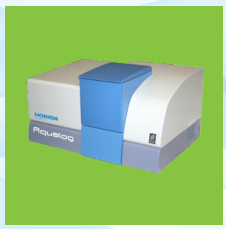
HORIBA Scientific

EPA Stage 2 Disinfection Compliance with Aqualog

FLSS-37

ELEMENTAL ANALYSIS
FLUORESCENCE
GRATINGS & OEM SPECTROMETERS
OPTICAL COMPONENTS
FORENSICS
PARTICLE CHARACTERIZATION
RAMAN
SPECTROSCOPIC ELLIPSOMETRY
SPR IMAGING



Applied Parallel Factor Analysis with Eigenvector Inc. *Solo* Software

Abstract

This application note describes the use of the Aqualog for monitoring regulated Dissolved Organic Matter (DOM) and disinfection by-product issues for drinking water treatment. The Aqualog was used to simultaneously measure the UV-VIS absorbance spectrum and fluorescence excitation emission matrix (EEM) and monitor DOM pertaining to EPA Stage 2 Disinfection By-product Rule (DBPR2) compliance [1] in a typical surface water source drinking water treatment plant (defined as Subpart H) . The method enabled near real-time monitoring of the EPA regulated parameters of Total Dissolved Organic Carbon (TOC), absorbance at 254 nm (UVA) and the Specific UV Absorbance (SUVA-TOC) as well as the Simulated Distribution System Trihalomethane (THM) Formation Potential (SDS-THMFP). The parameters were reported as a function of compliance rules associated with required % removals of TOC (as a function of alkalinity) and predicted maximum contaminant levels (MCL) of THMs. The single instrument method, which is compatible with continuous flow monitoring or grab sampling, provides a rapid (2-3 minute) and precise indicator of drinking water disinfectant treatability without the need for separate UV photometric and TOC meter measurements or independent THM determinations.

Introduction

Drinking water treatment plants that primarily use surface water sources are regulated according to Subpart H in the DBPR2. They are commonly subject to significant variations in the TOC in often unpredictable patterns associated with rainfall, snow-melt and other events that influence sporadic drainage of organic materials into the source water. TOC removal requirements are regulated by the DBPR2 because certain components are precursors to toxic disinfection by-products (DBPs) that may react over time in the distribution system with halogenated disinfectants. The regulated DBPs include trihalomethanes (THMs) and haloacetic acids (HAAs) which are suspected carcinogens. TOC removal is regulated as a function of alkalinity which influences the ability to remove TOC with coagulants. Conventional monitoring of treatability usually involves TOC determination which may also be coupled with the UVA to determine the specific UV absorbance or SUVA-TOC according to EPA method 415.3 [2]. SUVA-TOC is reported as an indicator of the aromatic content of the TOC which correlates with reactivity to halogenated disinfectants. The involvement of separate benchtop UV photometers and TOC meters or THM meter for these measurements is recognized as a bottleneck for rapid determination of DBP precursors and the SDS-THMFP. This bottleneck often results in the inability to effectively adjust coagulation and other treatment steps to natural fluctuations in the TOC. Online TOC and THM monitors are also recognized to require significant maintenance, calibration efforts and costs which may deter their routine application in many water utilities.

The reagent-free Aqualog method quickly generates a complete UV-VIS absorbance spectrum and fluorescence EEM which together contain the information required to evaluate the TOC composition and most importantly the aromatic composition of the TOC associated with the treatability regulations (SUVA-TOC) and the SDS-THMFP.

JOBIN YVON Technology

The analysis of the absorbance and EEM data involved the multivariate routine known as PARAFAC [3] which can be calibrated and automated to report in near real-time. Modeling of the data can also facilitate recognition of changes in the source water composition, contamination events or sampling errors as a function of goodness of fit and residual error patterns.

The results and discussion section show how the Aqualog can be calibrated with robust linear statistics to accurately determine the TOC and THMFP in direct comparison to instrumentation calibrated according to EPA-approved methods. Importantly, the analysis of TOC % removal requirements and THMFP require independent, parallel measurements of alkalinity, chlorine and pH. The data clearly illustrate the treatability and TOC determinations with the Aqualog are inherently more precise than the conventional SUVA-TOC method and much faster than the conventional SDS-THMFP tests which commonly require 2-10 days and extensive reagent treatment methods. The models were tested using two *Cyanophytes, M. aeruginosa, A. Flos-aquae*, two

Methods

Daily Alkalinity, UVA, pH, Chlorine, TOC and SDS-THMFP Determinations

Daily raw and finished Alkalinity, UVA, pH, chlorine, TOC and SDS-THMFP determinations were performed according to the following methods in reference [4]. Alkalinity (mg/l $CaCO_3$) was determined by titration according to Method 2320B. UVA was determined photometrically using a 5 cm path length cell according to Method 5910B. pH values were determined according to Method 4500-H*B. Chlorine residual (mg/l) was measured photometrically according to Method 4500-Cl G. TOC (mg/l) was measured using the UV Persulfate Oxidation Method according to Method 5310C. SDS-THMFP (µg/l) was determined according to Method 5710-C.

Aqualog Absorbance and Fluorescence EEMs

Duplicate daily raw source and finished water samples were filtered (0.45 µm) immediately before analysis. All samples were equilibrated to room temperature (25° C) nominally prior to analysis. Fluorescence EEMs and absorbance spectra were analyzed using an Aqualog (HORIBA Instruments, Inc.) from 250-600 nm using 3 nm for excitation intervals and 3.28 nm for emission using a medium gain and 2 s integration for emission detection. EEM data were corrected for the instrumental excitation and emission spectral response, detector dark currents, blank sample emission, inner filter effects and by masking of the first and second order Rayleigh scatter. The blank sample for emission and absorbance was a sealed TOC-free water sample (Starna 3Q-10) from Starna Scientific Inc.. All 3.5 ml samples were analyzed using 1 cm path length suprasil 4-way clear fluorescence quartz cuvettes. The EEM contours were normalized based on a standard 1 µm NIST-certified standard working solution (Starna QS-RM-00) of quinine sulfate dissolved in 0.1 M perchloric acid as prepared and sealed by Starna Scientific, Inc.

PARAFAC Analysis

Fluorescence EEM data were analyzed using the PARAFAC algorithm within the Eigenvector, Inc. *Solo* Package. All loadings were constrained to nonnegativity and the concentration loading areas were normalized to unity. Rayleigh masking was adjusted to 16 nm and 32 nm, for first and second order, respectively within *Solo*. The model was fit using the default PARAFAC algorithm parameters within *Solo*. The 3-component model data were validated using the built-in *Solo* split-half validation routine.

Results and Discussion

Daily Analysis of UVA (A254) and TOC

The results of the daily analysis for the photometric A254 and TOC data, collected independent of the Aqualog, for the raw and finished water grab samples are shown in Figure 1. Importantly, the UVA and TOC samples were filtered (0.45 µm pore size) so the TOC is equivalent to the dissolved organic carbon concentration (DOC) as defined by EPA Method 415.3 [2]. Figure 1A shows day to day variation in the A254 (5 cm path length) for the raw water varied by nearly an order of magnitude over the approximate 18 month period due to natural variation in the organics load of the source water. The finished water shows a diminished variation and reduced A254 due to the effects of the coagulation, sedimentation and filtration processes to remove the organics. Figure 1B plots the independent linear relationships between the A254 and TOC for the corresponding raw and finished water sample in Fig. 1A. Clearly, both the raw and finished water data exhibited significant linear relationships between the A254 and TOC. The slope of the line for the finished water was significantly shallower, by nearly a factor of 2, than that of the raw water. Notably, both the raw and finished models were fit assuming an intercept of 0 mg/l to indicate the majority of the TOC correlated with the components causing the extinction at 254 nm.

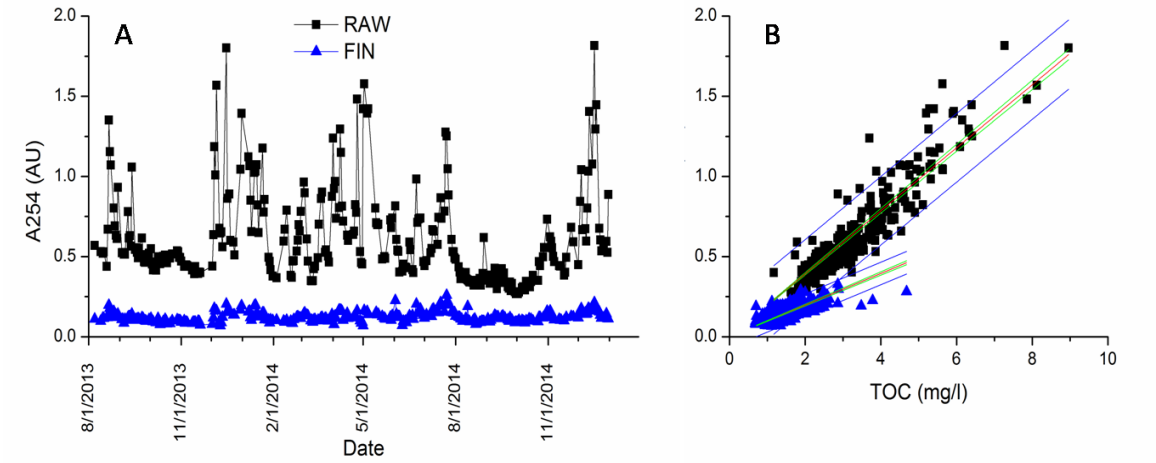


Figure 1. Daily measurements of A254 (A) and linear relationships between A254 and TOC (B) for corresponding raw (RAW) and finished (FIN) water samples. For panel B, the linear equation for the RAW samples was A254=0.196 • (TOC), adjusted r^2=0.975 and for the FIN samples A254 = 0.099 • (TOC), adjusted r^2=0.950. The linear fit predictions (red lines) are shown compared the 95% confidence intervals (green) and prediction intervals (blue).

Daily Analysis of EEMs and UV-VIS Absorbance with the Aqualog

In conjunction with the daily A254 and TOC data measurements, matching samples were analyzed using the Aqualog to collect the EEM and absorbance spectra. Figure 2 compares typical EEM and absorbance profiles for raw and finished water samples measured in the same daily sample set. The EEM data for the raw water exhibited around a 6.25 fold higher peak intensity than the finished water along with a broader and significantly red-shifted main emission band. The absorbance for the raw water also exhibited higher extinction at all wavelengths compared to the corresponding finished water sample.

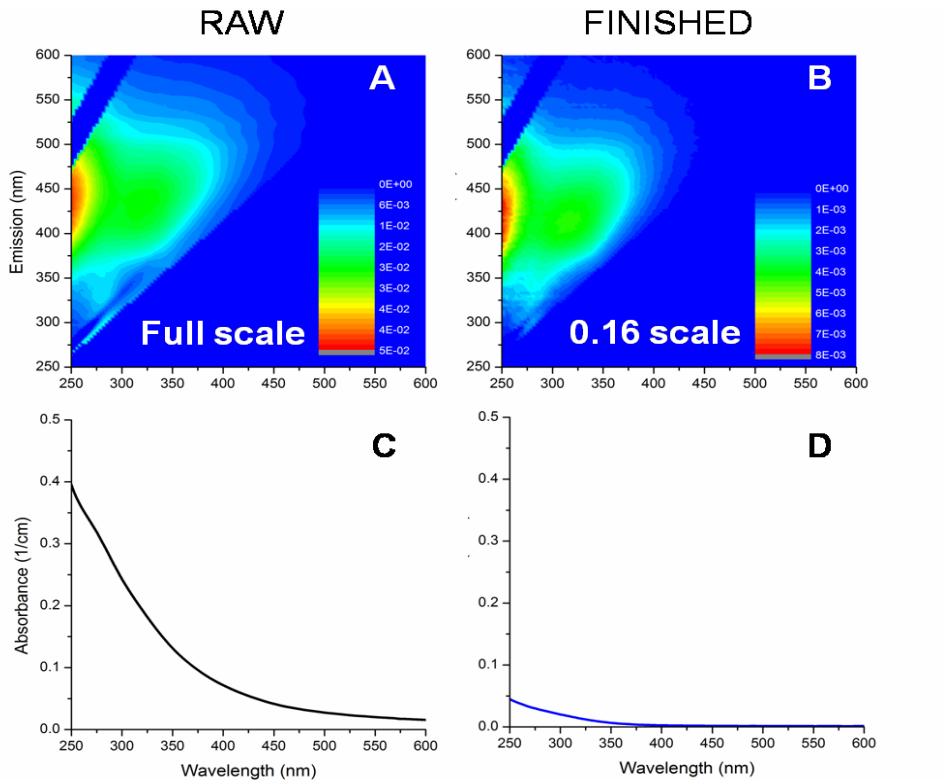


Figure 2. Comparison of typical Aqualog EEMs (top) and UV-VIS absorbance spectra (bottom) for corresponding raw (left) and finished (right) water samples measured on the same day.

To evaluate the quantitative changes in the EEMs associated with the treatment PARAFAC analysis was applied to all samples to decompose the excitation spectra, emission spectra and concentration loadings for the main fluorescent components. Figure 3 illustrates the three components resolved in the model each plotted as a contour representing the cross product of the excitation and emission spectral loadings. Component 1 was identified as a humic/fulvic component with relatively lower molecular weight and aromaticity compared to Component 2, which was also identified as a humic/fulvic component. Notably Component 2 exhibited a significantly broader and red-shifted excitation-emission contour than Component 1. Component 3 was identified as a protein-like component and exhibited the deepest UV excitation-emission contour.

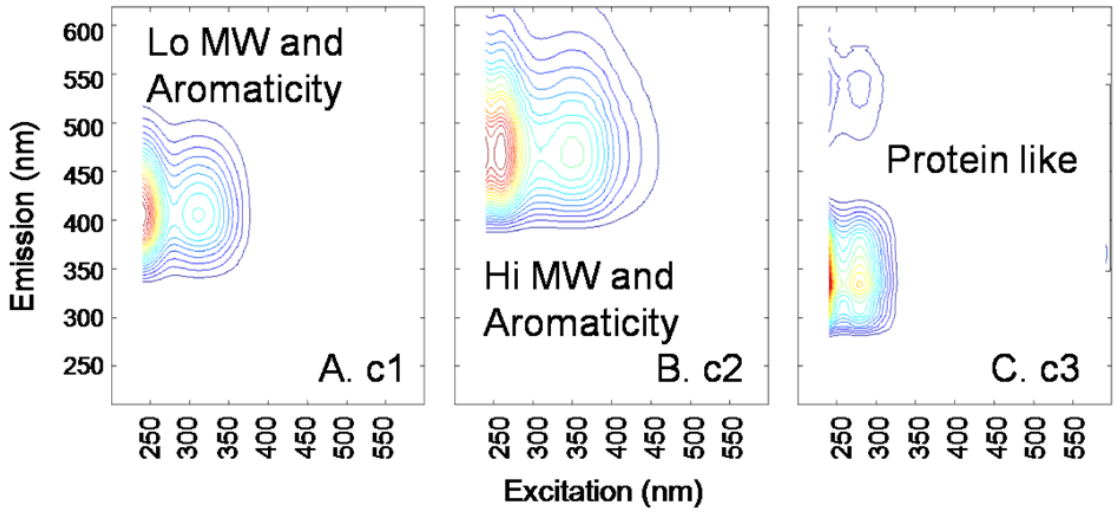


Figure 3. Excitation-emission contours for PARAFAC model components c1 (A), c2 (B) and c3 (C). The data set included *n*=1484 samples with duplicate daily measurements for each raw and finished sample. The model accounted for 97.3% of the variance, the split-half validation match was 98.6% and the core consistency was 94%.

Figure 4 compares the normalized PARAFAC concentration loadings for the three components for the daily raw and finished water samples. In the raw water, the main component was consistently Component 2 whereas in the finished water, Component 1 dominated consistently. The relative concentration of Component 3 remained largely unchanged between the treatments. The enhanced removal of Component 2 is consistent with the expected effects of coagulation to remove higher molecular weight organics more effectively than lower molecular weight species. Hence this pattern clearly correlated with the broader, red-shifted spectra for the main EEM bands in the raw water compared to the finished water shown in Fig. 1.

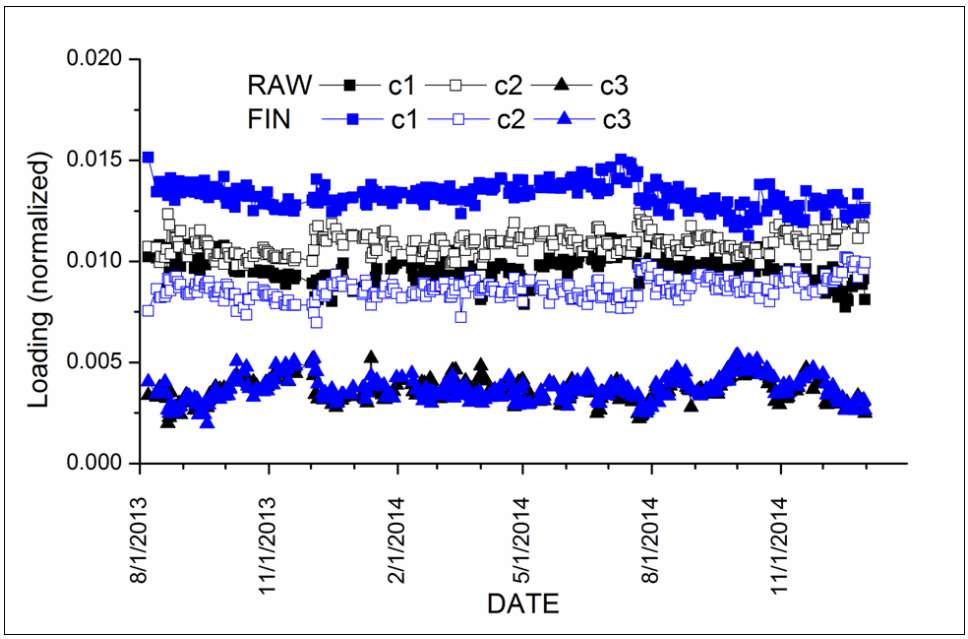


Figure 4. Normalized concentration PARAFAC loadings for c1-c3 for the daily raw (RAW) and finished (FIN) samples.

Evaluation of SUVA and Treatability with EPA Method 415.3

As shown in Figure 1 the linear relationship between A254 and TOC changes as a function of the coagulation treatment. This change is in fact the basis of the significance of SUVA and SUVA-TOC calculations which are reported as indicators of organic aromaticity and hence treatability with halogenated disinfectants as described in EPA Method 415.3 [1, 2]. Notably as shown in Figure 4 above the changes in aromaticity as a function of coagulation are directly quantified as the ratio of the PARAFAC components c1 and c2. Figure 5 therefore compares the PARAFAC c2:c1 ratio (Panel A) to the SUVA values for corresponding raw and finished water samples. Clearly the c2:c1 ratio is lower in the finished samples as is the SUVA ratio in Panel B. The SUVA threshold for treatability is generally recognized to be at values <4 and clearly the finished water samples were generally below this limit.

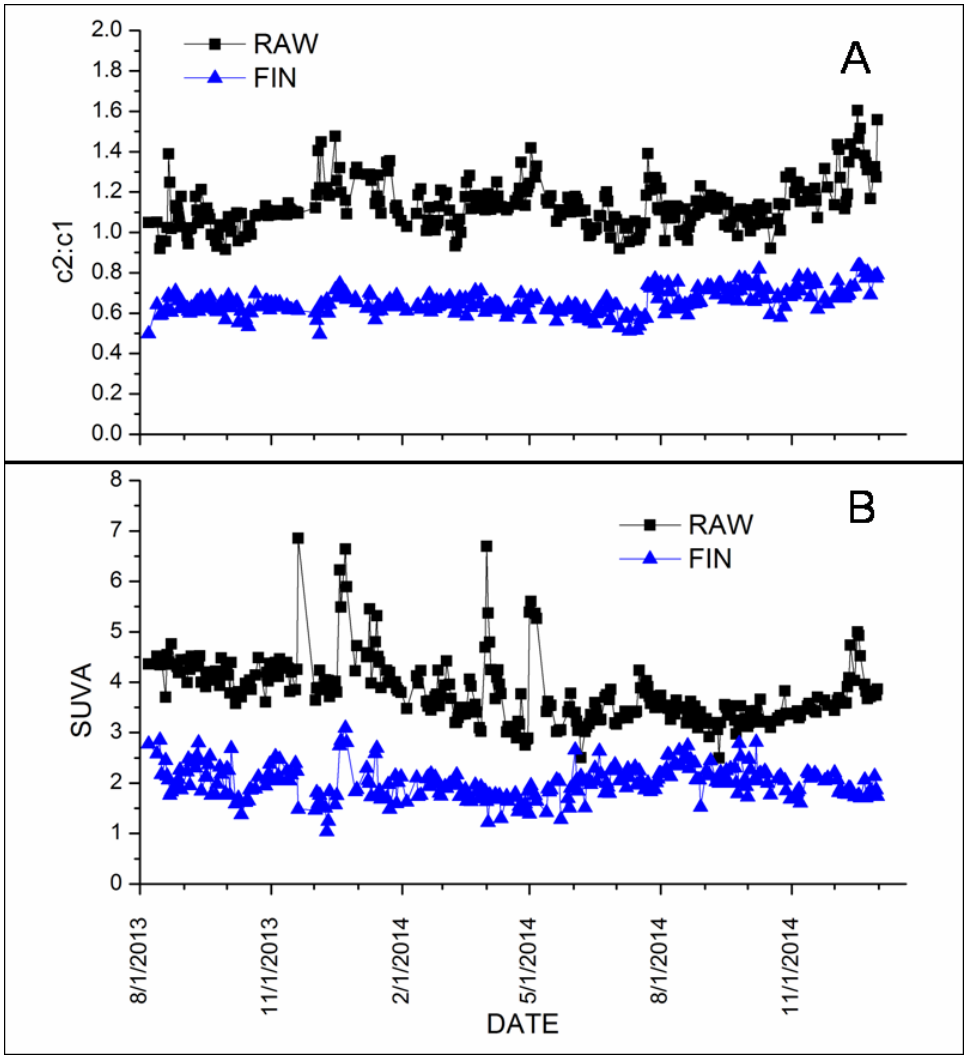


Figure 5. Comparison of the PARAFAC component concentration ratio c2:c1 (A) to SUVA (B) for the daily raw (RAW) and finished (FIN) water samples. SUVA was calculated using the data in Figure 1 using the formula in EPA Method 415.3; SUVA=100 • A254 (cm-1)/TOC (mg/l).

One key consideration is that the SUVA calculation requires separate complex photometric and TOC readings thus the precision and accuracy of the determination is subject to the propagation of the errors from both measurements. To evaluate the relative precision of the SUVA and c2:c1 ratios as indicators of treatability, Figure 6 shows that the mean, range and deviation of the SUVA calculation for the raw and finished water overlapped significantly. On the other hand, the c2:c1 mean and range exhibited no significant overlap to indicate a more precise estimate of aromaticity and treatability with a single instrument determination.

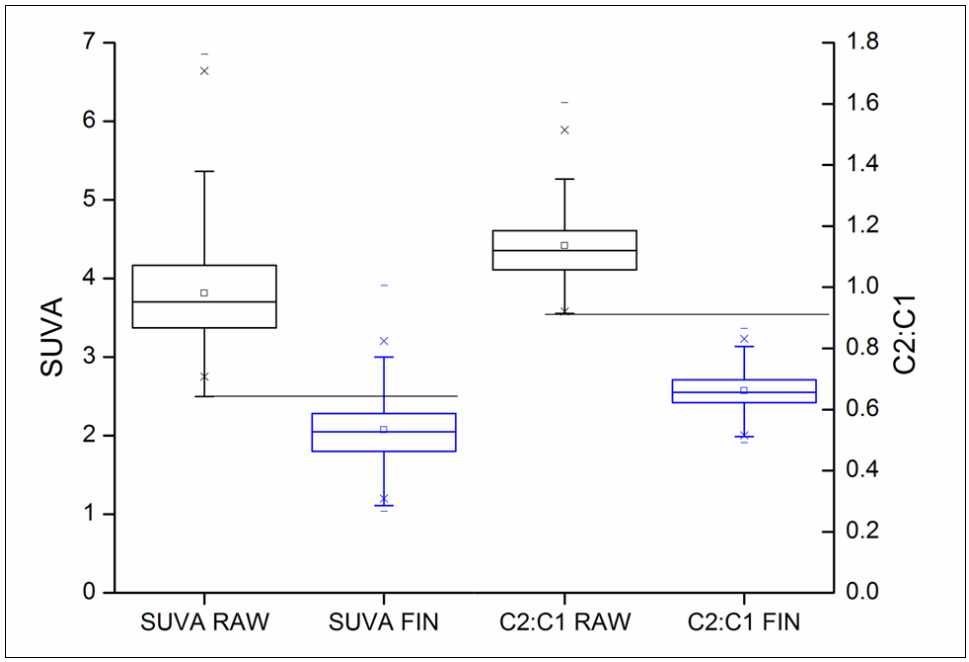


Figure 6. Box plot analysis of the means, maxima, minima and ranges for SUVA (left) and c2:c1 (right) for the raw and finished water samples corresponding to the data in Figure 5.

Evaluation of TOC and % Removal Requirements for EPA DBPR2

A key part of the DBPR2 regulation [1] involves TOC determinations as they relate to removal requirements and treatability. Figure 7A shows that using only the A254 and c2:c1 ratio as linear coefficients, a single robust linear model accurately predicts the TOC for both the raw and finished water samples. The basis of the linear relationship, which involves a fixed intercept value at 0 mg/l, is that the change in the slope of the relationship between A254 and TOC for the raw and finished water is simply determined stoichiometrically by the c2:c1 concentration ratio. As shown Figure 7A this relationship allows accurate measurement of the TOC on a daily basis for both the raw and finished water samples.

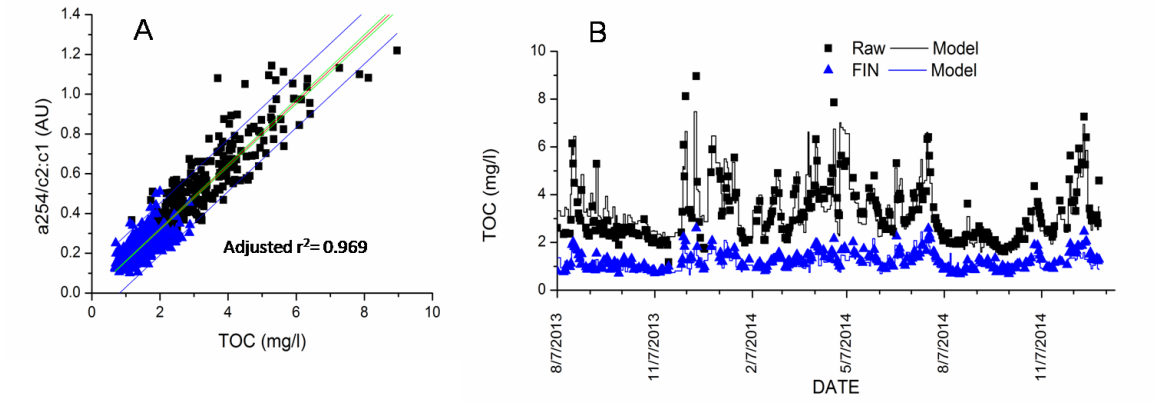


Figure 7. Model linear correlation of the TOC calculated using the A254 and c2:c1 concentration ratio (A) and the comparison of the model TOC calculations to actual daily TOC measurements for the raw (RAW) and finished (FIN) water samples. The linear relationship in panel A equates to TOC= *[A254 nm/ (c2:c1)] / Slope,* where the slope = 0.160.

The main regulation of the TOC determination centers on the requirement for removal of a specified fraction of TOC which is determined a function of both the TOC (mg/l) and alkalinity (mg/l) of the raw water as explained in Table 1. The data in Figure 8A illustrate both the TOC removal requirement calculations (expressed as a fraction) based on the independently measured alkalinity in Fig. 8A, and the Aqualog model TOC values for the raw and finished water shown in Fig. 8B. Figure 8B compares the daily TOC for the raw water, the calculated regulation target and the finished water. Clearly the target value was exceeded in all samples by the finished water treatment to indicate DBPR2 compliance. The treatment rule states that TOC removal requirements apply starting above 2 mg/l, thus in several samples in the latter part of 2014, the % removal requirement was actually 0.

Source Water TOC (mg/l)	Source Water Alkalinity (mg/l) as CaCO3		
	0-60	>60 to 120	>120
>2 to 4	0.35	0.25	0.15
>4 to 8	0.45	0.35	0.25
>8	0.50	0.40	0.30

Table 1. DBPR2 removal rules for TOC as a function of alkalinity in drinking water treatment systems defined by Subpart H that use conventional filtration [1].

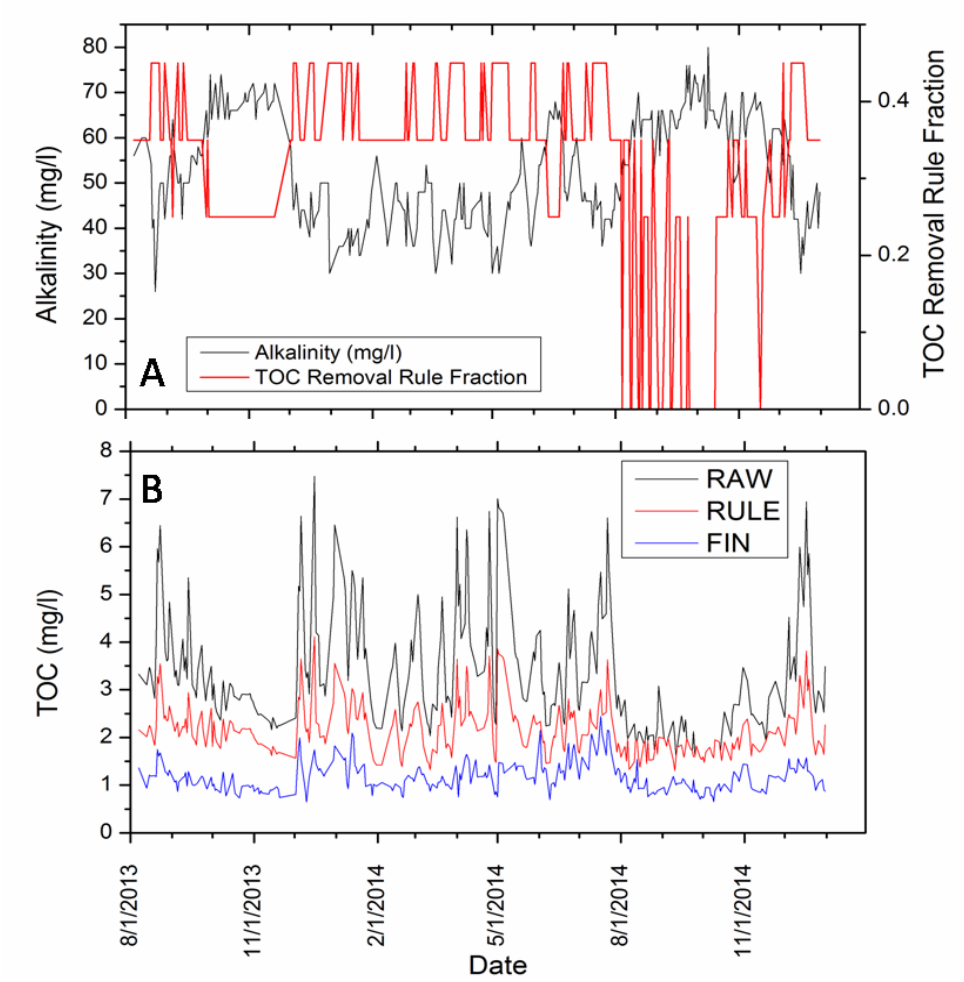


Figure 8. The daily alkalinity values for the raw water and calculated required removal fraction (A) and the Aqualog model TOC values for the raw water (RAW) and finished (FIN) and the calculated target removal (RULE) (B).

Evaluation of the SDS-THMFP to Predict DBPR2 compliance

The DBPR2 stipulates a maximum contamination limit (MCL) for THMs in the distribution system of 80 µg/l. The evaluation of the MCL is performed quarterly for all required local sampling sites in the distribution system as a Locational Running Annual Average (LRAA). Thus in order to predict compliance it is standard practice to perform regular simulated distribution system THM formation potential (SDS-THMFP) measurements. The 10 day SDS-THMFP is best viewed as a worst-case scenario for the distribution system and was evaluated for the raw and finished water samples. The test basically involves a saturating dosage of chlorine at a specified pH and alkalinity followed by an incubation period at a specified temperature to maximize the formation of THMs in the sample which are then evaluated. As shown in Figure 9A, it is possible to accurately predict the actual SDS-THMFP for the raw and finished water using a multiple linear regression involving the TOC and c2:c1 ratios, the latter as an indicator of aromaticity, as the 2 major linear coefficients. The independently measured chlorine residual, pH and alkalinity were significant additional linear coefficients. The data in Figure 9B clearly indicate the finished water exhibited a lower SDS-THMFP than the raw water samples and the average observed values

correspond closely to the MCL for THMs. Importantly, the green symbols show the actual TTHM site measurements to indicate the actual distribution system sites were all well below the MCL and thus within regulation. These data confirm that the SDS-THMFP is a useful representation of the worst case scenario because the actual MCL determinations historically average less than 60-80% of the observed SDS-THMFP values.

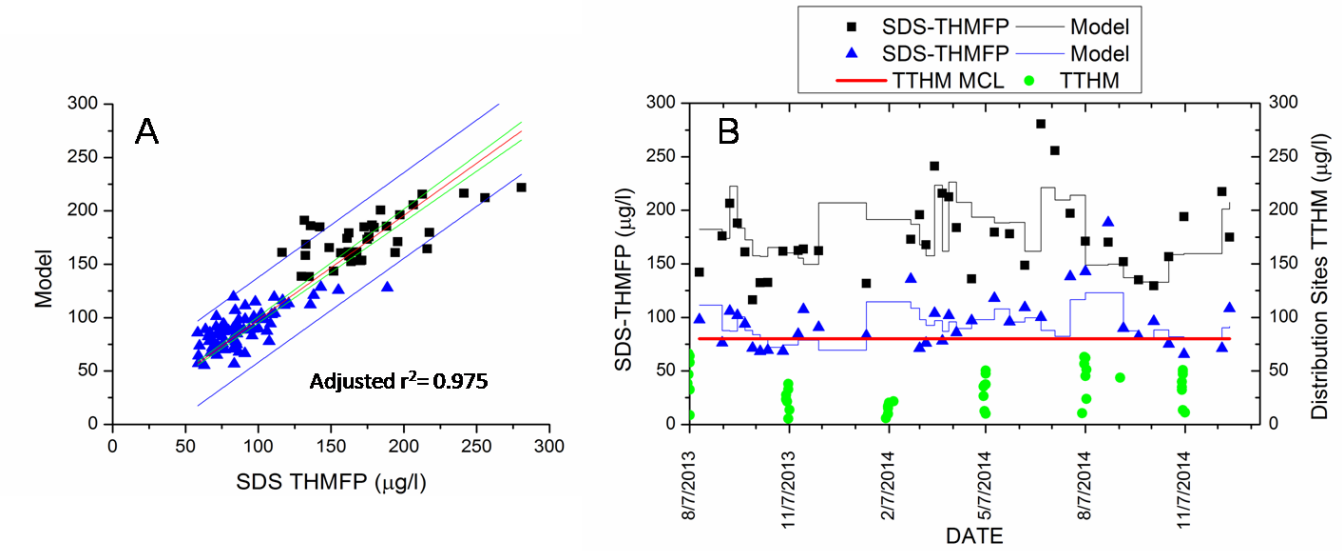


Figure 9. Multiple linear regression model of the SDS-THMFP for the raw and finished water samples (A) and comparison of the model and actual periodic SDS-THMFP measurements (B). The red line indicates the DBPR2 MCL for TTHM and the green symbols represent the actual distribution site values for TTHM.

Conclusions

The Aqualog facilitates in a single, reagent-free instrument method, the capability to monitor TOC and treatability (SUVA) as well as accurate predictions of SDS-THMFP when supplemented with pH, alkalinity and chlorine data. Importantly, the Aqualog's intrinsic ability to identify and quantify the high- and low-molecular weight humic/fulvic species provides a more, rapid precise indicator of treatability than conventional SUVA determinations which require separate photometric UVA and TOC measurements. Thus it is clear the Aqualog is of significant value to surface water treatment plants falling within the Subpart H designations for DBPR2 as a means of continuously evaluating compliance to these parameters. Potential application advantages could be realized for optimizing chemical dosing and other operational and analytical costs associated with DBPR2 compliance.

References

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