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High-performance size exclusion chromatography with a multi-wavelength absorbance detector study on dissolved organic matter characterisation along a water distribution system

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ABSTRACT

This study examined the associations between dissolved organic matter (DOM) characteristics and potential nitrification occurrence in the presence of chloramine along a drinking water distribution system. High-performance size exclusion chromatography (HPSEC) coupled with a multiple wavelength detector (200–280 nm) was employed to characterise DOM by molecular weight distribution, bacterial activity was analysed using flow cytometry, and a package of simple analytical tools, such as dissolved organic carbon, absorbance at 254 nm, nitrate, nitrite, ammonia and total disinfectant residual were also applied and their applicability to indicate water quality changes in distribution systems were also evaluated. Results showed that multi-wavelength HPSEC analysis was useful to provide information about DOM character while changes in molecule weight profiles at wavelengths less than 230 nm were also able to be related to other water quality parameters. Correct selection of the UV wavelengths can be an important factor for providing appropriate indicators associated with different DOM compositions. DOM molecular weight in the range of 0.2–0.5 kDa measured at 210 nm correlated positively with oxidised nitrogen concentration ($r = 0.99$), and the concentrations of active bacterial cells in the distribution system ($r = 0.85$). Our study also showed that the changes of DOM character and bacterial cells were significant in those sampling points that had decreases in total disinfectant residual. HPSEC-UV measured at 210 nm and flow cytometry can detect the changes of low molecular weight of DOM and bacterial levels, respectively, when nitrification occurred within the chloraminated distribution system.

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Introduction

The character of dissolved organic matter (DOM) is a key index used in drinking water quality management (Chow et al., 2008; Korshin et al., 2009). DOM is a complex molecular mixture variable in composition and functionality which depends on its source. The presence of DOM in waters can be one of the principal causes of microbes' growth. A decrease in disinfectant residual has also been suggested to be associated with interaction between disinfectant and DOM (Wilczak et al., 2003; Kristiana et al., 2013). The properties of DOM, particularly that of molecular weight, have been demonstrated to strongly affect natural organic matter reactivity in natural systems as well as different stages of the treatment process (Chow et al., 2008; Korshin et al., 2009; Kristiana et al., 2010). Hence, an effective determination of the molecular weight distribution of DOM is critical not only for improving the water treatment process in terms of removal but also for understanding the disinfection process downstream in the distribution system.

Although promoting various benefits and improvements for drinking water treatment processes and distribution system, the application of chloramine as secondary disinfectant is associated with a number of adverse effects on water quality (Lipponen et al., 2002; Motzko et al., 2009; Zhang et al., 2009; Bai et al., 2015). Nitrification management has drawn the most attention. A decrease in disinfectant residual and an increase in oxidised nitrogen concentrations (either nitrite or nitrate) as well as an increase in microbial risks are the common adverse effects owing to the occurrence of nitrification. Microorganism growth and regrowth and nitrite concentration increase have serious potential health risks (Lipponen et al., 2002; Krishna et al., 2013; Bai et al., 2015). Management of chloramine decay, maintenance of adequate disinfectant residual and determination of several operational, chemical and microbiological parameters throughout the water treatment process and distribution system are essential to ensure the supply of safe and high quality potable water to all consumers.

Nitrification is a two-step process. Ammonia is initially oxidised to nitrite, and nitrite is further oxidised to nitrate (Lipponen et al., 2002). These processes are associated with nitrifying microorganism occurrences and activity. An increased amount of ammonia in chloraminated waters is linked to nitrification in the drinking water distribution system. Increase in either nitrate or nitrite concentration is normally considered to be positively correlated with nitrification (Odell et al., 1996). Many researchers have also indicated that the level of microbes in pipe water is inversely related to the content of total disinfectant (Lipponen et al., 2002; Zhang et al., 2009). Monitoring and understanding treated water quality in the distribution system is hence required to effectively manage distribution system performance.

High performance size exclusion chromatography coupled with ultraviolet (UV) detection (HPSEC-UV) has been successfully and widely used for determining the performance of drinking water treatment processes, such as DOM removal evaluation, potential disinfection by-product (DBP) formation prediction and treated drinking water distribution management (Fabris et al., 2008; Chow et al., 2008; Xing et al., 2012; Kristiana et al., 2013). These previous studies have demonstrated that the low molecular weight DOM compounds are recalcitrant to

removal by conventional coagulation treatment. Some studies have also indicated that these low molecular weight fractions remaining in treated water are particularly associated with water quality degradation in distribution systems (Kristiana et al., 2010, 2013). In most cases, such measurements have generally focused on aromatic components by detection at a single wavelength in the UV range of 250–280 nm. The non-aromatic groups of DOM associated with low molecular weight fractions do, however, not absorb strongly at this range of wavelengths but can potentially impact water quality. HPSEC coupled with a multiple wavelength detector may further characterise DOM molecular weight distribution and yield more insight into the key information that is of importance in water quality investigations.

Additionally, flow cytometry in combination with a fluorescence staining method has been utilised to characterise microbes present in distribution system. Due to the ability to provide rapid, accurate and high throughput, this advanced analytical method has been frequently used to characterise bacterial removal throughout water treatment processes and distribution systems (Hoefel et al., 2005; Hammes et al., 2008; Ho et al., 2012).

In this paper, HPSEC coupled with a multiple UV wavelength detector, from 200 nm to 280 nm, was employed to characterise DOM as an indirect assessment tool for potential nitrification occurrence along an operating distribution system. This multi-wavelength HPSEC approach would be useful to investigate the impact of different fractions of DOM on nitrification, including those fractions of relatively lower molecular weight, less aromatic character and with a weak absorbance response in the 250–280 nm wavelength range. A key focus was on developing an organic characterisation tool for understanding how DOM impacts on water quality in chloraminated distribution systems. This study covers both aspects of 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, the study was designed to compare the interrelationship between samples in different sections of a distribution system supplied from the same water treatment plant.

1. Materials and methods

1.1. Sample site description

For this study, the Tailem Bend (TB) water treatment plant (WTP) and drinking water distribution system (DS) in South Australia were selected. This is a country water supply distribution system consisting of a single long trunk main with branches to several remote communities. Chloramine as secondary disinfectant to provide protection against microbial contamination is most suitable for this type of long distribution system to ensure disinfectant residuals reach the end of the system. The TB system sources its water from the River Murray and the raw water has variable colour (18 ± 20 HU January 2007–April 2015, $n = 429$ analyses) and DOC

concentration (5.4 ± 2.8 mg/L January 2007–April 2015, $n = 432$ analyses). Conventional treatment, including coagulation, flocculation, sedimentation and filtration followed by UV disinfection and chloramination are the main steps used at the TB WTP to produce good quality water to enter into the DS. The main focus of this study was on TB WTP and subsequently through the DS with different branches and different locations, including inlet and outlet of storage tanks and customer taps to provide a study of water quality changes within the distribution system using an operating water supply system.

1.2. Sampling procedure

Seventeen sampling points across the WTP and DS of the TB system were chosen based on the size and layout (position of tanks and customer taps (CTs) at the end of the major branches) with a full survey completed in May 2012 (Fig. 1). Six samples were collected from the WTP, including the raw water sample (TB-Raw), samples throughout the treatment processes (settled water, TB-WTP-1, post filtration prior to disinfection, TB-WTP-2, post disinfection prior to filtered water storage tank, TB-WTP-3, filter backwash water, TB-WTP-4, and supernatant, TB-WTP-5). The distribution system consists of multiple branches, three of them were selected based on available data of previous disinfectant decay study, including the main branch TB-Keith (7 sampling points including customer site, from TB-treated (located 1.5 km after WTP), and TB-B1-1 to TB-B1-CT) as well as branches TB-Lower Lakes (2 sampling points, TB-B2-1 and TB-B2-CT) and TB-Karoonda (2 sampling points, TB-B3-1 and TB-B3-CT). Extended sampling points focusing on Branch 2 (TB-Lower Lakes) was further completed in September 2014, since the analytical results of the first survey indicated that the Lower Lakes (LL) had the most degradable water quality

compared with the other two branches. Ten sampling points around many main communities were hence selected for further analysis, designated TB-LL-1 to TB-LL-10, as shown in Fig. 1. TB-B2-CT and TB-LL-6 were the samples collected at the same customer tap (CT) location.

1.3. Instrumental analysis

Samples for DOC and UV_{254} determinations were filtered through a $0.45 \mu\text{m}$ membrane. A 1 cm quartz cell was used for UV_{254} analysis. It is expressed in Abs/cm. DOC was measured using a Sievers 900 Total Organic Carbon Analyser (GE Analytical Instruments, USA). Specific UV absorbance ($SUVA_{254}$) expressed in $\text{L}/(\text{mg}\cdot\text{m})$ was calculated as UV_{254} divided by DOC multiplied by 100.

Total chlorine residual was determined using *N,N*-diethyl-*p*-phenylenediamine (DPD)–ferrous ammonium sulphate (FAS) titrimetric procedure (Standard Method 4500-Cl (F), APHA, 1998). Free ammonia concentrations were analysed using an ammonia-selective electrode (Standard Method 4500-NH₃ (D), APHA, 1998). Analysis of nitrate and nitrite were conducted through Standard Method 4500-NO₃ (I) and 4500-NO₂ (F), respectively (APHA, 1998).

Molecular weight profiles were determined using a Waters Acquity H-Class system with a photodiode array detector (Waters Corporation, USA) acquiring between 200 and 280 nm. The Shodex KW802.5 packed silica column (Showa Denko, Japan) was equilibrated at 30°C. Samples were filtered through a $0.2 \mu\text{m}$ membrane filter prior to analysis and 100 μL samples were injected. The mobile phase was 0.02 mol/L phosphate buffer at pH 6.8 adjusted to an ionic strength of 0.1 mol/L with sodium chloride. The system was operated at isocratic conditions with an eluent flow rate of 1.0 mL/min. Polystyrene

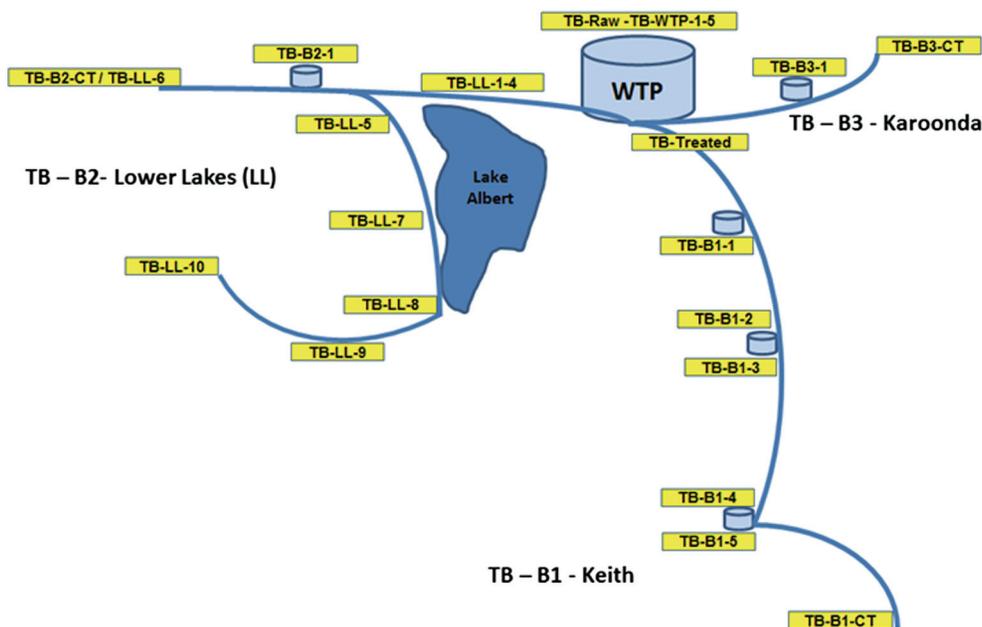


Fig. 1 – Schematic illustration of sampling point location for the Tailem Bend (TB) system including the water treatment plant (WTP) and three main branches of the drinking water distribution system (DS). B and CT indicate branch and customer tap, respectively.

sulfonate standards (Polysciences, USA) with molecular weights 4.6, 8, 18 and 35 kDa were used to calibrate the retention time response to apparent molecular weight (AMW).

Flow cytometry (FCM) analyses were conducted using a FACSCalibur flow cytometer (Becton Dickinson, USA) equipped with an air-cooled 15 mW argon ion laser, emitting at a fixed wavelength of 488 nm. Data were analysed using CellQuest software (Becton Dickinson, USA). Total numbers of bacteria were enumerated following staining of the bacteria with SYTO-9 and the BacLight bacterial viability kit (Molecular Probes, USA) as described previously (Hoefel et al., 2005). Results for FCM were presented as cells/mL.

1.4. Statistical analysis

Statistical and graphical analyses were made with R programming language (version 3.1.0, R Development Core Team). The relationship between HPSEC-UV profiles, chemical and microbial parameters was analysed by Pearson's Product Moment Correlation (PPMC). Both correlation factor (r) and probability (p) values were applied to determine the significance of correlation. Chromatographic data obtained from multi-wavelength HPSEC analysis were also explored and interpreted using R.

2. Results and discussion

2.1. General water quality analysis

Results of general water quality analyses for all samples are combined and illustrated in Fig. 2. Water samples taken through the WTP, DS and CT at the terminal sites of the system were included in order to understand both aspects of the system; treatment processes at the WTP and water quality change in the distribution system with an overall view of integrating the two together as well as determine potential factors associated with nitrification occurrence. UV_{254} , DOC and $SUVA_{254}$ as conventional DOM parameters were used to indicate DOM quality and quantity. As standard indicators for nitrification assessment, concentrations of free ammonia and both nitrate and nitrite were also analysed. Analytical results shown in Fig. 2a reveal that DOM removal was significant in the TB WTP process based on a comparison of raw (TB-Raw) and treated (TB-Treated) water samples, from 12.6 to 5.2 mg/L. DOC concentrations in both the first survey and the extended sampling points around the LL branch were relatively stable, in a range of 4.1–5.9 and 2.3–3.0 mg/L, respectively. The differences in treated water DOC concentrations between the first survey and the extended sampling points were due to the change in source water quality from the River Murray during the study period; approximately three magnitude reduction of DOC concentration was observed between 2012 and 2014. Braun et al. (2014) have illustrated drought followed by floods resulted in River Murray source water with high levels of natural organics and turbidity during 2010–2012. The river water quality between the period of September 2010–August 2012 was referred as floodwater with extreme organic intrusion, with DOC in a wide range of 4.6–19.1 mg/L and UV_{254} in a range of 0.139–0.799 Abs/cm. Higher DOC in source water challenges the conventional water treatment process and usually results in

slightly higher DOC concentration in treated water (Fabris et al., 2008; Braun et al., 2014). Hence, the DS samples collected in 2012 had higher DOC concentrations than samples captured in 2014. The values of UV_{254} and $SUVA_{254}$ of the first survey were also higher than those collected in 2014. These observations illustrate that the DOM from the first survey had more aromatic structures, since both UV_{254} and $SUVA_{254}$ are more representative of aromatic DOC groups (Her et al., 2008; Korshin et al., 2009). $SUVA_{254}$ values of both the first survey and extended samples were stable with minor variations within the distribution system (Fig. 2a). These observations show that water quality in DS was stable and indicate no measurable difference in DOC concentration passage through the distribution system.

The sums of nitrate and nitrite concentration and free ammonia concentration are presented in order to understand potential nitrification occurrence (Fig. 2b). It was notable to observe that the sums of nitrate and nitrite and free ammonia concentrations were relatively stable with a slight increase along the TB main branch 1 (TB-B1), from TB-Treated to the terminal customer tap site (TB-B1-CT). The changes of inorganic nitrogen in TB main branch 2 (TB-B2) and TB main branch 3 (TB-B3) were, however, obvious from TB-Treated to the terminal sites of TB-B2-CT and TB-B3-CT. Ammonia concentrations decreased dramatically from 0.52 mg/L at the sampling point (TM-B2-CT) to <0.01 mg/L at the terminal site customer tap (TB-B2-CT), where the sum of nitrate and nitrite concentration increased twofold. A similar trend was also observed in the extended DS samples focusing on the LL branch. The sums of nitrate and nitrite concentration increased sharply from <0.2 to >0.8 mg/L, while free ammonia disappeared below <0.01 mg/L at the last 5 sampling points along the DS. The various changes of inorganic nitrogen concentration, an obvious decrease in free ammonia and the increase in either nitrate or nitrite, could indicate that nitrification occurred in this TB system, Branch 2 Lower Lakes in particular, since nitrification is a microbial process in which ammonia is oxidised, forming nitrate and nitrite. Increases in nitrate and nitrite concentration are the standard parameters that are used as indicators of potential nitrification occurrence. These observations suggest that nitrification occurred in some sampling sites regardless of the initial treated water quality, and that the general DOM parameters, UV_{254} , DOC and $SUVA_{254}$, may not be sensitive enough to indicate water quality degradation linked to potential nitrification occurrence.

2.2. Application of HPSEC-UV in distribution systems

With the availability of multi-wavelength UV absorbance detection, the analytical information obtained from the HPSEC-UV profile has been improved compared with the traditional single wavelength detection. This multi-wavelength detector can give a more comprehensive perspective on the relative absorbance intensity of various molecular weight compounds at different wavelengths (Her et al., 2008; Liu et al., 2010; Yan et al., 2012). In this study, HPSEC coupled with a multiple UV wavelength (200–280 nm) detector analysis was used to characterise DOM for both the water treatment process and subsequently through the distribution system. AMW data were explored and plotted against the entire response range (200–280 nm) of the UV detector

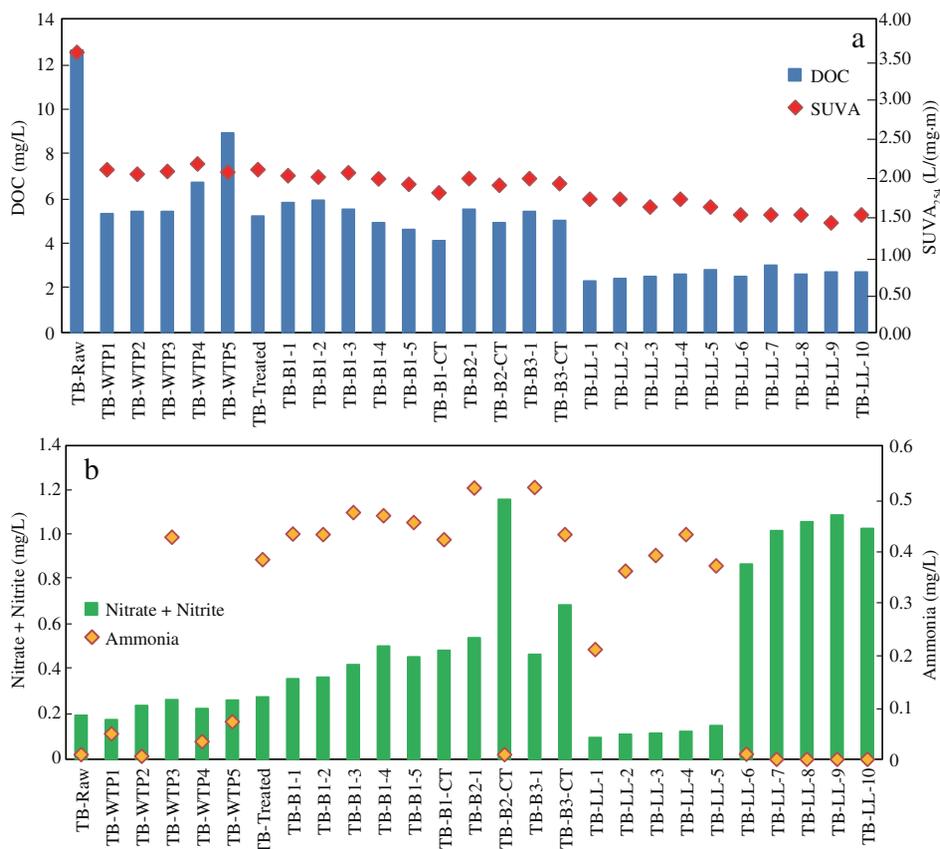


Fig. 2 – General water quality results, (a) DOC and SUVA₂₅₄ and (b) nitrate + nitrate and ammonia. DOC: dissolved organic carbon; SUVA: specific ultraviolet absorbance.

using R. These three-dimensional surface plots of the multi-wavelength HPSEC data revealed that there were significant differences in low AMW fraction (less than 0.5 kDa) of DOM in the distribution system samples and an increase in absorbance in the wavelength region less than 230 nm while the UV absorbance at the traditional range of 250–260 nm did not show any changes. This finding is supported by several previous studies suggesting the importance of using other wavelengths, such as less than 230 nm, for analysis different to the traditional 254 nm. Edwards et al. (2001) have reported the application of UV wavelengths in the range of 200–230 nm to estimate nitrate concentration in various water sources. Whitehead and Cole (2006) also addressed the fact that the wavelength around 210 nm correlated well with nitrate concentration, and also indicated microbial activity and nutrient content. Previous research studies have shown that when applying HPSEC-UV as DOM characterisation tool, UV absorbance spectra can be affected by the non-aromatic fraction of DOM with additional bands appeared at wavelength below 250 nm (Her et al., 2008; Korshin et al., 2009). Her et al. (2008) indicated the application of two wavelengths, 210 and 254 nm, is useful to estimate the contributions of functional groups (hydroxyl, carboxyl, carbonyl, ester), nitrogen containing compounds and the conjugated aromatic substituents. Korshin et al. (2009) also used the absorbance measured at two wavelength regions, 220–230 nm and 254–272 nm, to evaluate non-aromatic and aromatic compositions associated with DOM removal and DBP formation potential.

Based on a systematic multi-wavelength HPSEC data exploration with the combination of visual inspection and the findings from the above studies, 210, 230 and 254 nm were selected for this study to characterise various molecular weight fractions of DOM. The HPSEC-UV profiles at these wavelengths revealed that although DOM in all samples was mostly similar in the AMW ranges between 0.2 and 2 kDa, changes in HPSEC profiles in the higher AMW ranges between 1 and 2 kDa were observed across the WTP process and changes in the lower AMW ranges between 0.2 and 0.3 kDa were observed along the distribution system. Eight representative HPSEC profiles, including raw water, treated water, DS and CT waters, were chosen to illustrate this (Fig. 3).

Fig. 3a and b shows the HPSEC-UV profiles of raw water and treated water after TB treatment processes, respectively. Fig. 3a shows that there were two broad peaks located at AMW approximately 0.2–0.3 and 1–1.3 kDa. Fig. 3b shows that compounds with higher AMW (>1 kDa) were effectively removed as indicated by the reduction of UV absorbance at all three wavelengths, and a slight increase in the absorbance was also observed at lower AMW of 0.2–0.3 kDa measured at 210 nm. The removal of high AMW fraction was consistent with the DOC and SUVA₂₅₄ results suggesting that the aromatic fraction was mostly removed and lower AMW fraction of DOM was still present and entered into distribution system. In addition, SUVA₂₅₄ is generally well used to describe and evaluate DOM reactivity and treatability in waters (Chow

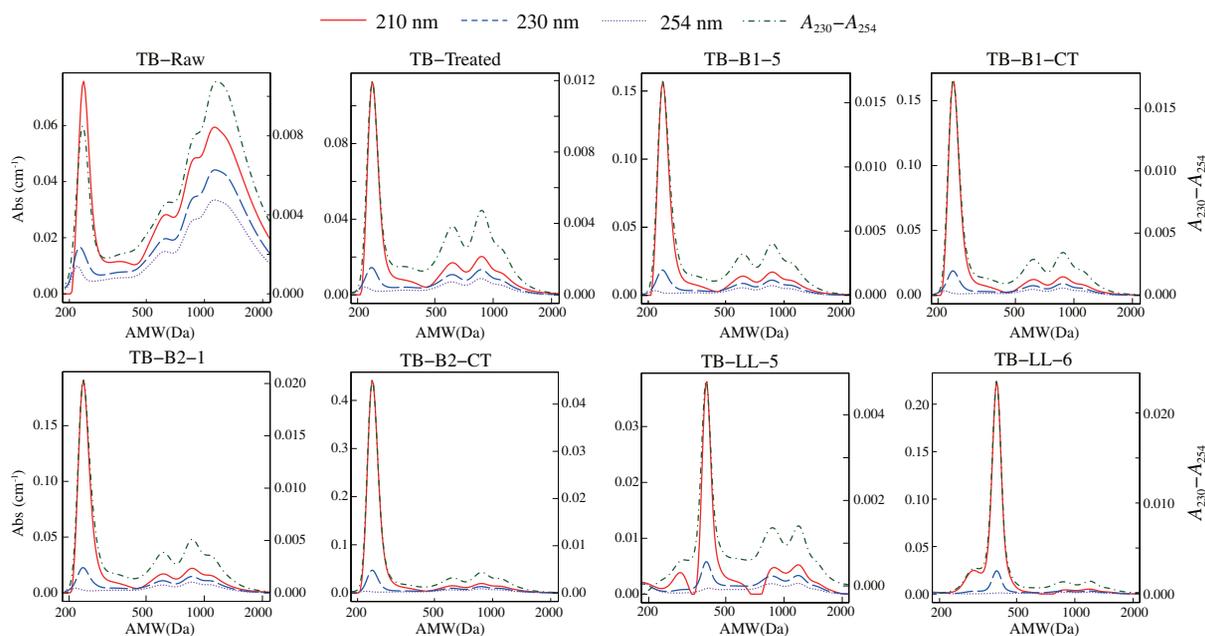


Fig. 3 – Comparison of high-performance size exclusion chromatography-ultraviolet (HPSEC-UV) profiles measured at different wavelengths (210 nm, 230 nm and 254 nm) and subtraction of A_{230} and A_{254} (a) TB-Raw (b) TB-Treated (c) TB-B1-5 (d) TB-B1-CT (e) TB-B2-1 (f) TB-B2-CT (g) TB-LL-5 and (h) TB-LL-6. AMW: apparent molecular weight; TB, B and CT indicate, Tailern Bend, branch and customer tap, respectively.

et al., 2008; Korshin et al., 2009), all DS samples had low $SUVA_{254}$ values and were in the range of 1–3 L/(mg·m) indicating that the remained fractions of DOM may have similar characteristics, relatively less aromatic in nature and possessing lower molecular weight components.

Fig. 3c–f presents the HPSEC-UV profiles of the first survey, two main branches 1 and 2 samples from DS and subsequent CT waters (end of distribution system). The peak located at lower AMW approximately 0.2–0.3 kDa, was so called the recalcitrant DOM and was observed in all these samples. This sharp peak was especially sensitive with higher signals at lower wavelengths, 210 and 230 nm, detection compared with the measurement at 254 nm. Applying a simple subtraction of absorbance intensities measured at 230 and 254 nm resulted in similar profile as measured at 210 nm. It is also worthwhile to point out that this salient feature was detected in all DS samples. Compared with the HPSEC-UV profile of TB-Treated water (Fig. 3b), both Fig. 3c and d shows that the absorbance signals of different AMW fractions were relatively consistent in TB-B1 DS at the beginning and end of the system. However the level of absorbance response in the AMW range of 0.2–0.3 kDa was increased in the TB-B2 DS samples (Fig. 3e and f), with approximately 3 times increase in absorbance signal at 210 nm at the terminal site CT water sample (Fig. 3f).

Similar changes in the level of absorbance response in the lower AMW range were also obtained from the extended DS samples around the LL branch collected in 2014. Although the DS samples around the LL branch has a stable water quality in terms of DOC and $SUVA_{254}$ values, the increases in the level of absorbance response in the lower AMW range of 0.3–0.5 kDa were also observed in the DS samples further away from the treatment plant. The samples obtained from TB-LL-1 to

TB-LL-5 had similar absorbance in this AMW region, whilst increased absorbance was observed in the downstream samples collected from TB-LL-6 to TB-LL-10. Fig. 3g and h showing the multi-wavelength HPSEC-UV profiles of TB-LL-5 and TB-LL-6, respectively, was used to illustrate the changes of absorbance signals and hence the organic character.

Liu et al. (2010) have demonstrated that more information can be extracted over a wider wavelength range measurement. These authors applied multi-wavelength HPSEC technique to investigate the differences between HPSEC-UV profiles, before and after water treatment, plotting AMW data against the entire response range (205–285 nm) of the UV detector instead of single wavelength detection at 254 nm. These authors also found low molecular acid and neutral compounds remained after treatment and these molecules with low AMW of 0.3 and 0.4 kDa absorb strongly at wavelength between 205 and 230 nm. The benefits of this multi-wavelength HPSEC method was also demonstrated in the current study with the increase of the peaks located at the low AMW region of the HPSEC-UV profile using the lower wavelength detection. This peak could be considered an indication of changes in organic compounds produced as a result of nitrification, and may be useful to indicate nitrification occurrence, since the absorbance signal changes in this AMW region coincided with the changes in sum of nitrate and nitrite concentration shown in Fig. 2b.

2.3. Association between DOM characteristics and nitrification

In order to ensure that all samples can be standardised and further investigate the association between DOM molecular weight distribution and potential nitrification occurrence, a

rapid and simple method of extracting HPSEC-UV information is needed to be developed for the rapid simultaneous analysis of DOM in various samples, raw, during treatment processes and treated water. The sum of absorbance intensities measured at 210 nm (A_{210}) in the range of AMW 0.2–0.5 kDa was hypothesised to be an indicator of potential nitrification occurrence.

Correlation analysis between the sum of absorbance intensities provided by HPSEC-UV profiles and conventional water quality parameters was further studied using simple linear regression. The sum of total area measured at 254 nm (A_{254}) could be applied to estimate DOC concentration ($R^2 = 0.96$, $p < 0.05$) (Fig. 4a). The active aromatic substances are generally the dominant proportion in DOM and are more sensitive to higher UV wavelengths (in the range of 250–280 nm) (Korshin et al., 2009). The sum of area measured at 210 nm in the lower AMW range (0.2–0.5 kDa) could also be used to estimate the sum of nitrate and nitrite concentration ($R^2 = 0.99$, $p < 0.05$) (Fig. 4b).

These findings indicate that lower AMW DOM was the main component associated with potential nitrification occurrence. There was an agreement between these observations and similar research finding reported by Wetzel et al. (1995) who also observed the importance of smaller and non-humic molecules as a source of energy for aquatic organisms. Our study also points out the advantage of using HPSEC to separate DOM based on molecular weight distribution and highlights the absorbance of the compounds of interest. HPSEC-UV analysis also showed the change of DOM molecular weight distribution in DS samples by the increase in absorbance signal at wavelength less than 230 nm. An earlier DOM study conducted by Chow et al. (2009) aimed to combine organic characterisation tools and biological analysis for distribution system managements and identified HPSEC with single wavelength detection at 260 nm can capture the

changes in AMW distribution of DOM in distribution systems. These authors also indicated that the chloramination process (mild oxidation) has little impact on DOM characteristics. In agreement with this earlier study, our study has also illustrated that there was no significant change in DOM characteristics along the chloraminated DS when measured at 254 nm, within the similar wavelength range of 250–280 nm. However, with the capability of the multi wavelength detector, our study confirmed the benefit of selecting wavelengths less than 230 nm can provide additional information of DOM characteristics and can also be used as an indicator of nitrification occurrence by detecting further changes in AMW distribution.

2.4. Microbiological analysis

In this study, the changes in microbial levels of waters in TB WTP and DS were also evaluated using FCM analysis. Concentrations of bacterial cell (total and active) in combination with total disinfectant residuals data are shown in Fig. 5. Changes in the bacterial cell concentrations were observed throughout the TB WTP processes. The active bacterial cell concentration of raw water (TB-Raw) was 1×10^7 cells/mL which was reduced significantly following treatment and disinfection. The conventional treatment removed physically 1 log reduction, leaving 1×10^6 cells/mL in the TB-WTP-2 sample and the disinfection process achieved 2 log removal, leaving 1×10^4 cells/mL in the TB-Treated sample (total of 3 log removal).

Although the total disinfectant residuals were lower in all TB DS water samples in comparison to the treated water sample (TB-Treated), the disinfectant concentrations were relatively stable with a slight fluctuation in TB-B1 DS. This resulted in stable bacterial cell concentrations throughout this branch. The total disinfectant residuals decreased

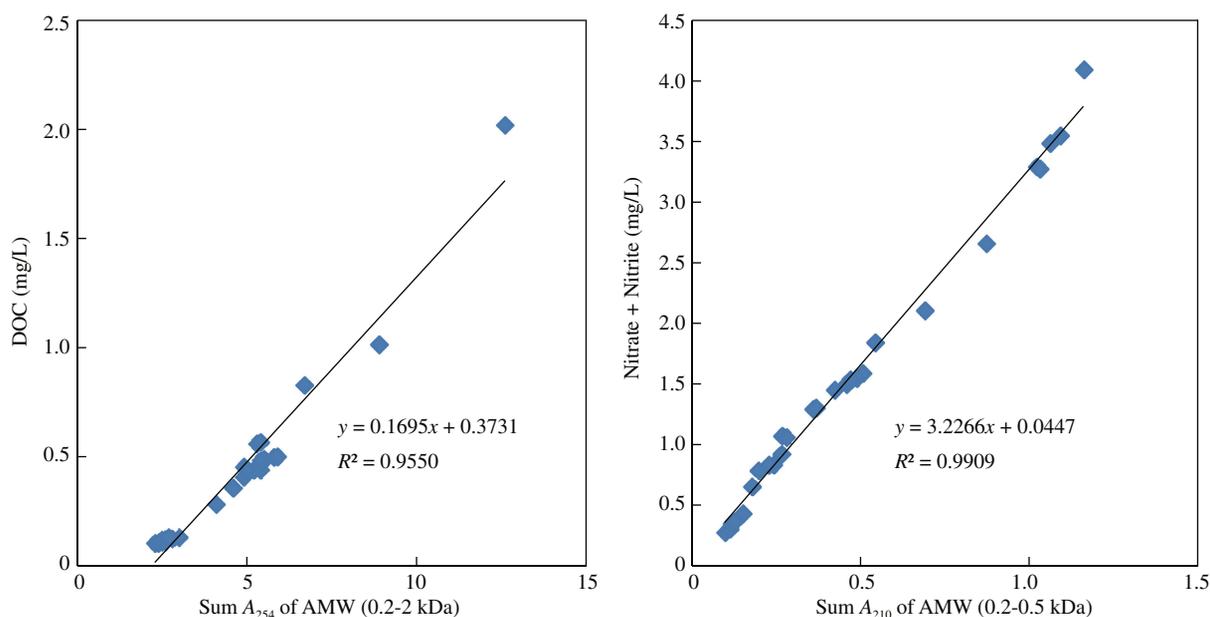


Fig. 4 – Correlation between HPSEC-UV indicators and conventional parameters, (a) dissolved organic carbon (DOC) concentration against the sum A_{254} of AMW in the range of 0.2–2 kDa, and (b) the sum of nitrate and nitrite concentration against the sum A_{210} of AMW in the range of 0.2–0.5 kDa.

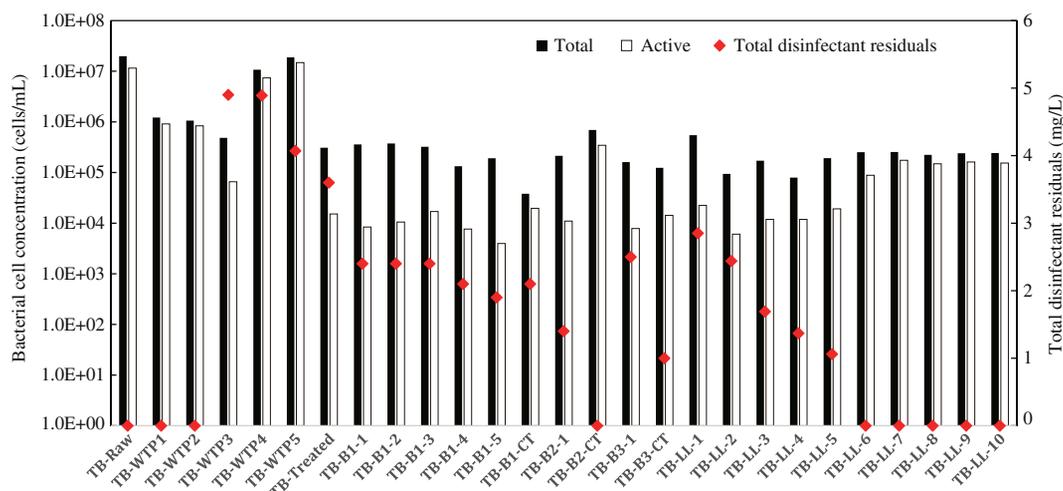


Fig. 5 – Concentrations of bacterial cells (total and active) determined by flow cytometry and corresponding total disinfectant residual results.

continuously along both TB-B2 and TB-B3 samples. An approximately twofold decrease in disinfectant residuals was observed between TB-Treated and TB-B2-1 samples, and disinfectant was absent at the terminal site TB-B2-CT. The concentrations of total and active bacterial cells in TB-B2-CT sample increased to 1×10^6 cells/mL and were similar to the result prior to disinfection (TB-WTP-2). The order of the total bacterial cell concentrations at the three terminal customer tap sites was TB-B2-CT > TB-B3-CT > TB-B1-CT. This order coincided with the orders of sum of nitrate and nitrite and sum A_{210} of AMW (0.2–0.5 kDa) whilst the total disinfectant residual was in reverse order. Although originating from the same WTP process, the quality of customer tap water could degrade differently during passage through the DS.

The results for the extended DS samples around the LL branch indicated that concentrations of active bacterial cells increased whilst total disinfectant decreased along the DS. The last five sampling points sharing similar concentrations of active bacterial cells could be a result of total disinfectant loss. A decrease in concentrations of total disinfectant residuals (<0.1 mg/L) and free ammonia (<0.1 mg/L) and an at least twofold increase in concentration of oxidised nitrogen (sum of nitrate and nitrite) occurred in TB-Branch 2 customer tap site (TB-B2-CT) and the last five sampling sites in the LL system. Our results agreed with previous research and indicate that the level of microbes in DS areas increases when total disinfectant decreases (Lipponen et al., 2002; Bai et al., 2015).

The relationships between the HPSEC-UV profile and chemical and microbiological water quality parameters were studied by statistical analysis. Table 1 shows the significance based on PPMC results. The sum A_{210} of AMW (0.2–0.5 kDa) in both WTP process and DS correlated positively with the sum of nitrate and nitrite concentration ($r = 0.99$, $p < 0.001$, $n = 27$). The sum A_{210} of AMW (0.2–0.5 kDa) in the DS also correlated positively with the concentrations of active bacterial cells ($r = 0.85$, $p < 0.001$, $n = 21$). This HPSEC-UV indicator correlated negatively with the concentration of ammonia and total disinfectant residuals, r being -0.74 and -0.78 ($p < 0.001$, $n = 21$), respectively.

All the above statistical results obtained high values of correlation factor and probability ($p < 0.001$) therefore imply that the low AMW fraction detected at this wavelength is illustrating a relationship with nitrification occurrence. These high levels of absorbance intensity measured at 210 nm could be an indication of the increase in microbiologically derived components that have a high proportion of non-aromatic groups. The sum of area measured at 210 nm in the lower AMW range (0.2–0.3 kDa) could, hence, be used to simplify complex HPSEC profiles and effectively represent DOM character changes within the DS.

3. Conclusions

The well designed case study has demonstrated an operating chloraminated distribution system, with careful planning and selection of sampling points was appropriate to be used to compare water quality of different branches. The findings also showed the package analytical techniques applied can provide early notice of potential water quality degradation. Our results showed linkages between decrease in total

Table 1 – Correlation coefficients between HPSEC-UV indicator and physiochemical and microbiological water parameters.

| Water parameter | Sum A_{210} of AMW (0.2–0.5 kDa) | | |
|-------------------------------------|------------------------------------|-------|--------|
| | n | r | p |
| Nitrate + nitrite (mg/L) | 27 | 0.99 | <0.001 |
| Ammonia (mg/L) | 21 | -0.74 | <0.001 |
| Total disinfectant residuals (mg/L) | 21 | -0.78 | <0.001 |
| Total bacterial cells (cells/mL) | 21 | 0.3 | >0.05 |
| Active bacterial cells (cells/mL) | 21 | 0.85 | <0.001 |

n = number of studied samples, TB WTP and DS samples ($n = 27$), DS samples ($n = 21$).

disinfectant residual and degradation of water quality within the distribution system, such as higher concentration of nitrate and nitrite and higher level of microbial risks. These changes also coincide with the changes of the molecular weight distribution of DOM. Multi-wavelength HPSEC analysis demonstrated the occurrence of absorbance change of the lower AMW compounds (0.2–0.5 kDa) of DOM within the distribution system detected at less than 230 nm, this was not observed when traditional single wavelength, 254 nm, was only used for DOM detection. Our studies have also shown a positive correlation between low AMW (0.2–0.5 kDa) of signal measured at 210 nm and both changes in oxidised nitrogen concentration and bacterial activity. This study suggests both detector wavelengths (210 and 254 nm) are important to provide complete information on the physico-chemical properties of DOM, and HPSEC-UV provides a convenient and effective way for simultaneous analysis of changes in DOM characteristics and potential nitrification occurrence in drinking water distribution systems.

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