



Use of log-transformed absorbance spectra for online monitoring of the reactivity of natural organic matter



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ABSTRACT

This study examined the significance of water quality monitoring parameters obtained via logarithmic transformation of the absorbance spectra of raw and treated drinking water. The data were generated using samples of the influent, settled and filtered water acquired weekly over a six months period at two full scale treatment plants. Examination of the weekly plant samples combined with the data of laboratory fractionation and chlorination experiments showed that the slopes of the log-transformed spectra are correlated with typically reported water quality parameters (e.g., its specific absorbance at 254 nm, SUVA₂₅₄); yet the determination of spectral slopes is considerably simpler and potentially information-rich. The spectral slopes determined for the range of wavelength 280–350 nm were shown to be correlated with the yields of trihalomethanes (THMs) and haloacetic acids (HAAs). These results support the notion that multi-wavelength monitoring of the absorbance spectra of drinking water and their interpretation via logarithmic transformation constitutes a promising practically implementable approach for online water quality monitoring.

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1. Introduction

Online monitoring and control are important and ultimately indispensable for drinking water operations because they allow for continuous surveillance of source and treated water quality and detection of chemical (Hall et al., 2007; Izydorczyk et al., 2009; Storey et al., 2011; Arad et al., 2013) and microbiological threats (Strathmann et al., 2013; Lopez-Roldan et al., 2013; Hammes et al., 2012; Hammes and Egli, 2010; Prest et al., 2014; Foladori et al., 2015). They can also provide early warning indications of unexpected contamination, process failure or other unusual events thus improving the efficiency of drinking water treatment operations and enhancing public health protection (Storey et al., 2011; Kuklina et al., 2013; Banna et al., 2014; Byrne et al., 2014).

Currently available online systems provide reliable information about common water quality parameters such as turbidity, free and combined chlorine, conductivity, pH, oxidation/reduction potential,

chloride, nitrate and ammonia. These parameters are measured using commercially produced sensors that can also provide data for water absorbance at single wavelength (typically 254 nm) or for wider range of wavelengths, and in selected case for fluorescence (Storey et al., 2011; Banna et al., 2014). Absorbance and fluorescence-based parameters suitable for online monitoring have been particularly useful for monitoring concentrations of natural or effluent organic matter in drinking water and wastewater, respectively (Reckhow et al., 1990; Korshin et al., 1997a; Świetlik and Sikorska, 2004; Chow et al., 2007; Matilainen et al., 2011; Audenaert et al., 2013; Valencia et al., 2013; Shutova et al., 2014; Murshed et al., 2014; Bridgeman et al., 2015). Despite the recent developments of a variety of more sensitive and robust sensors and data acquisition systems for online water quality monitoring, its applications for real-time control of trace-level organic contaminants in water remain very challenging (Korshin et al., 1997b; Roccaro et al., 2008, 2009; Gerrity et al., 2012; Zietzschmann et al., 2014; Liu et al., 2015; Anumol et al., 2015). Among such contaminants, disinfection by-products (DBPs) notably trihalomethanes (THMs) and haloacetic acids (HAAs) are strictly regulated (Roccaro et al., 2005) due to their ubiquity, toxicity and carcinogenicity (Richardson et al., 2007).

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All aspects of the formation and speciation of THMs, HAAs and other DBPs are affected by the concentration and reactivity of natural organic matter (NOM), bromide, ammonia, chlorine dose, pH, temperature and reaction time (Reckhow et al., 1990; Leenheer and Croue, 2003; Cowman and Singer, 1996; Hua et al., 2006; Obolensky and Singer, 2008; Pan and Zhang, 2013; Roccaro et al., 2013, 2014). The complexity of NOM halogenation and challenges of its modeling necessitate the use of easily measurable surrogate parameters deemed to be indicative of NOM reactivity in DBP formation. Among such parameters, the absorbance of light at 254 nm (A_{254}) and its value normalized by the concentration of dissolved organic carbon (DOC) and denoted as $SUVA_{254}$ are most typical (Croue et al., 1999; Kitis et al., 2001, 2002). Due to its strong correlation with NOM aromaticity, $SUVA_{254}$ is a good predictor of the yields of total organic halogen (TOX), THM and HAA albeit the performance of $SUVA_{254}$ as an indicator of NOM reactivity has limitations (Weishaar et al., 2003; Ates et al., 2007; Hua et al., 2015). Another challenge for online determination of $SUVA_{254}$ is that it requires that DOC concentrations be measured simultaneously with A_{254} values but this is done less typically. As a result, $SUVA_{254}$ values tend to be measured offline using water grab samples and online $SUVA_{254}$ data are rarely available.

Surrogate NOM characterization parameters other than $SUVA_{254}$ have been suggested as well. For instance, the molar absorbance of NOM at 280 nm (ϵ_{280}) determined by the normalization of water absorbance at 280 by the molar concentration of DOC has been shown to be correlated with the aromaticity and apparent molecular weights of DOM (Chin et al., 1994; Gu et al., 1995; Peuravuori and Pihlaja, 1997). The aromaticity and reactivity of NOM have also been estimated using ratios of absorbances at 280 and 350 nm as well as at 203 and 253 nm (Korshin et al., 1997a). Other spectroscopic parameters, for instance the derivative of absorbance at 290 nm or the second derivative of absorbance at 310 have been recently suggested to provide additional options for online drinking water monitoring (Byrne et al., 2014).

An alternative approach based on the measurements of changes of NOM absorbance before and after chlorination have also been employed to probe the formation of TOX and individual DBPs (Korshin et al., 1997b, 2002; Roccaro et al., 2008, 2011). The differential spectra calculated as the difference of NOM absorbance at any specific wavelength before and after chlorination tend to have a maximum at ca. 272 nm and the intensity of these spectra is strongly correlated with DBP concentrations (Korshin et al., 1997b; Roccaro and Vagliasindi, 2009, 2010).

Recent research has shown that the use of NOM reactivity indicators determined using absorbance measurements at a single or dual wavelengths can be enhanced via determinations of multi-wavelength parameters. For instance, logarithms of NOM absorbance measured for water samples originating from pristine environments or generated in drinking water operations decrease quasi-linearly with the observation wavelength (Helms et al., 2008; Yan et al., 2014a, 2015a, 2015b; Gao et al., 2015). The slopes of the log-transformed absorbance spectra of NOM discussed in these and related publications are determined as

$$S_{\lambda_1-\lambda_2} = \left| \frac{d \ln A(\lambda)}{d\lambda} \right|_{\lambda_1-\lambda_2} \quad (1)$$

where $\ln A(\lambda)$ is the natural logarithm of NOM absorbance at any specific wavelength, while λ_1 and λ_2 define the range of wavelength in which the spectral slope is calculated.

The slopes of log-transformed NOM absorbance spectra determined, for instance in the range of wavelengths 275–295 nm ($S_{275-295}$) or 350–385 nm ($S_{350-385}$) tend to decrease with as the apparent molecular weight of NOM increases (Helms et al., 2008).

Recent research has shown that the spectral slopes determined in the range of wavelength 350–400 nm ($S_{350-400}$) tend to decrease as a result of NOM chlorination and the extent of this change is correlated with the formation of DBPs (Yan et al., 2014a). Pronounced changes of the $S_{275-295}$ and $S_{350-385}$ values have been observed for NOM oxidized by chlorine, chlorine dioxide and ozone and correlated with attendant decreases of the antioxidant capacity of NOM (Wenk et al., 2013).

Given that the prior studies demonstrate that the slope and possibly other parameters characterizing log-transformed absorbance spectra of NOM can be predictive of NOM reactivity, it is relevant to examine the performance of this approach for drinking water produced in realistic treatment conditions. Accordingly, the goals of this study were i) to establish major trends in the behavior of spectral slopes of log-transformed absorbance spectra of raw and treated water produced at representative drinking water plants; ii) to examine relationships between the spectral slopes and commonly measured parameters such as $SUVA_{254}$; iii) to examine the significance of measurements of the spectral slopes for predicting NOM reactivity in DBP formation and iv) to establish the utility of long-transformed spectra in online water quality monitoring.

2. Materials and methods

2.1. Waters, standards, reagents and resins

Experiments were conducted using water samples sent to the UW research laboratory from two full-scale drinking water treatment plants (WTP) denoted as A and B. WTP A is a conventional surface water treatment plant that uses a sequence of coagulation with alum, flocculation, sedimentation followed by filtration and primary disinfection with chlorine. Chloramine is used as a secondary disinfectant. A cationic coagulant aid polymer can be added before the flocculation/sedimentation step. The filtration is done using dual media filters, and PACl can be fed as a filter aid when necessary. Chlorine is injected before the filtration step at a dose needed to ensure a 1.5 mg/L free chlorine residual in the filter effluent. Additional chlorine is added as needed at the clear well to provide a 3.7 mg/L total chlorine residual. Fluoride, orthophosphate, ammonia and lime are added to convert the chlorine to chloramine and for corrosion control. The treatment sequence used at WTP B is similar to that at Plant A, the only major difference being the presence of an open reservoir located between the sedimentation basins and the filters in Plant B.

Influent, settled and filtered samples from WTP A (denoted as AS and AF, respectively) and WTP B (denoted as BS and BF, respectively) were collected over a 23-week (March to July) observation period and sent to the UW laboratory overnight. Samples of settled water were taken at a point located upstream from chlorine injection. Samples of filtered water were taken from the clearwell. Residual chlorine in the filtered water samples was immediately quenched by sodium sulfite. For uniformity, same amount of sodium sulfite was added to all weekly samples during their collection. DBP analysis of the weekly samples showed that only trace level of DBPs were present in any of them prior to chlorination carried out in the UW laboratory. Upon receipt, the samples sent from the treatment plants were processed to determine concentrations of total and dissolved organic carbon, pH, absorbance and fluorescence spectra and other water quality parameters.

2.2. Experimental and analytical methods

2.2.1. Fractionation and chlorination

All chemicals used in the laboratory experiments were ACS reagent grade. Solvents used in extractions were high-purity grade.

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