Development of fluorescence sensors for DBPs control in drinking water

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Abstract. Chlorination of drinking water has been recognized as one of the most effective public health measures ever. However, chlorine reacts with Natural Organic Matter (NOM) present in all surface waters to produce disinfection by-products (DBPs). Trihalomethanes (THMs) and haloacetic acids (HAAs) are the most prominent classes of DBPs, but a vast array of yet unidentified compounds contribute to about 60% of the total organic halogen have been found in disinfected water. Due to the complexity and heterogeneity of NOM, several surrogate parameters have been used to quantify NOM reactivity in halogenation reaction and DBPs formation. Differential absorbance and fluorescence were also strongly correlated with DBPs formation. The goal of this study is to explore the performance and applicability of fluorescence based surrogates to control DBPs and DBPs precursors during the water chlorination at varying operating conditions. Obtained results highlight that selected fluorescence signals are powerful parameters for in situ monitoring of the organic precursors of DBPs.

Keywords: Disinfection; chlorination; disinfection by-products; monitoring.

1. Introduction

Fluorescence excitation-emission matrix (EEM) spectroscopy, also known as three-dimensional fluorescence (3DEEM) or fluorescence fingerprinting, is one of the most predominant methods because of its information-rich data, visual maps and multidimensional information provided (Li et al., 2020). Indeed, fluorescence is often measured through a range of excitation and emission wavelengths using Excitation-Emission Matrix Spectroscopy (EEMs), producing a 3-D fluorescence intensity landscape in which the presence of distinctive peaks can provide indications of sources, behaviour, and biogeochemical cycling of DOM (Murphy et al., 2010), responsible for DBPs formation. The analysis of 3-D fluorescence data containing additional information such as the relative content of a component can be interpreted by fluorescence intensity (FI), fluorescence index or other derived expressions. For instance, Bugden et al. (2008), used the slope ratio and the intensity ratios to interpret 3-D fluorescence data based on specific peak FI value in order to detect oil and chemically dispersed oil in seawater. 3-D fluorescence can yield important information on the chemical nature of NOM, especially for the aromatic organic materials. The aromatic carbon compounds can yield the carbonaceous DBPs, such as trihalomethanes (THMs), trichloroacetic acid and other (C-DBPs). Fulvic acid also has a significant impact on the formation of THMs, haloacetic acids, and aldehydes, while 2,3,5-tribromopyrrole can be produced from humic acid (Richardson et al., 2003). This implies that there should be a relationship between the fluorescence fractions and TOC or DBPs.

2. Materials and methods

Information on methods employed to analyze fluorescence can be found in prior studies (Roccaro et al., 2009; Sgroi et al., 2000).

3. Results and discussion

The removal of EEM during the treatment trains at a DWTP indicates the removal of DOM and DBP precursors. For instance, Figure 1 shows the decrease of fluorescence EEM over the treatment train at a selected WTP. As expected, the decrease in EEM is significant during the DWTP, demonstrating that fluorescence EEM can be used to track the fate of DOM during the treatment train. Based on the EEM information and on prior research (Roccaro et al., 2009), selected fluorescence peaks were identified to study the DBPs formation. The selected fluorescence sensors were validated by correlating the data obtained from the laboratory spectrofluorometer (Shimadzu RF-5301PC) and those obtained by the sensor fluorescence. The fluorescence intensities obtained from the laboratory spectrofluorometer were extracted from the 3-D EEMs and elaborated to obtain fluorescence raw data (Arbitrary Units, AU) and corrected data by inner filter effect (IFE) and blank corrections, and Raman normalisation (Raman Units, RU). Figure 2 shows the strong linear correlation between two selected fluorescence sensors and lab-scale spectrofluorometer data of different water samples, including surface water, and tap water to investigate the sensor sensitivity. As shown in Figure 2, the strong linear correlation was found regardless of the type and content of DOM. The developed sensors will be employed in full or pilot scale water systems to monitor the DBPs and their organic precursors.

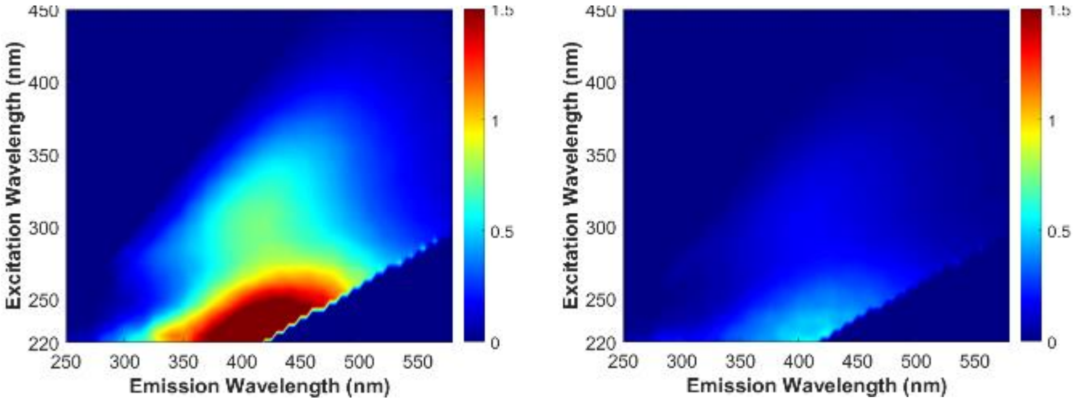

Figure 1. Fluorescence EEM changes during the WTP (Raw water vs. treated water)

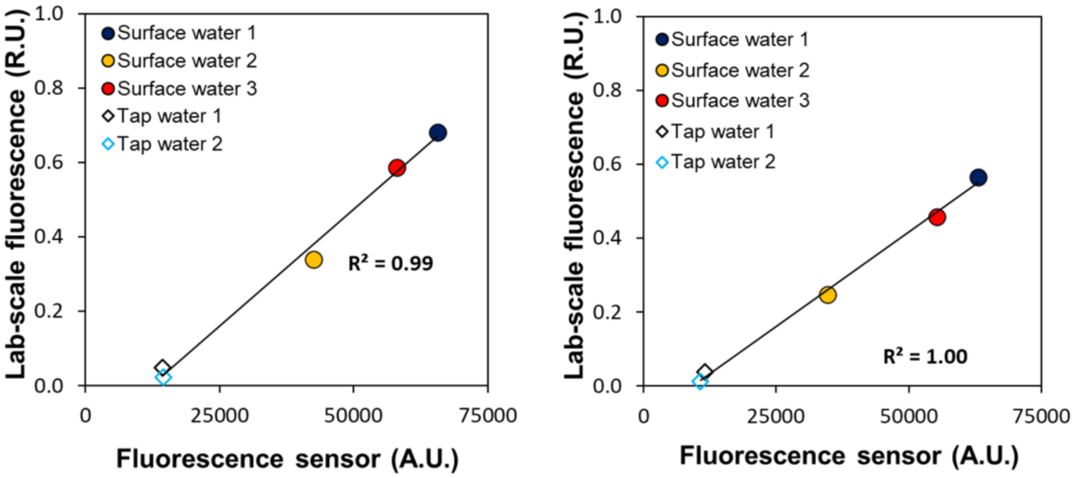

Figure 2. Linear correlation between two selected fluorescence indexes measured by sensors (A on the left and B on the right) and lab-scale spectrofluorometers of different water matrices

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