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Relationships between DBP concentrations and differential UV absorbance in full-scale conditions

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ABSTRACT

Differential UV spectroscopy, defined as the difference in UV absorbance spectra before and after chlorination, has shown great potential to predict disinfection by-product (DBP) concentrations at laboratory scale. However, so far, no results have been reported on the full scale application of differential UV spectroscopy in drinking water treatment facilities. The objectives of this study are to determine if relationships can be developed between differential UV absorbance and DBP concentrations, for both regulated and unregulated DBPs, in a full-scale facility and to determine if these relationships vary throughout the year with variations in raw water quality and treatment conditions. The results show that linear and power relationships between differential UV absorbance and DBP concentrations can be developed ($0.62 \leq R^2 \leq 0.99$), although differences between relationships obtained in lab- and full-scale conditions need further investigation. Finally, the relationships obtained are different from one sampling campaign to another, which raises the question of whether it is possible to determine relationships that are stable enough to be used as adequate feedback on DBP concentrations.

1. Introduction

The monitoring of disinfection by-products (DBPs) for regulatory compliance usually requires grab sampling and analyses of the samples for individual species. While these methods involve costs and delays for water utilities, researchers have developed empirical (Sadiq and Rodriguez, 2004, 2011) and kinetic (Gallard and von Gunten, 2002; Korshin et al., 2004; Sohn et al., 2004) models based on operational and water quality parameters (e.g. chlorine dose, natural organic matter indicators, temperature, pH, contact time and others), to provide more frequent estimates of DBP concentrations. These estimates are not valid for regulatory compliance, but could be used to evaluate the impact of raw water variations or operational changes on DBP formation, to plan sampling campaigns in distribution networks, or simply to provide more frequent feedback on plant performances in terms of DBP precursor removal and occurrence.

An alternative approach for estimating DBP concentrations, differential UV absorbance (ΔA), has been proposed by Korshin et al. (1996). The approach consists in measuring UV absorbance before chlorination and after a given contact time. In laboratory conditions, the difference in UV absorbance at a wavelength of 272 nm between the two measurements has been shown to be linearly proportional to the concentration of many regulated DBPs, including trihalomethanes (THMs) and haloacetic acids (HAAs) (Korshin et al., 2002a; Li et al., 1998; Uyak and Demirbas, 2014), as well as some unregulated DBPs (Korshin et al., 2004, 2002a, 2002b; Roccaro and Vagliasindi, 2010). Reported correlations between ΔA and DBP concentrations, obtained through laboratory batch chlorination experiments, are at least as strong as results obtained by empirical and kinetic models (Korshin et al., 2002b, 2002a; Li et al., 1998; Roccaro et al., 2008a; Roccaro and Vagliasindi, 2009, 2010). Also, while UV absorbance of low specific UV absorbance (SUVA)

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waters may not be proportional to the formation potential of DBPs, ΔA has shown to be a good surrogate to DBP measurements in waters with various SUVAs (Korshin et al., 2002a; Korshin and Chang, 2008; Roccaro et al., 2008b). It has been shown that DBP concentrations are better correlated to ΔA at 272 nm than at 254 nm, a wavelength at which UV absorbance is more widely monitored (Roccaro and Vagliasindi, 2009). However, to the best of our knowledge, full scale applications of ΔA have not been reported in peer-reviewed literature.

Previous work (Marcoux et al., 2017) has shown that about 80% of the DBPs measured in the distribution network, in some cases, are already formed when the water leaves the plant and enters the distribution network. Therefore, ΔA could lend itself as a useful tool for the estimation of DBPs to characterize their formation at the treatment plant. The objectives of this study are first to determine the applicability of DBP - ΔA relationships as a surrogate for grab sampling and analyses of individual DBPs, and secondly to provide a better understanding of regulated and non-regulated DBP formation throughout the plant. This paper presents a first attempt at applying ΔA in a full-scale facility for DBP monitoring purposes.

2. Methodology

2.1. Case study

The facility in this study has been worked on previously (Marcoux et al. (2017)) and is located in the City of St-Jérôme, Quebec, Canada and takes its water from the Du Nord River that flows south from the Laurentian Mountains. The treatment plant (Fig. 1) consists of a slightly modified conventional treatment train. Potassium permanganate ($KMnO_4$) is used on the raw water as a pre-oxidant. Coagulation and settling is conducted on five parallel trains: two ballasted ACTIFLO® (Veolia Water Technologies, Canada) floc settlers and three conventional settling basins. Interchlorination with sodium hypochlorite takes place after settling but before filtration in all settling trains at around 1 h before primary disinfection with chlorine. The flow on conventional settlers is held almost constant, while the flow treated by the ballasted floc settlers is adjusted to account for daily variations in water demand. 12 dual-media (i.e. sand and activated carbon) filters treat water from the ballasted floc and conventional settlers (six for each stream). Backwash and filter ripening waters are sent to waste and do not contribute to DBP levels in the plant. Once the filter effluents are mixed, primary disinfection is conducted with sodium hypochlorite before entering the contact tank. Chlorination is followed by UV disinfection, also for primary disinfection, and chlorine dioxide, for oxidation purposes. The total reservoir volume between the effluent of the filters and the entrance of the distribution system is about 36 000 m^3, providing a hydraulic retention time of about 20 h for an average flow of 45 000 m^3/day. There is no other reservoir in the distribution network.

2.2. Sampling strategy

This study is based on intensive seasonal multi-point daily sampling campaigns that were designed according to the different location of the various chlorination points and the water residence time within this treatment plant. Four intensive 24 h sampling campaigns were carried out on October 2015 (fall), December 2015 (early winter), March 2016 (early spring), and July 2016 (summer), for seasonal characterization of DBP formation. Regulated DBPs (THMs and HAAs) were measured in each campaign, while non-regulated DBPs (haloacetonitriles (HANs), chloropicrin (CPK) and haloketones (HKs)) were measured only in the last two campaigns. Other water quality and operational parameters, including differential UV absorbance (ΔA), were also measured in each campaign. Samples were taken at 15 points throughout the plant (Fig. 1), 10 of which were located after the first chlorination point. Sampling locations were chosen to adequately characterize the impact of coagulation on natural organic matter (NOM) (RW, S1, S2, S4, S5) and to provide DBP concentrations after short and long reaction times in the reservoirs, before (S3, S6, S7, S8) and after (S9, S10, S11,

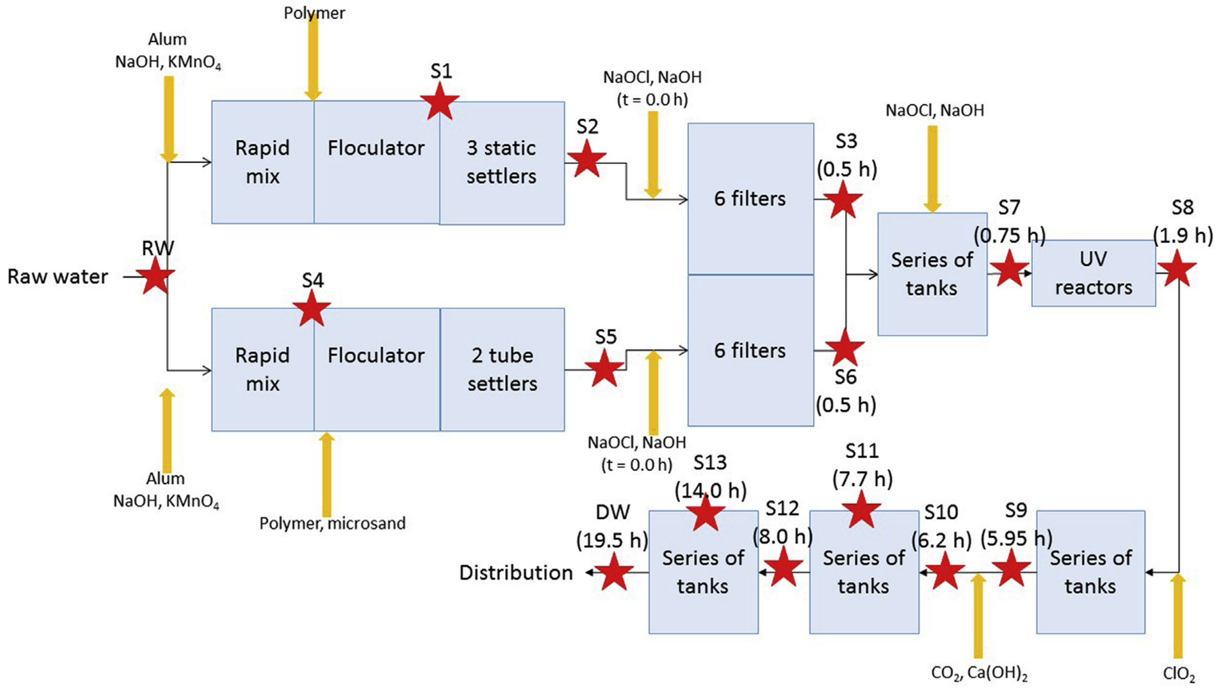

Fig. 1. Flow chart of the treatment plant under study, with location of sampling points and estimated average travel time after first chlorination point.