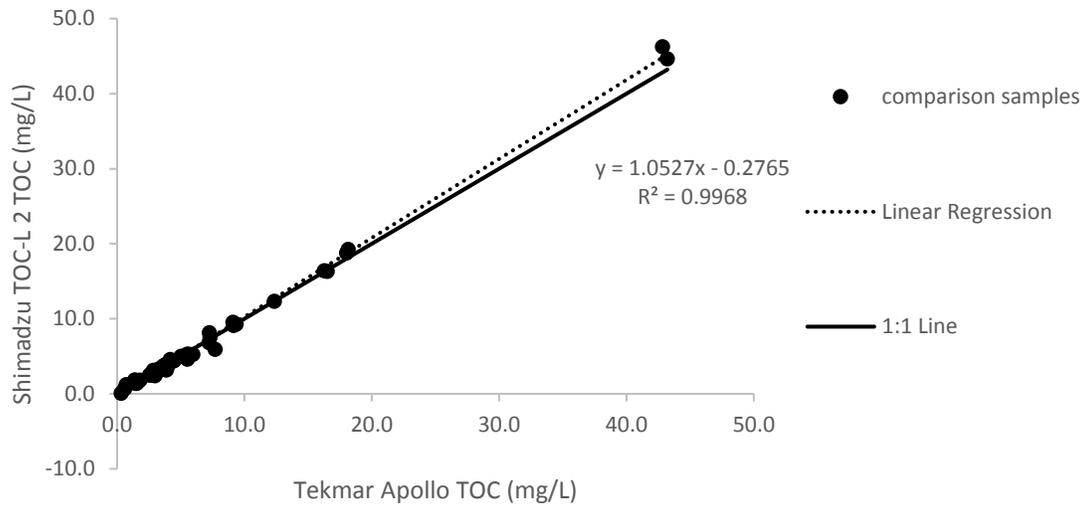
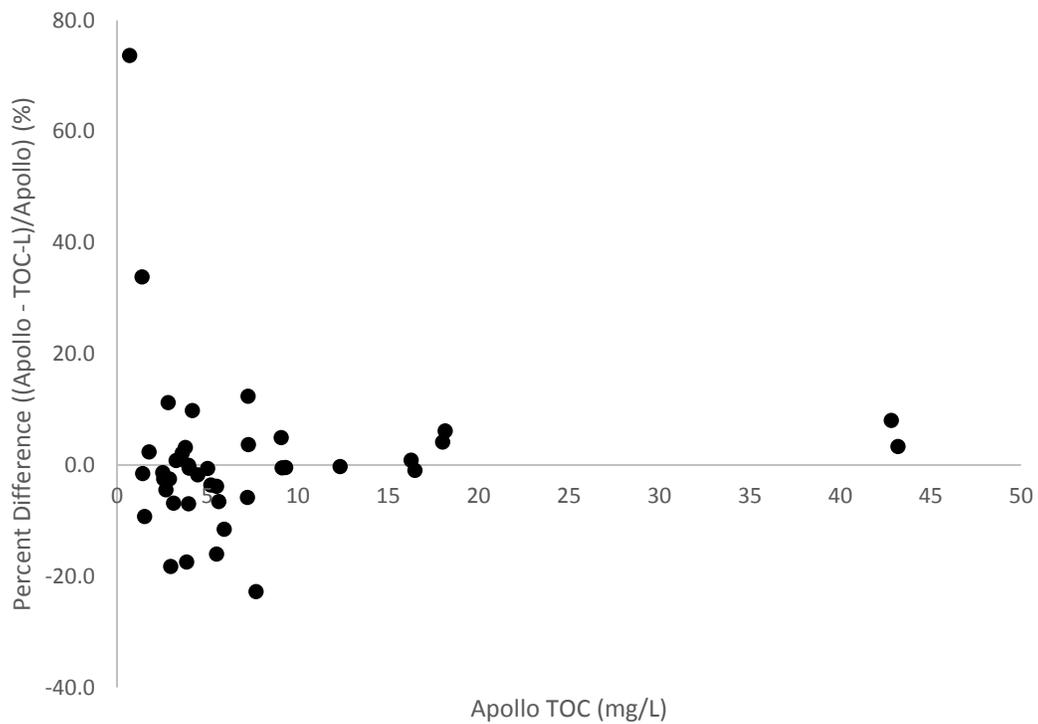


Figure 4. Percent difference of total organic carbon (TOC) measurements from environmental samples on the existing Apollo instrument and the replacement TOC-L 2 instrument versus the TOC measured on the Apollo, in milligrams per liter carbon (mg/L C).



4.5 Results of other quality-control samples

DOC QC samples from the BQS OBSP and PT samples from EC were analyzed on the Phoenix and TOC-L instruments, as described in section 3.1 and table 6. The mean percent recovery for these QC samples on the Phoenix was 105 percent and the mean percent recovery for these QC samples on the TOC-L was 93 percent. The results for the EC PT samples were within the defined acceptable limits provided by EC for all results on the Phoenix and all results on the TOC-L.

The results of these QC samples mirror the difference seen in results of environmental samples between instrument platforms. The OBSP samples are made using spiked reagent water with KHP as the sole carbon source. This type of carbon is highly soluble in water, and full recovery is expected on both instruments because KHP is not prone to precipitation during IC removal. The EC samples are prepared in natural water matrices, and are more complex. The carbon in the EC samples is expected to be in many naturally occurring forms, including hydrophobic compounds. A precipitation of hydrophobic DOC to vessel walls is expected during acidification and sparging to remove IC. This precipitated fraction is recovered on WCO instruments, like the Phoenix, but not on HTOC instruments, like the TOC-L. This supports the conclusion that the difference observed between the old and new instruments for environmental comparison samples is a combination of high bias on the Phoenix and low bias for some forms of carbon on the TOC-L.

Table 6. Percent recovery of DOC on both the Phoenix and TOC-L instruments for other QC samples

[DOC, dissolved organic carbon; mg/L, milligrams per liter; BQS, Branch of Quality Systems; OBSP, organic blind sample project; EC, Environment Canada; PT, performance test sample; percent recovery equals result divided by expected carbon value times 100]

Sample name	Expected DOC value (mg/L)	Sample source	Phoenix result (mg/L)	Phoenix percent recovery	TOC-L 1 result (mg/L)	TOC-L 1 percent recovery
OBSP1A	2.17	BQS OBSP	2.52	116	2.17	100
OBSP1B	5.45	BQS OBSP	5.45	112	5.36	98.4
MI110 -1	3.57	EC PT	3.50	98.0	3.18	89.0
MI110 -2	6.40	EC PT	6.80	106	5.91	92.3
MI110 -3	4.36	EC PT	4.66	107	4.07	93.3
MI110 -4	5.70	EC PT	6.00	105	5.31	93.2
MI110 -5	9.44	EC PT	10.2	108	8.88	94.1
MI110 -6	1.81	EC PT	1.86	103	1.57	86.6
MI110 -7	3.44	EC PT	3.45	100	3.18	92.6
MI110 -8	3.02	EC PT	3.06	101	2.80	92.7
MI110 -9	1.91	EC PT	1.84	96.2	1.71	89.5
MI110 -10	10.14	EC PT	10.7	106	9.55	94.2

A purchased TOC CRM sample was analyzed on the Apollo and TOC-L with every analytical batch, as described in section 3. The results of this analysis indicate that when high amounts of suspended solids are present, precision and accuracy degrades for both the Apollo and the TOC-L as shown in table 7. Customers who submit samples with high levels of suspended solids may see poor precision and accuracy. This represents little change from the Apollo instrument, but is an important consideration for data users.

Table 7. Accuracy and Precision on both the Apollo and TOC-L instruments for a suspended solid CRM

[mg/L, milligrams per liter; CRM, certified reference material purchased from ERA, catalog number 542; TOC, total organic carbon; n, number of replicates analyzed; %, percent; % recovery equals result divided by expected carbon value times 100; RSD, relative standard deviation]

Sample Name	Instrument	Expected TOC value (mg/L)	n	Mean TOC result (mg/L)	Mean % recovery	Mean RSD
CRM	Apollo	5.8	12	3.5	60.1	23.9
CRM	TOC-L 2	5.8	9	1.8	31.5	18.6

5 SUMMARY

Customers may experience a shift in analytical results for DOC analyses reported with the new instruments. This is because the Phoenix instrument exhibits a slight high bias and the TOC-L exhibits a slight low bias. Both instrument platforms produce data that is of acceptable quality for carbon analyses of this nature, as demonstrated by the acceptable performance on EC PT and BQS OBSP samples, as well as other analytical QC samples. Results from samples analyzed on the TOC-L beginning October 1, 2017 are expected to appear, on average, 10.76 +/- 1.80 percent lower compared to historical results obtained on the Phoenix instrument, for natural waters containing hydrophobic forms of DOC.

Comparison data suggests that customers will experience little to no change in analytical results for TOC analyses. There is evidence that when samples contain high levels of suspended solids, accuracy and precision of TOC measurements are biased across old and new instrument platforms.

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7 ATTACHMENTS

Attachment 1 Measured dissolved organic carbon (DOC) on both the Tekmar Phoenix (existing instrument) and Shimadzu TOC-L (replacement instrument)

Attachment 2 Measured total organic carbon (TOC) on both the Tekmar Apollo (existing instrument) and Shimadzu TOC-L (replacement instrument)

/signed/
Jeff McCoy, Chief
National Water Quality
Laboratory

Supersedes: N/A

Key words: dissolved organic carbon, DOC, total organic carbon, TOC, bias, variability, instrument validation

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Attachment 1

Measured dissolved organic carbon (DOC) on both the Tekmar Phoenix (existing instrument) and Shimadzu TOC-L (replacement instrument)

[LC, laboratory code; LabID, NWQL assigned sample identifier; mg/L, milligrams per liter; percent difference equals (measurement on Phoenix minus measurement on TOC-L 1) divided by measurement on Phoenix times 100; WS, surface water; WG, groundwater; OAQ, artificial quality-control sample (blank water); WGQ, groundwater quality-control sample; WSQ, surface-water quality-control sample; N/A, not applicable]

LC	Medium	LabID	Phoenix result (mg/L)	TOC-L 1 result (mg/L)	Percent difference
2612	WS	20170600067	<0.23	<0.23	N/A
2613	WG	20170730103	<0.23	<0.23	N/A
2613	OAQ	20170720001	<0.23	<0.23	N/A
2613	WG	20171640193	<0.23	<0.23	N/A
2613	WG	20170800062	<0.23	<0.23	N/A
2612	WG	20170590028	<0.23	<0.23	N/A
2612	OAQ	20171460031	<0.23	0.33	N/A
2612	OAQ	20171460029	<0.23	0.39	N/A
2612	OAQ	20170730045	<0.23	<0.23	N/A
2612	WG	20170600051	0.23	<0.23	N/A
2612	OAQ	20170540081	0.25	<0.23	N/A
2612	WG	20170810036	0.28	0.25	-8
2612	WG	20170660063	0.32	<0.23	N/A
2612	WG	20171640135	0.33	0.32	-2
2612	WG	20170810081	0.37	0.54	44
2612	WS	20170730094	0.41	0.48	18
2612	WG	20170810080	0.45	0.40	-11
2612	WS	20170730093	0.48	0.55	13
2612	WG	20171640059	0.65	0.48	-26
2612	WGQ	20171640039	0.67	0.40	-40
2612	WS	20171630026	0.82	0.68	-17
2612	WG	20171640038	0.82	0.49	-40
2612	WS	20170730078	0.89	0.95	7
2612	WS	20170660039	0.92	0.82	-12
2612	WS	20171630025	1.18	0.97	-18
2612	WS	20170660050	1.23	1.13	-8
2612	WS	20171640065	1.25	0.92	-26
2612	WG	20171640052	1.29	1.03	-20
2613	WG	20171530127	1.37	1.31	-5
2613	WS	20170760090	1.40	1.43	2

Attachment 1

Measured dissolved organic carbon (DOC) on both the Tekmar Phoenix (existing instrument) and Shimadzu TOC-L (replacement instrument)

[LC, laboratory code; LabID, NWQL assigned sample identifier; mg/L, milligrams per liter; percent difference equals (measurement on Phoenix minus measurement on TOC-L 1) divided by measurement on Phoenix times 100; WS, surface water; WG, groundwater; OAQ, artificial quality-control sample (blank water); WGQ, groundwater quality-control sample; WSQ, surface-water quality-control sample; N/A, not applicable]

LC	Medium	LabID	Phoenix result (mg/L)	TOC-L 1 result (mg/L)	Percent difference
2613	WG	20171530126	1.45	1.35	-7
2613	WS	20170680049	1.54	1.30	-15
2613	WS	20170720003	1.55	1.47	-6
2613	WS	20170820096	1.60	1.51	-5
2613	WG	20171580052	1.60	1.36	-15
2612	WG	20170750151	1.66	1.56	-6
2612	WS	20170540089	1.74	1.55	-11
2612	OAQ	20170540090	1.79	1.61	-10
2612	WS	20170590022	1.81	1.80	-1
2612	WSQ	20170590024	1.89	1.84	-3
2612	WSQ	20170590023	1.97	1.87	-5
2613	WS	20170730034	2.08	2.03	-3
2613	WS	20170760089	2.10	1.87	-11
2613	WS	20170820095	2.21	2.00	-10
2613	WS	20170800078	2.28	2.52	10
2612	WG	20171640051	2.36	1.88	-20
2612	WS	20171460046	2.38	2.21	-7
2612	WS	20171630027	2.41	2.12	-12
2613	WS	20170810077	2.44	2.38	-3
2612	WS	20170730033	2.44	2.23	-9
2612	WS	20170660044	2.48	2.18	-12
2613	WS	20170800028	2.51	2.36	-6
2612	WSQ	20170660040	2.64	2.40	-9
2613	WS	20170800026	2.67	2.16	-19
2612	WS	20170660073	2.73	2.61	-4
2612	WS	20170600039	2.85	2.32	-18
2612	WS	20171460033	2.88	2.62	-9
2612	WS	20170690106	2.98	2.62	-12
2612	WS	20171460036	2.98	2.87	-4

Attachment 1

Measured dissolved organic carbon (DOC) on both the Tekmar Phoenix (existing instrument) and Shimadzu TOC-L (replacement instrument)

[LC, laboratory code; LabID, NWQL assigned sample identifier; mg/L, milligrams per liter; percent difference equals (measurement on Phoenix minus measurement on TOC-L 1) divided by measurement on Phoenix times 100; WS, surface water; WG, groundwater; OAQ, artificial quality-control sample (blank water); WGQ, groundwater quality-control sample; WSQ, surface-water quality-control sample; N/A, not applicable]

LC	Medium	LabID	Phoenix result (mg/L)	TOC-L 1 result (mg/L)	Percent difference
2612	WS	20170660041	3.00	2.40	-20
2612	WS	20171640064	3.05	2.65	-13
2613	WS	20170820092	3.20	2.97	-7
2612	WS	20171460047	3.22	3.06	-5
2613	WS	20170800037	3.25	3.13	-4
2613	WS	20170800038	3.28	3.16	-4
2612	WS	20171460030	3.32	3.40	2
2613	WS	20170720002	3.47	3.41	-2
2612	WS	20170600036	3.49	2.88	-18
2613	WSQ	20170810096	3.51	3.30	-6
2613	WS	20170680045	3.54	2.98	-16
2613	WS	20170810097	3.56	3.33	-6
2612	WS	20170600040	3.62	2.87	-21
2612	WS	20170660057	3.68	3.50	-5
2612	WS	20170730032	3.72	3.40	-9
2613	WS	20170810078	3.88	3.64	-6
2612	WS	20171460032	3.95	3.62	-8
2613	WS	20170800036	4.04	3.85	-5
2612	WS	20170660049	4.06	3.54	-13
2612	WS	20171460018	4.14	3.74	-10
2612	WS	20170540069	4.17	3.44	-17
2612	WS	20170600042	4.27	4.02	-6
2613	WS	20170680047	4.29	3.82	-11
2612	WS	20170540092	4.34	3.43	-21
2612	WSQ	20170540070	4.36	3.59	-18
2612	WS	20170600041	4.38	3.63	-17
2613	WS	20171590187	4.44	3.77	-15
2612	WS	20170590062	4.46	3.60	-19
2612	WS	20170590029	4.62	4.27	-8
2613	WS	20171590021	4.70	4.26	-9

Attachment 1

Measured dissolved organic carbon (DOC) on both the Tekmar Phoenix (existing instrument) and Shimadzu TOC-L (replacement instrument)

[LC, laboratory code; LabID, NWQL assigned sample identifier; mg/L, milligrams per liter; percent difference equals (measurement on Phoenix minus measurement on TOC-L 1) divided by measurement on Phoenix times 100; WS, surface water; WG, groundwater; OAQ, artificial quality-control sample (blank water); WGQ, groundwater quality-control sample; WSQ, surface-water quality-control sample; N/A, not applicable]

LC	Medium	LabID	Phoenix result (mg/L)	TOC-L 1 result (mg/L)	Percent difference
2613	WS	20171590217	4.77	4.22	-12
2612	WS	20170590071	4.83	3.84	-20
2613	WS	20170680048	5.40	4.78	-12
2613	WS	20170820097	5.42	5.14	-5
2612	WS	20170590039	5.50	4.73	-14
2612	WS	20170540080	5.52	4.46	-19
2613	WS	20171590023	5.80	4.45	-23
2613	WS	20170690089	5.96	5.23	-12
2612	WS	20170540094	5.97	5.02	-16
2612	WS	20170660048	5.98	5.97	0
2612	WS	20170590030	6.18	5.41	-13
2613	WS	20171590275	6.24	5.32	-15
2613	WS	20170810102	6.37	5.65	-11
2613	WS	20171590216	6.50	5.95	-8
2613	WS	20171590116	6.52	5.58	-14
2613	WS	20170800027	6.53	6.39	-2
2612	WS	20171460019	7.15	6.47	-9
2613	WS	20171590276	7.16	5.82	-19
2613	WS	20171590274	7.18	6.44	-10
2612	WS	20170600070	7.28	5.33	-27
2613	WS	20170680043	7.40	5.91	-20
2612	WS	20170540093	7.44	6.07	-18
2613	WS	20170820093	7.45	7.31	-2
2612	WS	20171460020	8.42	7.48	-11
2612	WS	20171460021	9.64	8.56	-11
2613	WS	20170800025	10.0	9.7	-3
2612	WS	20170600071	10.5	8.9	-15
2613	WS	20171590022	12.3	10.5	-15
2613	WS	20170680041	17.4	15.0	-14
2613	WS	20170680042	19.3	17.1	-12
2612	WS	20170590061	21.0	17.2	-18

Attachment 2

Measured total organic carbon (TOC) on both the Tekmar Apollo (existing instrument) and Shimadzu TOC-L (replacement instrument)

[LC, laboratory code; LabID, NWQL assigned sample identifier; mg/L, milligrams per liter; percent difference equals (measurement on Apollo minus measurement on TOC-L 2) divided by measurement on Apollo times 100; WS, surface water; WG, groundwater; OAQ, artificial quality-control sample (blank water); WGQ, groundwater quality-control sample; WSQ, surface-water quality-control sample; N/A, not applicable]

LC	Medium	LabID	Apollo result (mg/L)	TOC-L 2 result (mg/L)	Percent difference
3211	WG	20171370208	<0.7	<0.7	N/A
3211	WS	20172210103	<0.7	<0.7	N/A
3211	OAQ	20172230038	<0.7	<0.7	N/A
3211	OAQ	20172230054	<0.7	<0.7	N/A
3211	OAQ	20172200227	<0.7	0.7	N/A
3211	WS	20171380030	0.7	1.2	73.7
3211	WS	20171380116	1.4	1.9	33.8
3211	WS	20171380029	1.4	1.4	-1.5
3211	WS	20171380028	1.5	1.4	-9.2
3211	WS	20172200224	1.8	1.8	2.4
3211	WS	20171370155	2.5	2.5	-1.4
3211	WS	20171380123	2.6	2.5	-2.5
3211	WS	20172200238	2.7	2.6	-4.4
3211	WS	20171380112	2.8	3.1	11.2
3211	WS	20171430039	2.9	2.8	-2.5
3211	WS	20171380124	3.0	2.4	-18.2
3211	WS	20171430038	3.1	2.9	-6.8
3211	WS	20172210108	3.3	3.3	0.9
3211	WS	20171380036	3.6	3.7	2.2
3211	WS	20171380113	3.8	3.9	3.2
3211	WS	20171380125	3.9	3.2	-17.4
3211	WS	20171380114	4.0	3.7	-7.0
3211	WS	20172230052	4.0	4.0	0.0
3211	WS	20172230053	4.0	4.0	-0.5
3211	WS	20171380037	4.2	4.6	9.8
3211	WS	20171370104	4.5	4.4	-1.7
3211	WS	20171370105	5.0	5.0	-0.6
3211	WSQ	20171370106	5.2	5.0	-3.6
3211	WS	20171380122	5.5	4.6	-16.0
3211	WS	20171370107	5.5	5.3	-3.8
3211	WS	20172220036	5.6	5.3	-6.6
3211	WS	20171380108	5.9	5.3	-11.5

Attachment 2

Measured total organic carbon (TOC) on both the Tekmar Apollo (existing instrument) and Shimadzu TOC-L (replacement instrument)

[LC, laboratory code; LabID, NWQL assigned sample identifier; mg/L, milligrams per liter; percent difference equals (measurement on Apollo minus measurement on TOC-L 2) divided by measurement on Apollo times 100; WS, surface water; WG, groundwater; OAQ, artificial quality-control sample (blank water); WGQ, groundwater quality-control sample; WSQ, surface-water quality-control sample; N/A, not applicable]

LC	Medium	LabID	Apollo result (mg/L)	TOC-L 2 result (mg/L)	Percent difference
3211	WS	20172230039	7.2	6.8	-5.8
3211	WS	20172210104	7.3	8.2	12.4
3211	WS	20172160081	7.3	7.6	3.7
3211	WS	20171370154	7.7	5.9	-22.8
3211	WS	20171380090	9.1	9.5	4.9
3211	WS	20172210058	9.1	9.1	-0.5
3211	WS	20171380138	9.3	9.3	-0.4
3211	WS	20171380140	12.3	12.3	-0.2
3211	WS	20171380089	16.3	16.4	0.9
3211	WS	20171380088	16.5	16.3	-1.0
3211	WSQ	20171380141	18.0	18.8	4.2
3211	WS	20171380139	18.2	19.3	6.1
3211	WSQ	20172200219	42.8	46.3	8.1
3211	WS	20172200220	43.2	44.7	3.4