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Q5 Developing a chloramine decay index to understand 2 nitrification: A case study of two chloraminated drinking water 3 distribution systems

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ABSTRACT

The management of chloramine decay and the prevention of nitrification are some of the 17
 critical issues faced by water utilities that use chloramine as a disinfectant. In this study, 18
 potential association between high performance size exclusion chromatography (HPSEC) 19
 data obtained with multiple wavelength UV detection from two drinking water distribution 20
 systems in Australia and nitrification occurrence was investigated. An increase in the 21
 absorbance signal of HPSEC profiles with UV detection at $\lambda = 230$ nm between apparent 22
 molecular weights of 200 to 1000 Da was observed at sampling sites that experienced rapid 23
 chloramine decay and nitrification while its absorbance signal at $\lambda = 254$ nm decreased. A 24
 chloramine decay index (C.D.I) defined as the ratio of area beneath the HPSEC spectra at two 25
 different wavelengths of 230 and 254 nm, was used in assessing chloramine decay 26
 occurrences. The C.D.Is of waters at locations that experienced nitrification were 27
 consistently higher than locations not experiencing nitrification. A simulated laboratory 28
 study showed that the formation of nitrite/nitrate and/or soluble microbial products and/or 29
 the release of extracellular polymeric substances (EPS) during nitrification may contribute 30
 to the C.D.I increase. These findings suggest that C.D.I derived from HPSEC with multiple 31
 wavelength UV detection could be an informative index to track the occurrence of rapid 32
 chloramine decay and nitrification. 33

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Introduction

49 One of the major goals of the drinking water industry is to
 50 supply high quality drinking water to the community that is
 51 free of pathogens and has none or minimal levels of chemical
 52 and physical contaminants. This goal is achieved by appropri-
 53 ate water treatment processes including the use of chemical

disinfectants to remove harmful microorganisms in the drink- 54
 ing water and ensure that the treated water is safe to drink. In 55
 recent years, monochloramine has been widely used for 56
 secondary disinfection to minimize disinfection by-product 57
 (DBP) formation and to meet disinfection requirements in 58
 distribution systems (Duirk et al., 2005; Vikesland et al., 2001). 59
 However, a major concern with the use of monochloramine as a 60

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secondary disinfectant is the decay of monochloramine and nitrification occurrence. Nitrification is a biological process in which sequential oxidation of ammonia (released as a result of chloramine decay) to nitrite, and nitrite to nitrate occurs. When chloramine residual is low, i.e., less than 1 mg/L, the chance of nitrification occurring in water systems is higher (Liu et al., 2005; Nguyen et al., 2012; Wilczak et al., 1996; Zhang and Edwards, 2009). Once nitrification starts, it is difficult to maintain an acceptable chloramine residual because nitrification can increase chloramine decay and affect the disinfectant residual needed to ensure a safe drinking water supply. While there are various factors such as treated water quality, concentration of residuals, and residence time that have affect the efficiency of chloramine disinfection, it is becoming evident that the chloramine disinfection efficiency in water distribution systems is also dependent on the presence of extracellular polymeric substances (EPS) in biofilms (Wang et al., 2013; Xue et al., 2014). EPS can accelerate the decay of disinfection agents such as chlorine or chloramine (Wonoputri et al., 2015; Xue et al., 2014). The management of chloramine decay and the prevention of nitrification are critical for water utilities managing chloraminated drinking water distribution systems (WDS) (Huang et al., 2016; Wilczak et al., 1996; Yang et al., 2008; Zheng et al., 2016). Nitrification is still not fully understood, and therefore research is needed to determine the influencing factors on nitrification and then monitor and control these in order to manage nitrification.

The detection and monitoring of nitrification episodes is usually carried out through measuring water quality parameters referred to as indicators of nitrification. A decrease in the disinfectant residual (Pintar et al., 2005), a decrease in dissolved oxygen (Odell et al., 1996; Wilczak et al., 1996; Zhang et al., 2009), or an increase in nitrite and nitrate concentrations (Pintar et al., 2005; Wilczak et al., 1996; Zhang et al., 2009), and microbial decay factor (F_m) (Sathasivan et al., 2005) are the most frequently recommended indicators of nitrification incidents. On the other hand, it has been reported that ammonia is not a sensitive nitrification indicator because ammonia concentration will change at various stages of nitrification (Jian et al., 2007; Liu et al., 2005; Wilczak et al., 1996; Yang et al., 2008). In addition, heterotrophic plate count (HPC) bacteria are recommended as a water quality indicator in Australia (Ho et al., 2012; Hoefel et al., 2003; Vitanage et al., 2002). This is listed as one of the indicators of nitrification (Odell et al., 1996) because HPCs have been observed to rise during nitrification in chloraminated drinking water distribution systems (Bal Krishna et al., 2013; Skadsen, 1993). However, other factors can lead to high HPCs beside nitrification, so HPCs cannot be used in isolation as one of the indicators of nitrification (Zhang et al., 2009). The other water quality parameters such as pH, alkalinity and temperature have been used as indicators of nitrification, but correlations between these parameters and nitrification occurrences are typically not very strong (Odell et al., 1996).

The aim of this study was to enhance the understanding of nitrification and chloramine decay in real water distribution systems. The approach taken was to collect water samples from different sites throughout two full scale Australian drinking water distribution systems, Tailem Bend-Keith (TBK) in South Australia and the Mundaring system in Western Australia, and

analyze the samples by high performance size exclusion chromatography (HPSEC). HPSEC has been widely used to provide useful information on the quality of drinking water and is an analytical method to evaluate the apparent molecular weight (AMW) distribution of NOM (Chow et al., 2008; Huang et al., 2016; Pelekani et al., 1999; Zheng et al., 2016). HPSEC is a useful organic characterization tool and has found wide application in water treatment optimization, because it is a relatively inexpensive analytical method that requires a small sample volume with minimal pre-treatment. HPSEC is a separation technique based on molecular size by elution through beds of porous beads. Molecules that are too large to penetrate the pores of the beads are excluded and passed through the column with the solvent, while molecules that penetrate the beads are temporarily retained, and thus are separated from the larger molecules (De Nobili and Chen, 1999). Despite HPSEC limitations such as the selection of appropriate calibration standards, interactions of organic matter with the column material, it has been widely applied for NOM characterization and also for better understanding of the water chemistry in different drinking water treatment processes (Chow et al., 2009; Fabris et al., 2008; Matilainen et al., 2006; Perminova et al., 2003; Sandron et al., 2015; Zhao et al., 2009).

To date, little is known about the relationships or association between water quality parameters obtained from HPSEC analysis, chloramine residual and nitrification in drinking water distribution systems. In this study, we investigated the potential of HPSEC combined with chemometrics analysis as a technique for assessment of drinking water quality in two chloraminated distribution systems to determine whether there is any specific pattern or fingerprint in the HPSEC spectra of samples collected from locations that experienced rapid chloramine decay and nitrification. Potential association between HPSEC data with chloramine decay and/or nitrification occurrence was investigated. In addition to real drinking water samples, a set of synthetic samples to study the possible causes of the HPSEC behavior in locations that experienced rapid chloramine decay and nitrification were investigated in the laboratory. A comprehensive study on the application of HPSEC analysis for prediction of monochloramine residual decay and nitrification could lead to significant improvement in control and operation of disinfection dosing through responses to changing water quality.

1. Materials and methods

1.1. Water sources description

Laboratory studies of nitrification usually use bioreactors to grow nitrifying bacteria and biofilms; therefore it is difficult for researchers to simulate exactly the real nitrification conditions in those studies. Laboratory experiments cannot reproduce what happens in real drinking water distribution systems because the efficiency of nitrifying bacteria in water systems is strongly affected by nutrient levels and the presence of certain metals (Abbassi et al., 2014; Speitel et al., 2011; Zhang and Edwards, 2010). Sampling from a continuous water distribution system in which pipes are the natural bioreactor has the advantage of

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