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Characterization of natural organic matter in water for optimizing water treatment and minimizing disinfection by-product formation

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Introduction

Natural organic matter (NOM) present in source water has significant impact on water treatment processes and on the quality of drinking water. NOM is a complex mixture of diverse groups of organic compounds, humic and fulvic acids, proteins, peptides, carbohydrates, and heterogeneous materials decayed from terrestrial vegetation and aquatic organisms (Edwards, 1997; Barrett et al., 2000; Hwang et al., 2000). The presence of NOM in source water is a critical factor in the determination of both coagulant and disinfectant doses for water treatment (Edzwald, 1993; Matilainen et al., 2010; Rakruam and Wattanachira, 2014; Huang et al., 2015). NOM can act as a carbon source for the growth of microorganisms in water distribution systems (Edwards, 1997; Zhao et al., 2014). In addition, many classes of organic compounds in NOM can react with disinfectants to form various disinfection by-products (DBPs). The type and amount of DBPs produced during water disinfection are highly dependent on the concentration and constituents of NOM in the source water (Barrett et al., 2000; Hua and Reckhow, 2007a; Krasner et al., 2006; Bull et al., 2011; Richardson and Postigo, 2012; Wang et al., 2016). Therefore, characterization of NOM in water is important for optimizing processes of water treatment and for minimizing the formation of toxic DBPs.

1. Techniques for the characterization of NOM

Examination of water color and turbidity, measurements of absorbance at an ultraviolet (UV) wavelength (*e.g.*, 254 nm), and determination of dissolved organic carbon (DOC) can offer limited information about NOM in a water sample (Bennett and Drikas, 1993; APHA et al., 1998; Matilainen et al., 2011). Advanced instrumental techniques, such as gas chromatography mass spectrometry (GC–MS) (*e.g.*, pyrolysis GC–MS), nuclear magnetic resonance (NMR) (*e.g.*, C^{13} solid state NMR), infrared spectroscopy (*e.g.*, diffuse reflectance infrared Fourier transform), fluorescence spectroscopy, high performance size exclusion chromatography (HPSEC), and liquid chromatography with high resolution mass spectrometry (Vuoria et al., 1998; Her et al., 2003; Allpike et al., 2005; Chow et al., 2008; Peleato and Andrews, 2015; Tang et al., 2016; Richardson and Postigo, 2016), can provide further information on the composition of NOM.

In a recent study by Huang et al. (2016), the authors combined HPSEC separation with multi-wavelength absorption

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detection to characterize dissolved organic matter (DOM) in a live water distribution system. The high performance size exclusion chromatography enabled the separation of DOM on the basis of apparent molecular weight (AMW) (Fig. 1). Absorbance detection simultaneously at multiple UV wavelengths, *e.g.*, 210, 230, and 254 nm, provided complementary detection of DOM classes that may or may not contain aromatic moieties. Applications of this technique contributed to the characterization of molecular size fractions of DOM.

2. Characterization of DOM in a live water distribution system

While previous studies (Liu et al., 2010; Xing et al., 2012) have used HPSEC to characterize various organics related to the drinking water supply, Huang et al. (2016) applied the method to examine a drinking water distribution system in South Australia. From the water treatment plant to the consumers' water taps, the water supply distribution system consisted of a single long trunk main with branches to several remote communities. The source water was from River Murray. The main steps of the conventional treatment were coagulation, flocculation, sedimentation, filtration, UV disinfection, and chloramination. Chloramine was used as the secondary disinfectant to ensure that disinfectant residuals reached the end of the long distribution system and to provide protection against microbial contamination. The authors collected water samples from 17 sampling points across the water treatment plant and throughout the water distribution system. These samples from a live water distribution system allowed for the characterization of the changes of DOM, disinfectant residuals, and microbial cell counts. These measures also made it possible to study the associations between DOM and other water quality parameters.

The high performance size exclusion chromatography-ultraviolet (HPSEC-UV) analyses of raw water (Fig. 1a) and treated water (Fig. 1b) show two broad peaks, corresponding to apparent molecular weight (AMW) of approximately 200–300 and 1000–1300 Da. The lower intensity of the higher AMW fraction (1000–1300 Da) in the treated water (Fig. 1b) as compared to the raw water (Fig. 1a) suggests that the water treatment processes were able to remove or destroy some of the higher molecular weight DOM. However, the treatment processes did not result in a decrease of the lower AMW (200–300 Da) DOM. In general, across treatment processes in the water treatment plant, changes were observed in the higher AMW fraction (1000–2000 Da). Along the water distribution system, changes were observed in the lower AMW fraction (200–300 Da). A comparison of the signals obtained from the detection at different wavelengths (210, 230, and 254 nm) also suggests that the treatment processes preferentially removed or destroyed the aromatic fraction of DOM (absorbance at 254 nm). These results are consistent with previous findings (Korshin et al., 2009; Xing et al., 2012).

3. Determination of microbial cells in the water distribution system

Huang et al. (2016) also measured the changes in microbial levels of water in the water treatment plant and in the distribution system. This was done by using flow cytometry analysis of fluorescently stained bacteria with SYTO-9 and with a bacterial viability kit (Hoefel et al., 2005). They found that the active bacterial concentration in the raw water was 1×10^7 cells/mL. This was significantly decreased following the steps of water treatment and disinfection. Specifically, with the conventional water treatment (before disinfection), the active bacterial concentration was reduced to 1×10^6 cells/mL. The subsequent disinfection process further reduced the active bacterial concentration to 1×10^4 cells/mL. Thus, the overall water treatment processes resulted in a total of 3 log removal of the active bacterial cells.

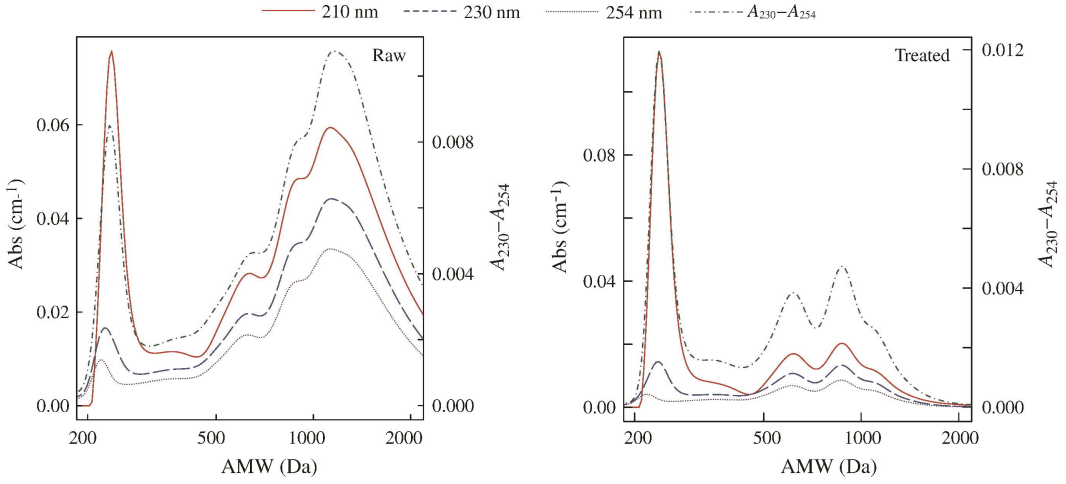

Fig. 1 – Chromatograms obtained from the high performance size exclusion chromatography (HPSEC)-ultraviolet (UV) analyses of raw water (left graph) and treated water (right graph). Apparent molecular weight (AMW) was calibrated against the retention time response from polystyrene sulfonate standards. UV absorbance (Abs) was detected at 210, 230, and 254 nm. The vertical axis on the right shows the difference between the absorbance at 230 nm and the absorbance at 254 nm ($A_{230} - A_{254}$). Reproduced with permission from Huang et al., 2016.

To understand the relation between the disinfectant residuals and the bacterial concentration in water from the distribution system, Huang et al. (2016) also measured the concentrations of the total chlorine residual in the water samples (APHA et al., 1998). They found that the order of the total bacterial cell concentrations at three customer tap water locations coincided with the reverse order of the total disinfectant residual. These results are consistent with previous research indicating that the level of microorganisms increases with decrease of total disinfectant (Lipponen et al., 2002; Bai et al., 2015).

4. Understanding the association between DOM and nitrification

Further to the observation that the total bacterial cell concentrations in the water distribution system correlated in reverse order with the total disinfectant residual, Huang et al. (2016) also found that the order of the total bacterial cell concentrations coincided with the order of the sums of nitrate and nitrite. An increase in oxidized nitrogen concentrations (nitrate or nitrite), a decrease in disinfectant residual, and an increase in microbial concentrations are common adverse effects associated with the occurrence of nitrification (Wilczak et al., 1996; Schreiber and Mitch, 2007; Zhang et al., 2009). Nitrification involves oxidation of ammonia to nitrite, and further oxidation of nitrite to nitrate (Zhang et al., 2009). These processes are associated with the occurrence and activity of nitrifying microorganisms.

Management of nitrification is critical particularly when chloramine is used as the secondary disinfectant. Nitrification is related to many water quality parameters (Fig. 2), and management of nitrification requires understanding of NOM in water and its relation to the decay of chloramine. Chloramine offers longer lasting disinfection and greater stability over chlorine, which is particularly important in distribution systems that are characterized by long residence times and high temperatures. While offering greater stability over chlorine, chloramine is still unstable and degrades over time. Nitrification can reduce the pH and alkalinity of the water and the nitrite produced by nitrification can increase chloramine decay. Furthermore, reaction of chloramine with DOM in drinking water results in decreases in the concentration of the disinfectant residual needed to ensure a safe drinking water supply. The growth and regrowth of microorganisms have serious potential health risks. Therefore, management of chloramine decay and the prevention of nitrification are critical for water utilities managing chloraminated drinking water distribution systems.

Formation of DBPs from reactions between DOM and the disinfectants is also a concern. While chloramine produces only a fraction of the common DBPs (*e.g.*, trihalomethanes, haloacetic acids, and chloral hydrate) that are produced by chlorine (Mitch and Sedlak, 2002; Swietlik et al., 2004; Hua and Reckhow, 2007b; Lin et al., 2015), a number of new DBPs of

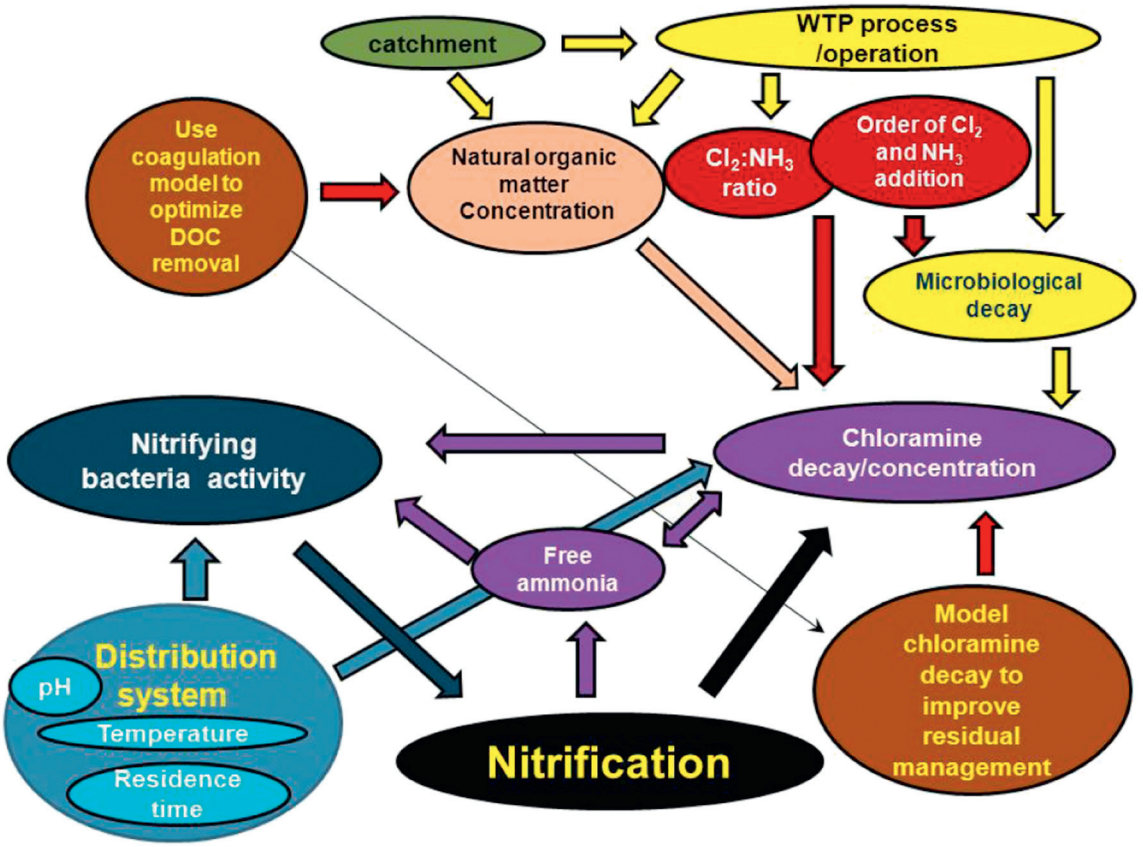

Fig. 2 – Schematic showing relations of nitrification with other water quality parameters when chloramine is used as the secondary disinfectant. Figure courtesy of Mr. David Cook, Senior Scientist, Australian Water Quality Centre, SA Water, Australia.

higher toxicity have been detected in chloraminated drinking water (Gerecke and Sedlak, 2003; Krasner et al., 2006; Richardson et al., 2007; Li et al., 2015).

5. Concluding remarks

It is important to characterize NOM in water because NOM influences water treatment processes, reduces the concentration of disinfectant residuals, forms disinfection by-products, and affects the quality of drinking water. By using HPSEC coupled with a multiple wavelength UV absorbance detection, Huang et al. (2016) were able to characterize DOM as an indirect assessment tool for potential nitrification occurrence along an operating distribution system. This approach was applied to investigate the impact of different fractions of DOM on nitrification. The DOM fractions included those of relatively lower molecular weight, less aromatic character and with a weak absorbance response in the 250–280 nm wavelength range. This study revealed general water quality parameter changes associated with nitrification occurrence in the distribution system and their associations with changes in the DOM molecular weight profile. Due to the nature of an operating system with possible changes in both environmental and operational conditions along the distribution system, it is important to conduct studies like this to compare the samples in different sections of a distribution system and to analyze interactions among the key water quality parameters. Such studies will contribute to a better understanding of how DOM impacts water quality in chloraminated distribution systems.

The type and character of NOM are complicated and vary with location and season (Sharp et al., 2006). The interactions of chloramine with complicated NOM in source water have resulted in the formation of new DBPs (Mitch and Sedlak, 2002; Choi and Valentine, 2002; Krasner et al., 2006; Qin et al., 2010; Shah and Mitch, 2012). Further research is needed to understand the formation of the new DBPs, characterize their precursors, survey their occurrence, investigate their transformation, study their human health effects, and minimize their formation, achieving the ultimate goal of ensuring the supply of safe drinking water.

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