Seasonal variation in the nature of DOM in a river and drinking water reservoir of a closed catchment[☆]

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ABSTRACT

Dissolved organic matter (DOM) in surface waters used for drinking purposes can vary markedly in character depending on its source within catchments and the timing and intensity of rainfall events. Here we report the findings of a study on the character and concentration of DOM in waters collected during different seasons from Myponga River and Reservoir, South Australia. The character of DOM was assessed in terms of its treatability by enhanced coagulation and potential for disinfection by-product i.e. trihalomethane (THM) formation. During the wet seasons (winter and spring), water samples from the river had higher DOC concentrations ($\bar{X}$: 21 mg/L) and DOM of higher average molecular weight (AMW: 1526 Da) than waters collected during the dry seasons (summer and autumn: DOC: 13 mg/L; AMW: 1385 Da). Even though these features led to an increase in the percentage removal of organics by coagulation with alum (64% for wet compared with 53% for dry season samples) and a lower alum dose rate (10 versus 15 mg alum/mg DOC removal), there was a higher THM formation potential (THMFP) from wet season waters (treated waters: 217 μ g/L vs 172 μ g/L). For reservoir waters, samples collected during the wet seasons had an average DOC concentration ($\bar{X}$: 15 mg/L), percentage removal of organics by alum (54%), alum dose rates (13 mg/mg DOC) and THMFP (treated waters: 207 μ g/L) that were similar to samples collected during the dry seasons (mean DOC: 15 mg/L; removal of organics: 52%; alum dose rate: 13 mg/mg DOC; THMFP: 212 μ g/L for treated waters). These results show that DOM present in river waters and treatability by alum are highly impacted by seasonal environmental variations. However these in reservoir waters exhibit less seasonal variability. Storage of large volumes of water in the reservoir enables mixing of influent waters and stabilization of water quality.

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1. Introduction

The concentration of dissolved organic matter (DOM) presented in surface waters (e.g., streams and reservoirs) is influenced by the

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climate and season changes (Chen et al., 2015; Mattsson et al., 2009). It has been reported that during storm events, there is an increase in DOM concentration in stream water (Evans et al., 2005) and in reservoir water (Chen et al., 2015) and this is attributed to flushing of the upper organic soil horizons (Ritson et al., 2014). DOM concentrations (measured as dissolved organic carbon, DOC) within streams have been found to have a positive relation with stream discharge (Billett et al., 2006). Highest concentrations of DOC released into subsurface waters and lateral flows occur after the first major rainfall event in the break-of-season during late autumn/early winter, demonstrating the importance of fresh litter

material in generating high amounts of soluble organic matter (Chow et al., 2011).

Storm events lead to an increase in the percentage of humic-like and aromatic organic compounds present in catchment runoff as reported by Carstea et al. (2009) and Stutter et al. (2012). Goslan et al. (2002) reported an increase in the percentage of the hydrophobic acid fraction in waters of a reservoir inlet (Albert, Yorkshire) during the winter season compared to other seasons. Chen et al. (2015) also reported that DOM present in reservoir waters (Bohunsan Reservoir, South Korea) during the wet season has higher SUVA (specific UV absorbance) with lower apparent of small molecular weight (MW) fraction than during dry season. Increasing water temperatures can lead to an increase in microbial activity and consequently greater formation of hydrophilic compounds (Lumsdon et al., 2005). Further, with increasing UV irradiation during the dry season there is increase in the photo-degradation rates of coloured DOM (Zepp et al., 2007) mainly aromatic organic compounds. Aromatic compounds have been found to be susceptible to photo-oxidation (Ritson et al., 2014).

Natural organic matter (NOM) present in drinking water sourced from reservoir catchments may lead to health risks. These risks include formation of disinfection by-products (DBPs), including trihalomethanes (THMs), haloacetic acids, iodo-acids, halonitromethanes, nitrosamines, and dichloroacetamide that form when NOM reacts with chemical disinfectants (Chu et al., 2010; Richardson and Postigo, 2012). For chlorinated waters, THM levels have been found to be highest in concentration compared to other by products (King et al., 2000a). In comparison to other DBPs, THM have the highest skin permeability (Carter et al., 2015) and the toxicity of disinfected waters can be evaluated based on THM concentrations (Allard et al., 2015). THM levels have also been linked to several health effects such as elevated rates of bladder and brain cancers (Agency, 2012; King et al., 2000b; Richardson et al., 2007; Siddique et al., 2015; Villanueva et al., 2007), still-births and miscarriages (King et al., 2000a; Richardson, 2005). A recent study (Min and Min, 2016) has reported that blood THM levels (mainly brominated THM) were significantly linked with the total number of adults' cancer mortality in the United States.

The removal of organics that are the precursors of DBPs of health concern, is therefore of high importance. Coagulation and flocculation are the most widely used processes for removal of DOM from drinking water (Matilainen et al., 2010) even though it can only be partially removed. Enhanced coagulation refers to maximizing total or dissolved organic carbon (TOC or DOC) removal from drinking water by increasing the coagulant dose and controlling the coagulation pH level to the coagulation optimum (White et al., 1997). Optimum DOC removal can be defined as the point of diminishing returns in terms of chemical use, where an additional 10 mg/L of coagulant results in less than 0.15 mg/L DOC reduction (van Leeuwen et al., 2005). The treatability (or removal capacity) of organics present in drinking water by coagulation/flocculation is affected by a range of factors of the raw water quality including pH, alkalinity and the character of the DOM (Chow et al., 1999, 2009).

Although many studies have shown that the presence of DOM in surface waters is influenced by a combination of biophysical properties of a catchment within the watershed and the timing and intensity of rainfall events, there is a paucity of studies on the effect of these characteristics on the quality of water for domestic consumption. Here we report the findings of a study on the changes in the character and concentrations of aquatic DOM during different seasons and rainfall events in an enclosed catchment's river and reservoir (Myponga, South Australia). The character of DOM was also assessed in context of potential treatability by coagulation/flocculation treatment and THM formation potential.

2. Methodology

2.1. Study area

This study was conducted in the Myponga reservoir-catchment (35°18' to 35°25'S and 138°24' to 138°33'E) which is part of the Mount Lofty Ranges watershed, 50 km south of Adelaide, South Australia, Australia. Water samples were collected from the Myponga River and Myponga Reservoir between March 2014 and February 2015. Samples were transported to the laboratory at ambient temperature in ~2 h and stored at 4 °C until analyzed. The rainfall pattern of Myponga, shown in Fig. 1a, is strongly seasonal with hot dry summers and cool wet winters.

2.2. The concentration and character of DOM

For determination of the concentration of DOM measured as DOC and UV absorbance, water samples were passed through 0.45 µm pre-rinsed sterile cellulose membrane filters prior to analyses. DOC concentration was determined using a TOC analyser (Model 900, Sievers Instruments). UV-Visible light absorbances were measured using a spectro-photometer (UV-120, MIOSTECH Instruments) for wavelengths from 200 nm to 700 nm, using a quartz cuvette of 1 cm path length. Color in Hazen Units (HU) was determined by absorbance at 456 nm using a 5 cm path length, glass cuvette and a platinum/cobalt standard (50 HU). Specific UV absorbance or SUVA (the ratio of absorbance at 254 nm/m to the concentration of DOC), (Edzwald and Tobiasson, 1999) and Specific color (SpCol, the ratio of color in HU to DOC concentration), (van Leeuwen et al., 2005) were determined.

Separation of organic compounds based on apparent molecular weight (MW) distributions was performed using HPSEC (A Waters 2690 Separation Module and Waters 996 photodiode array detector) with UV detection at 260 nm wavelength, as described by Chow et al. (2008). Column size and type, flow rate and other relevant information for the HPSEC-UV detection method have been previously reported (Chow et al., 2008). Water samples for HPSEC analysis were passed through 0.22 µm sterile cellulose membrane filters prior to the analysis. The weight-averaged molecular weight ($AMW = \sum n \times MW / \sum n$) was calculated as described by Chow et al. (2008). HPSEC chromatograms were analyzed using a peak fitting technique (Peak Fit software, Version 4, Systat Software Inc.) to resolve overlapping peaks as reported by Aslam et al. (2013). Peaks detected by absorbance at UV260 nm had MWs of 58,300 (Peak 1), 8600 (Peak 2), 4450 (Peak 3), 2700 (Peak 4), 1750 (Peak 5), 1250 (Peak 6), 830 (Peak 7), 515 (Peak 8) and 390 (Peak 9) Da.

Apparent MW distributions of humic-like compounds were measured using HPSEC with fluorescence detection, as described by Aslam et al. (2013). Excitation and emission wavelengths (320ex/430em) were used to investigate the MW distributions of humic-like compounds (Chen et al., 2003). HPSEC chromatograms were analyzed by a peak-fitting technique. Peak fitting of the chromatographs of humic-like compounds produced peaks with average MWs of 2345 Da (Peak 1), 1600 Da (Peak 2), 1175 Da (Peak 3), 810 Da (Peak 4), 485 Da (Peak 5) and 370 Da (Peak 6).

2.3. Enhanced coagulation and THM formation potential

For testing of the treatability of the organics by alum, DOC concentrations of water samples, as collected from Myponga River and reservoir, were treated by coagulation/flocculation process at ambient temperature and pH 6 ± 0.1 (Chow et al., 2009) using aluminium sulfate (alum; $Al_2(SO_4)_3 \cdot 18H_2O$). An enhanced dose (ED) of alum was estimated by mEnCo[®] model (van Leeuwen et al., 2005; van Leeuwen et al., 2009). The mEnCo[®] model was

Fig. 1. (a) Rainfall data between March 2014 and February 2015; DOC concentrations in river (b) and reservoir (c) waters and SUVA and SpCol values for river (d) and reservoir (e) waters, respectively.

developed for raw waters such as rivers and reservoirs used for portable supply.

Total THMFP and formation of constituent THM compounds (four chloro/bromo compounds) were determined for treated waters by a headspace sampler (Perkin Elmer, TurboMatrix 110) and gas chromatograph with electron-capture detection (Perkin Elmer Clarus[®] 500 GC). THM compounds were formed after 20 mg/L chlorine addition under controlled laboratory conditions of 35 °C and pH 7.4, and held for 4 h as reported by [Fabris et al. \(2008\)](#) and by [Ng et al. \(2013\)](#). Br concentration presented in raw waters was measured using Standard Method 4110 ([Rice et al., 2012](#)).

2.4. DOM loading

The DOC loading from reservoir input (Myponga River) into the reservoir and reservoir output (from the Myponga water treatment plant; WTP), were calculated using Beale's stratified ratio estimator ([Beale, 1962](#); [Ran et al., 2013](#)), equations (1)–(3). According to [Quilbé et al. \(2006\)](#), this method is a good for estimating different pollutants when daily measurement of flow is recorded but only a few data of the concentrations of pollutants are available.

$$L_D = \mu_{Q_1} \times \frac{\mu_{DOC}}{\mu_{Q_2}} \left[\frac{1 + \frac{1}{n} \times \frac{S_{Q_2 DOC}}{\mu_{DOC} \times \mu_{Q_2}}}{1 + \frac{1}{n} \times \frac{S_{Q_2}^2}{\mu_{Q_2}^2}} \right] \quad (1)$$

$$S_{Q_2 DOC} = \frac{1}{n-1} \times \sum_{i=1}^n DOC_i \times Q_i - (n \times \mu_{Q_2} \times \mu_{DOC}) \quad (2)$$

$$S_{Q_2}^2 = \frac{1}{n-1} \times \sum_{i=1}^n Q_i^2 - (n \times \mu_{Q_2}^2) \quad (3)$$

where: L_D , DOC loading (DOC concentration $\times$ water flow, g/d); μ_{Q_1} , mean daily water flow (m^3/d); μ_{DOC} , mean DOC concentration (g/ m^3); μ_{Q_2} , mean daily water flow for the days on which DOC was measured (m^3/d); n , number of the days on which DOC was measured; DOC_i , individual DOC concentration (g/ m^3); Q_i , individual daily water flow (m^3/d); $S_{Q_2 DOC}$, variance value of DOC loading for the days on which DOC was measured; $S_{Q_2}^2$, standard deviation of water flow for the days on which DOC was measured.

3. Results and discussion

3.1. DOM concentration and character in raw waters

Using equations (1)–(3), the total DOC transported by the Myponga River determined over the study period was 122.7 ton/y (annual average, 26.1 mg/L) and the total loading in the reservoir output was 70.9 ton/y (annual average, 15.0 mg/L). The concentrations of DOC in river waters showed seasonal variation with the highest values [mean value: 26.5 mg/L (1028 kg/d)] occurring in the winter season (June–August 2014) followed by the spring season [September–November 2014; mean: 14.8 mg/L (84 kg/d)], autumn [March–May 2014; mean: 12.9 mg/L (62 kg/d)] and summer [December 2014–February 2015; mean: 12.1 mg/L (18 kg/d)], shown in Fig. 1b. This finding is similar to that reported by Evans et al. (2005) and Billett et al. (2006). Evans et al. (2005) reported an increase in DOM concentrations in stream waters during storm events and Billett et al. (2006) reported that DOC concentrations in streams have a positive relation with stream discharge.

In contrast, DOC concentrations in reservoir waters showed a different trend (Fig. 1c), with the mean organic concentration found to be similar between various seasons [mean: 16 mg/L (173 kg/d) for autumn, 15 mg/L (132 kg/d) for winter, 15 mg/L (210 kg/d) for spring, and 14 mg/L (261 kg/d) for summer]. These smaller variations are attributed to the high water holding capacity (time) of Myponga Reservoir (mean 4.6 y). The holding time, ratio of average holding capacity to the outflow rate (at WTP) of the Myponga Reservoir were calculated based on the average holding capacity of $85.5 \pm 5.4\%$ of the maximum storage capacity (22,902,833 m^3) and the outflow rate of 4,787,440 m^3/y .

UV-Vis spectroscopy was performed to characterize DOM, based on the presence of UV absorbing and chromophoric organic constituents, including aromatic groups as reported by Weishaar et al. (2003) and Korshin et al. (2009). SUVA and SpCol of DOM present in river and reservoir waters are shown in Fig. 1d and 1e respectively. These two parameters are used in the drinking water industry to characterize DOM as a means of assessing treatment needs in the supply of potable water.

For river waters, mean values of SUVA were 3.36 ± 0.39 L/(mg m) in autumn, 3.70 ± 0.30 L/(mg m) in winter, 3.70 ± 0.30 L/(mg m) in spring and 3.85 ± 0.29 L/(mg m) in summer. This parameter was higher at the wet season compared with the end of the dry season,

Fig. 1d. The highest SUVA [~ 4.2 L/(mg m)] occurred at the end of June and July while the lowest SUVA level [~ 2.65 L/(mg m)] occurred in March for the period of investigation. SpCol levels showed the same trend with values higher for water samples collected at the start of the wet season (~ 9.5 HU L/mg) compared with the end of the dry season (~ 3.9 HU L/mg), Fig. 1d. Storm events led to an increase in the percentage of humic-like and aromatic organics compounds in stream/river waters as reported by Carstea et al. (2009) and Stutter et al. (2012).

Mean SUVA levels in the reservoir waters (Fig. 1e) were slightly lower in the dry season [3.15 ± 0.22 L/(mg m)] compared with the wet season [3.36 ± 0.11 L/(mg m)]. SpCol levels showed the same trend with values lower for waters collected in autumn and summer than other seasons [means: 4.01 ± 0.32 HU L/mg for autumn, 4.56 ± 0.39 HU L/mg for winter, 5.0 ± 0.47 HU L/mg for spring and 3.87 ± 0.40 HU L/mg for summer months], Fig. 1e. Warmer water temperatures lead to increase in microbial activity and consequently greater formation of hydrophilic compounds (Lumsdon et al., 2005). Further, with increasing UV irradiation levels during the dry season there is increase in the photo-degradation rates of coloured DOM (Zepp et al., 2007) mainly aromatic organic compounds (Ritson et al., 2014).

Organic constituents of the river and reservoir waters were analyzed by HPSEC with UV detection. The mean AMW of organics of river waters collected in the wet seasons (winter-spring: 1526 ± 125 Da) was higher than of the dry seasons (summer-autumn: 1385 ± 129 Da), Fig. 2a. Similar to SUVA and SpCol, the highest AMW value (~ 1721 Da) was found in waters collected between the end of June and July while the lowest AMW value (~ 1239 Da) was found in water collected in March. For reservoir waters, the mean AMW values were similar for the wet (1332 ± 32.7 Da) and dry (1290 ± 46 Da) seasons.

In order to resolve peaks from HPSEC chromatographs, a peak fitting technique was applied and the relative abundance of each peak area determined, shown in Supplementary data, Fig. S1. For river waters, relative abundances of HMW peaks (P1:P4: MW > 2 KDa) were lower in flow collected during the dry season (summer-winter: $10 \pm 4.2\%$) than in the wet season (winter-spring: $17 \pm 6.2\%$), Fig. S1. In contrast, the relative abundances of LMW peaks (P7:P9: MW < 1.0 KDa) were similar between wet and dry seasons ($20 \pm 1.4\%$ during wet seasons and $22 \pm 2.5\%$ during dry seasons). For reservoir waters, the abundances of organics of HMW and LMW (peaks) were similar between the wet and dry seasons (wet seasons: $8 \pm 0.8\%$ for P1:P4 and $24 \pm 1.4\%$ for P7:P9; dry seasons: $8 \pm 1.6\%$ for P1:P4 and $23 \pm 1.1\%$ for P7:P9).

Organic constituents of the river and reservoir waters were also analyzed by HPSEC with fluorescence detection to estimate the molecular weight distributions of humic-like compounds. The AMW of organics of river waters collected in the wet seasons (winter-spring: 1008 ± 6.7 Da) were higher than of the dry seasons (summer-autumn: 923 ± 21.3 Da), Fig. 2b. Mean AWM-humic level in the reservoir waters were slightly higher in the wet season [971 ± 19 Da] compared with the dry season [938 ± 29 Da]. For the reservoir waters, the lowest AWM-humic level (882 Da) was found in water samples collected in the summer season.

Peak fitting was performed and the relative abundance of each peak area determined. For river waters, the relative combined abundances of peaks P4:P6 (MW < 1 KDa) were greater in flows collected in the dry seasons ($40 \pm 2.3\%$) than in the wet seasons ($32 \pm 1.8\%$), Supplementary data (Fig. S2). The relative abundances of peaks P2:P3 (1 KDa < MW < 1.3 KDa) were lower in flows collected in the dry seasons ($60 \pm 2.3\%$) than in the wet seasons ($66 \pm 3.3\%$). Peak 1 (2345 Da) did not appear in flows collected in the dry seasons while in the wet seasons, this peak was detected with a mean relative abundance of $2 \pm 1.6\%$ (Fig. S2).

Fig. 2. Average AMW of UV absorbance compounds (a) and of humic-like compounds (b) of river and reservoir waters.

For reservoir waters, the relative abundances of peaks P4:P6 were similar in flows collected in the dry seasons ($39 \pm 2.2\%$) compared with the wet seasons ($36 \pm 1.8\%$). Also, the % of peaks P2:P3 and P1 were similar in waters collected in the dry seasons ($59 \pm 2.4\%$ for P2:P3 and $1 \pm 0.9\%$ for P1) to those of the wet seasons ($62 \pm 2.3\%$ for P2:P3 and $2 \pm 1.9\%$ for P1). The highest abundances of LMW compounds were in flows in January (Fig. S2).

3.2. Alum dose and DOC removal

Percentage removals of DOC from water by alum treatment at ED (%DOC_{Rem}) under standardized conditions and alum dose rates (mg alum per mg DOC removed) applied at ED (Al/DOC), are presented in Fig. 3. Average percentage removals of DOC from river waters ($58 \pm 10\%$) were slightly higher than reservoir water ($53 \pm 3\%$), while the Al/DOC for the river waters (13 ± 3 mg/mg DOC

removed) was similar to the reservoir waters (13 ± 1 mg/mg DOC removed), as shown in Fig. 3b.

For river waters, %DOC_{Rem} by alum treatment were greater for water samples collected during wet seasons ($64 \pm 5\%$) than waters collected during the dry seasons ($53 \pm 10\%$). The Al/DOC data showed a consistent trend with values lower in waters collected during wet seasons (10 ± 2 mg/mg DOC removed) than waters collected during the dry seasons (15 ± 3 mg/mg DOC removed). Coefficient of variation values for these waters collected during the wet and dry seasons were calculated and these are 9.4% and 20% for %DOC_{Rem} and Al/DOC respectively. This shows that organic compounds present in surface waters of the wet seasons were more amenable to removal by coagulation than the waters collected during dry seasons, and this corresponds with the DOM characters. Organics collected during wet seasons had high relative abundances of high MW humic and aromatic compounds compared

Fig. 3. Average data of (a) %DOC_{Rem} and (b) Al/DOC from jar tests of river and reservoir waters.

with organics collected during dry seasons (Figs. 1 and 2, S1 and S2).

In contrast, water samples collected from the reservoir during wet seasons had similar %DOC removals and Al/DOC values compared to that collected during dry seasons (%DOC_{Rem}: $54 \pm 4\%$ for wet seasons vs $52 \pm 2\%$ for dry seasons; Al/DOC: 13 ± 2 mg/mg DOC for wet seasons vs 13 ± 0.8 mg/mg DOC for dry seasons). Coefficient of variation values of reservoir waters collected during the wet and dry seasons were 1.9% and 0.1% for %DOC_{Rem} and Al/DOC respectively. For river waters, the lowest alum dose rates (7.7 Al/DOC) was for water collected at end of June (the start of catchment runoff, Supplementary data, Fig. S4). For reservoir waters, the lowest alum dose rate (10 Al/DOC) with the highest DOM removal ratio (59.4%) was for water collected at end of the winter season, coinciding to the higher relative abundance of organics of high MW-humic compounds (Figs. 2 and S2). Sachse et al. (2005) reported that as a result of low temperature, autochthonous precursor activities are reduced in winter and DOM is mainly from allochthonous inputs. The latter is likely to be more amenable to removal by coagulation (Fabris et al., 2008).

3.3. Characterization of DOM in alum treated waters

SUVA and SpCol values of ED alum treated waters are shown in Table 1. Alum treated waters had lower SUVA and SpCol values than raw waters, as expected. This is attributed to the greater effectiveness of coagulation in removal of aromatic and hydrophobic compounds, as reported by Ødegaard et al. (2010) and others. For river waters, those collected during wet seasons had higher residual aromatic constituents after ED [SUVA: 2.0 ± 0.2 L/(mg m); SpCol: 2.5 ± 0.5 HU L/mg] compared with residual organics in waters collected during the dry seasons [SUVA: 1.5 ± 0.3 L/(mg m); SpCol: 1.3 ± 0.2 HU L/mg]. In contrast, for reservoir waters, there were no differences in the SUVA and SpCol levels of treated waters for waters collected during various seasons [SUVA: 1.8 ± 0.1 L/(mg m) for the dry season and 1.8 ± 0.1 L/(mg m) for wet season; SpCol: 1.2 ± 0.3 HU L/mg for dry season and 1.5 ± 0.4 HU L/mg for wet season].

For river waters, there were no differences in the mean AMW of treated waters for raw waters collected during the wet and dry seasons (784 ± 76 Da for wet season and 800 ± 29 Da for dry season). However, the mean AMW-humic component was found to be higher in waters collected during wet seasons compared with the dry season (705 ± 33 Da vs 640 ± 40 Da). For reservoir waters, there were no differences in the AMW and AMW-humic levels of treated waters [AMW: 848 ± 13 Da for wet season samples and 817 ± 50 Da for dry season; AMW-humic: 698 ± 9 Da for the wet season and 691 ± 6 Da for dry season].

Table 1
DOM concentration and character for ED alum treated waters from river and reservoir.

	DOC Residual (mg/L)		SUVA [L/(mg m)]		SpCol (HU L/mg)	
	Reservoir	River	Reservoir	River	Reservoir	River
Mar. 14	7.65	8.91	1.97	1.69	1.19	NA
April 14	8.70	6.14	1.75	1.67	1.19	1.22
May 14	NA	6.99	NA	1.13	NA	1.09
June 14	6.92	7.42	1.66	1.91	1.29	1.93
July 14	6.94	10.62	1.94	2.30	2.03	2.44
Aug 14	6.68	5.71	1.87	1.96	1.03	2.34
Sep 14	6.62	4.89	1.89	1.88	1.51	2.22
Oct 14	NA	5.20	NA	1.75	NA	3.42
Dec 14	6.01	4.30	1.66	1.36	1.00	1.25
Jan 15	6.90	5.08	1.72	1.79	1.30	1.54

From the resolved peaks of organics in waters before and after alum treatment (at ED), the percentage removals of each peak were determined, shown in Fig. 4a. High molecular weight (HMW) peaks, P1:P5 (MW > 1750 Da) identified by HPSEC-UV detection can generally be easily removed by coagulant treatment (Allpike et al., 2005; Chow et al., 2008; Soh et al., 2008; Wang et al., 2010). These peaks (MW > 1750 Da) present in waters collected during different seasons were completely removed from waters by alum treatment.

The percentage removals of compounds of LMW (peaks of MW < 1 KDa) in river waters ($33 \pm 14\%$) were similar to removals of compounds in reservoir waters ($30 \pm 7\%$), Fig. 4a. The percentage mean reduction of P6 (1250 Da) was higher for river waters compared to reservoir waters ($75 \pm 9\%$ for river vs $66 \pm 8\%$ for reservoir). Samples collected during dry and wet seasons of surface waters (reservoir or river) had similar percentage removals of P6 (reservoir: $65 \pm 10\%$ for dry season vs $67 \pm 7\%$ for wet season; river: $75 \pm 8\%$ for dry season vs $75 \pm 9\%$ for wet season). Samples collected during the dry seasons had lower removals of compounds of LMW peaks (MW < 1 KDa) compared with samples collected during wet season (reservoir: $24 \pm 1\%$ for dry season vs $35 \pm 6\%$ for wet season; river: $22 \pm 12\%$ for dry season vs $41 \pm 9\%$ for wet season).

The percentage removals of resolved peaks with alum treatment at ED determined by HPSEC-fluorescence detection are shown in Fig. 4b. HMW humic-like compounds (P1:P2; MW > 1200 Da) were easily removed from waters collected during the various seasons. Removals of LMW humic-like compounds (P4:P6; MW < 1000 Da) by coagulation from surface waters collected during the wet season were similar to that of waters collected during the dry season (reservoir: $36 \pm 8\%$ for dry season vs $35 \pm 1\%$ for wet season; river: $34 \pm 9\%$ for dry season vs $34 \pm 10\%$ for wet season). In contrast, samples collected during dry season had higher removals of P3 (1175 Da) compound(s) compared with samples collected during wet season for both river and reservoir waters (reservoir: $71 \pm 10\%$ for dry season vs $62 \pm 1\%$ for wet season; river: $86 \pm 3\%$ for dry season vs $72 \pm 9\%$ for wet season). These results are consistent with findings from the study of Aslam et al. (2013), who reported that most low molecular weight humic-like compounds are recalcitrant to treatment by alum and remain in treated water.

3.4. Trihalomethane formation potential for treated waters

Total THMFP and constituent THM compounds for river and reservoir waters after ED alum treatment are shown in Fig. 5. Average total THMFP for alum treated waters sourced from the river ($\bar{X} \pm \text{SD}$: 202 ± 26 µg/L) was similar to treated waters sourced from the reservoir ($\bar{X} \pm \text{SD}$: 209 ± 8 µg/L). Average specific THMFP values (the ratio of THMFP to DOC concentration) for treated river waters (32 ± 5 µg/mg DOC) was also similar to that for treated reservoir waters (30 ± 2 µg/mg DOC). Further, no apparent difference was found in the percentages of chlorinated compounds (e.g., %CHCl₃) between treated river and reservoir waters (%CHCl₃: $36 \pm 8\%$ for river waters vs $35 \pm 2\%$ for reservoir waters).

Treated waters of those sourced from the river collected during dry seasons had residual DOM of lower THMFP (172 ± 2 µg/L) than organics of waters collected during wet seasons (217 ± 18 µg/L). However no apparent difference was found in the mean specific THMFP values (31 ± 3 µg/mg DOC for dry seasons vs 32 ± 6 µg/mg DOC for wet seasons). These findings indicate that residual DOC concentration is a key factor that determines THM formation levels in treated waters. Residual DOC concentrations in waters collected during dry and wet seasons were 5.6 ± 0.5 mg/L and 7.2 ± 2.0 mg/L respectively.

The relative abundances of THM chlorinated species were different between waters collected during dry and wet seasons

Fig. 4. Percentage removals of resolved peaks determined by HPSEC with UV-detection (a) and with fluorescence-detection (b).

Fig. 5. Average constituent THM compounds (µg/L) for ED alum treated waters from river and reservoir waters.

with slightly lower potentials in samples collected in the dry seasons than wet seasons (e.g., %CHCl₃: 31 ± 6% for dry seasons vs 38 ± 8% for wet seasons). However for treated waters from the reservoir, no significant differences were found between waters collected during dry and wet seasons for total THMFP

concentration (212 ± 10 µg/L for dry seasons vs 208 ± 7 µg/L for wet seasons) and the relative abundances of THM chlorinated species (e.g., %CHCl₃: 34 ± 4% for dry seasons vs 35 ± 1% for wet seasons) as shown in Fig. 5. However, Specific THMFPs were found to be slightly higher in reservoir treated waters collected during wet season

compared with the dry season ($30 \pm 1 \mu\text{g}/\text{mg}$ DOC vs $27 \pm 2 \mu\text{g}/\text{mg}$ DOC).

From studies conducted to determine the impacts of catchment characteristics on the quality of waters used for domestic supply, we previously reported the influence of the vegetation (native, pine, grasslands) and soil texture (sandy/clayey) on the characters and concentrations of DOMs present in surface and sub-surface runoff waters collected from various zero-order catchments (ZOCs), Myponga Reservoir-catchment (Awad et al., 2015). The DOC concentration, DOM character by UV-absorbance and HPSEC of subsurface (~ 30 cm) water samples collected over two seasons (winter and spring) of 2014 are presented in Figs. S3 and S4 (Supplementary data). In summer-autumn seasons, runoff and subsurface water flows were not found to occur in any of the ZOCs. At the start of the wet seasons, DOC concentrations and the relative abundances of coagulable organics (aromatic and high MW peaks organic compounds) were found to be much higher than at the end of the wet season (these features decreased with time, Figs. S4 and S5). The highest concentration of DOC released into subsurface waters and lateral flows occurred after the first major rainfall event, as similarly reported by Chow et al. (2011).

Compared to ZOC waters, river waters showed the same trend, with the highest organic concentration (Fig. 1b) occurring at the end of June and in July (the start of catchment runoff, Figs. S3 and S4). Evans et al. (2005) and Ritson et al. (2014) reported an increase in DOM concentrations in stream waters during storm events as a result of flushing of the upper organic soil horizons. Further, the highest relative abundances of coagulable organics (aromatic and high MW peaks organic compounds) also occurred at the end of June and in July. These features (concentration and character of DOM) led to a higher percentage removal of organics by coagulation and using a lower alum dose rate (Fig. 3). However, these features led to an increase in the total THM formation potential (Fig. 5). These results indicate that DOM present in river waters and their treatability by alum are highly impacted by catchment runoff and by seasonal variation.

In contrast, for reservoir waters, no apparent differences were found in the DOC concentrations between samples collected during the wet and dry seasons (Fig. 1c). Further, aromatic compounds and MW distributions in reservoir waters (Figs. 1e and 2) appeared to be more constant during the collection period compared with river waters (Figs. 1d and 2). Wei et al. (2008) reported that SUVA levels of reservoir waters (East-Lake, China) collected during different seasons had similar values. However, Wei et al. (2008) also reported differences in the MW distributions during the collection period. In our research, similarity in these features (concentration and character of DOM) led to consequently similar percentage removals of organics by alum, similar alum dose rates (Fig. 3) and THMFP (Fig. 5) between samples collected during the dry and the wet seasons. This may be attributed to storage of larger water volumes within the reservoir enabling mixing of influent waters and stabilization of water quality.

4. Conclusions

Catchment runoff and flow patterns combine to have a significant effect on the concentration and character of organics in river waters. DOC concentration and relative abundance of coagulable organics were highest in the waters collected during the first flush from the ZOCs studied and consequently in the river water. Waters collected during wet season have higher DOC concentrations, higher relative abundance of aromatic, HMW and humic-like compounds than waters collected during dry season. Consequently, river waters collected during wet season were found to have higher THMFP formation, and higher percentage removal of

organics by coagulation and at a lower alum dose rate compared with waters collected during dry seasons.

Storage of large volumes of water in the reservoir enables mixing of influent waters and stabilization of water quality. This resulted in no measurable differences in the reservoir output water quality (at the water treatment plant) between the dry and wet seasons. DOM in reservoir waters and its treatability were found to be less seasonally variable compared with river waters.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2016.10.054>.

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