Comparing three Australian natural organic matter isolates to the Suwannee river standard: reactivity, disinfection by-product yield, and removal by drinking water treatments.

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Abstract

Water treatments that provide efficient removal of organic and inorganic disinfection by-product (DBP) precursors across variable natural organic matter (NOM) sources are desirable. Treatments that effectively remove inorganic DBP precursors such as bromide, which significantly shift the speciation of DBP formation towards more toxic DBPs, are of particular interest and have been less investigated.

This study characterized NOM isolated from three major drinking water sources in Southeast Queensland (SEQ), Australia, and compared it to the International Humic Substances Society (IHSS) Suwannee River NOM isolate (SR) in terms of DBP precursor removal treatments and DBP formation. Each NOM isolate was used to make synthetic water samples with otherwise identical water quality parameters, that were treated with enhanced coagulation

(EC) or EC followed by; anion exchange (MIEX® resin), powdered activated carbon (PAC), granular activated carbon (GAC) or silver impregnated activated carbon (SIAC), to investigate the removal of DBP precursors (bromide and DOC), minimisation of DBPs, as well as the change in specific chlorine demand. EC/SIAC treatment was the most effective method of DBP control studied, due to the efficient simultaneous NOM and bromide adsorption of the SIAC ($99\pm1\%$ bromide removal regardless of NOM source). This treatment also resulted in $>92\%$ removal of each of the measured DBPs across all NOM sources, with the exception of DBAN and 1,1-DCP, which achieved $>80\%$ removal across all NOM sources. Increases in tribromomethane (TBM) and dibromoacetonitrile (DBAN) formation were observed after all other treatment/NOM-isolate combinations, due to increased Br:DOC ratio after treatment, whereas chlorinated DBPs were generally well-controlled by all treatment/NOM-isolate combinations. Differences in reactivity of the individual NOM isolates were found to be related to both the origin of the isolate and the treatment employed, however, bromide removal capacity for each treatment was independent of NOM source.

Key words: DBP, enhanced coagulation, MIEX, SIAC, halide removal, NOM removal.

1. Introduction

Natural organic matter (NOM) is a complex heterogeneous mixture of organic compounds derived from terrestrial and aquatic sources, present in all natural waters (Swietlik and Sikorska 2006, Yohannes et al. 2005). It is composed of humic substances, hydrophilic acids, carboxylic acids, carbohydrates, amino acids, lipids and proteins and can contain aromatic, aliphatic, phenolic, and quinonic regions with varying molecular sizes and properties (Yohannes et al. 2005). NOM concentrations and reactivity can vary greatly between different natural waters depending on source, climate and land use. NOM reacts with disinfectants and halides (bromide, iodide) present in the source water to form disinfection

by-products (DBPs), some of which have been associated with deleterious reproductive effects and specific forms of cancer (Richardson et al. 2007). Generally, brominated DBPs (Br-DBPs) are both more genotoxic and carcinogenic than their chlorinated counterparts (Richardson et al. 2007). DBPs occurring in drinking water are of public health concern, and strategies for their continued control are imperative. One strategy to minimize DBP formation is the removal of organic and inorganic precursors (such as NOM and bromide, respectively) before disinfection. While many drinking water treatment plants (DWTPs) employ a technique such as enhanced coagulation (EC) to remove organic matter, the use of treatments that reduce both organic and inorganic precursors is less established (Watson et al. 2012). Recent research has highlighted correlations between specific NOM fluorophores and formation of particular classes of DBPs, and further to this, changes in NOM character throughout treatment processes (as observed through changes in fluorescence) are understood to lead to changes in DBP formation (Fabbri et al. 2019, Li et al. 2017, Watson et al. 2018, Yan et al. 2018). It follows that variable NOM sources being subjected to similar water treatment processes may give rise to different DBP profiles, assuming all other relevant water quality parameters remain constant, and there is a need to identify water treatment methods that may be expected to be effective for DBP mitigation across widely variable NOM sources. The International Humic Substances Society (IHSS) has isolated NOM from the Suwannee River in southeast Georgia, and this is often employed in laboratory studies (Watson et al. 2015, 2016). The Suwannee river is a unique acidic blackwater stream sourced from the Okefenokee Swamp, with very high NOM concentrations, primarily composed of allochthonous-derived humic substances (Averett et al. 1994, Croue et al. 2000). NOM from drinking water sources can vary markedly in organic content, and is commonly derived from both allochthonous and autochthonous sources (Sullivan et al. 2005).

In this study, NOM was isolated and characterised from three major drinking water sources in Southeast Queensland (SEQ), Australia. These three isolates, along with the Suwannee river NOM isolate, were compared in terms of NOM and bromide removal from a standardised synthetic water using an EC primary treatment followed by; MIEX[®], powdered activated carbon (PAC), granular activated carbon (GAC) or silver impregnated activated carbon (SIAC) secondary treatment. DBP formation potential was also assessed at each stage of treatment, for each isolate, and compared to the DBP formation potential of ‘no treatment’ (NT) samples. Although some recent studies have reported excellent bromide removal for SIAC, it is still unclear if the removal capacity is dependent on NOM properties (Chen et al. 2017, Watson et al. 2016). The main objective of this study, was to compare SIAC to more conventional treatments, and to determine, in general, how different water treatment protocols responded to different NOM sources, with all other water quality parameters being kept constant, in terms of NOM and bromide removal, and DBP formation.

2. Methods

2.1 Reagents

Chemicals were purchased from the following suppliers – Accustandard: mixed standard of trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), tribromomethane (TBM), 2.0 mg/mL in methanol; 1,2-dibromopropane, 5 mg/mL in methanol; mixed standard of dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), bromochloroacetonitrile (BCAN), dibromoacetonitrile (DBAN), 1,1-dichloropropanone (1,1-DCP), 1,1,1-trichloropropanone (1,1,1-TCP), CH, trichloronitromethane (TCNM), 1 mg/mL in acetone. Acros organics: phosphate buffers (Na_2HPO_4 and KH_2PO_4) (99%), ascorbic acid (ACS grade). Sigma-Aldrich: $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (98%), NaOCl ($\geq 4\%$), MgSO_4 ($\geq 99.5\%$), $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (98%), NaHCO_3 (99.7-100.3%), methyl *tert*-butyl ether (MtBE) ($\geq 99.8\%$), NaBr ($\geq 99.0\%$). ThermoFisher: NaCl (99.95%). Merck: HCl (32%). Chem-supply: NaOH

($\geq 98\%$). Malcron chemicals: sodium sulfate (anhydrous) 99.7%. Suwannee river (whole) NOM isolate was purchased from the International Humic Substances Society (batch number 1R101N). Commercial DPD test kits (HACH) were used for the analysis of free chlorine (method 8021). Norit 18 $\times$ 40AG1 (0.1% Ag) SIAC and Norit GCN1840 GAC was donated by Cabot Norit, Amersfoort, The Netherlands. Used, regenerated, MIEX[®] resin was obtained from a South Australian water treatment plant (WTP). Norit W35 PAC was purchased from Sigma-Aldrich. NOM isolates were developed in our laboratory, and the procedure for this is detailed herein.

2.2 Site descriptions

The three major drinking water sources for the SEQ region were selected for this study. Samples were collected from the influent to each DWTP and sourced from Tingalpa Reservoir (TR), Brisbane River (BR) and Advancetown Lake (AL). Samples were transported in 50 $\times$ 20 L HDPE containers directly to the laboratory, where they were stored at 4 °C until processing (within 24 h). Standardised synthetic water samples were used for these experiments, therefore, the NOM, halide, inorganic constituent and DBP concentrations reported herein do not reflect the natural waters from which they originated.

2.3 NOM Isolation process

The NOM isolation process employed was performed in accordance with the Suwannee River NOM isolation method presented by Serkiz and Perdue (Serkiz and Perdue 1990), with minor modifications. Specifically, 1000 L of raw water from each sampling site was filtered through successive in-line 5, 1 and 0.5 μ m polypropylene sediment filters, then subjected to continuous reverse osmosis (RO) and cation exchange in order to concentrate the organic matter in the sample and remove metal cations such as Ca^{2+} and Al^{3+} that may cause precipitates on the RO membranes. Permeate was discarded until a final volume of

approximately 20 L was attained (Figure SI 1 and Table SI 1). The RO concentrates were desalted using Spectra/Por Biotech cellulose ester dialysis membrane (molecular weight cut-off 100 Da) and then freeze-dried using a 25 L Genesis SQ Super XL-70 freeze drier, after which the isolates were stored under vacuum until use.

2.4 Synthetic water samples

For each NOM isolate, 6 synthetic water samples were prepared, allowing one for each treatment scenario. Additionally, 6 blank samples were prepared, again allowing one for each treatment scenario. This gave a matrix of 30 synthetic waters of standardised water quality characteristics that were utilised for all DBP formation potential and DBP precursor removal experiments. This matrix of experiments was run in duplicate. Synthetic water samples were prepared by dosing 1L of laboratory-purified water with standard concentrations of; dissolved organic carbon (DOC) (i.e. the weight of each NOM isolate used per sample was standardised to give approximately equal DOC concentration in solution between samples), bromide, chloride, sodium carbonate, calcium sulfate and magnesium sulfate. Bromide concentration was 450 µg/L and DOC concentration was approximately 10 mg/L. Alkalinity concentration was 138 mg/L as CaCO₃, while calcium sulfate and magnesium sulfate were both added at 73 mg/L. Sodium chloride was added to give a Br⁻/Cl⁻ ratio of 1:300 by weight, to mimic a natural water (Magazinovic 2004). After making the waters, the pH was adjusted to 7 with dilute HCl. Finally, bromide, DOC and alkalinity concentrations were measured to obtain accurate starting concentrations for these parameters. Each 1 L sample was stored in an amber glass bottle at 4 °C until use (within 24 h).

2.5 Water treatments

2.5.1 EC treatment

EC with alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) was conducted in accordance to US EPA's Enhanced Coagulation and Enhanced Precipitative Softening Guidance Manual (USEPA 1999, Watson et al. 2015). Each 1L synthetic water sample was dosed with 60 mg/L alum, then rapidly mixed for 1.5 min at 200 rpm, flocculated for 13.5 min at 30 rpm, then settled for 60 min before vacuum filtering through Whatman No. 1 filter papers, which were chosen to simulate sand filtration at the WTP (Hudson 1981).

2.5.2 PAC treatment

After EC, 1 L samples were dosed with 60 mg/L of Norit W35 PAC, then subjected to jar test using a Platypus Jar Tester for 30 min at 100 rpm, settled for 5 min, then vacuum filtered through Whatman No. 1 filter papers (Watson et al. 2015). PAC dose was optimised by testing synthetic water samples pre-treated by EC at doses ranging from 0 to 120 mg/L and determining the lowest dose with greatest DOC removal.

2.5.3 MIEX® treatment

MIEX® was a used resin sourced from a South Australian DWTP that was regenerated with a 10% NaCl solution prior to use in jar tests. After EC, 1L samples were dosed with 10 mL/L of regenerated and settled MIEX® resin, subjected to jar test using a Platypus Jar Tester for 30 min at 100 rpm, settled for 5 min, then vacuum filtered through Whatman No. 1 filter papers. This jar testing protocol is similar to previously published methods (Hsu and Singer 2010, Johnson and Singer 2004, Watson et al. 2015).

2.5.4 GAC and SIAC treatments

GAC (Norit GCN1840; particle size < 0.425 mm, surface area = 1100 m²/g, iodine number: 1000) and 0.1% SIAC (Norit 18 × 40AG1; silver content = 0.1%, water extractable silver content = 0.01 mg/L, particle size < 0.425 mm, surface area = 1050 m²/g, iodine number:

950) were soaked overnight in ultrapure water and rinsed prior to use to remove fines. Aqueous activated carbon slurries were then loaded into columns with a total volume of 6.36 cm³ (10 cm height $\times$ 0.9 cm diameter) with a final wet weight of 6 g of activated carbon in each column. After EC, approximately 125 bed volumes of sample was passed over each column, at a flow rate that allowed an empty bed contact time (EBCT) of 10 min (0.6 mL/min)(Watson et al. 2016). Analyses were conducted by comparing the influent onto the columns with the treated sample after the whole volume had been passed over the column.

2.6 DBP formation potential test

Two aliquots of 225 mL were taken at each stage of treatment for use in chlorine demand tests and DBP formation potential tests. To evaluate the formation potential of DBPs, first the specific chlorine demand for each sample was determined using Standard Method 5710 [44]. The second aliquot of sample was then buffered at pH=7 with phosphate buffer (10 mM) and dosed with 4% sodium hypochlorite, at a dose equal to the chlorine demand plus 2 mg/L Cl₂, in order to obtain a final residual chlorine concentration similar to what would be found in a real application of drinking water disinfection. Chlorinated samples were then kept headspace free in amber glass bottles with gentle mixing for 72 h, at constant temperature (23 $\pm$ 1 °C) [45], after which residual free chlorine was measured using the DPD method [46] and then quenched with an excess of ascorbic acid (5 mg/L of ascorbic acid added per 1 mg/L of free chlorine).

2.7 DBPs analysis

Samples were prepared for DBP analysis using a liquid-liquid extraction, then analysed by gas chromatography (GC) with electron capture detector (ECD) as described (Krasner et al. 2006). Briefly, 2 $\times$ 30 mL aliquots of each sample were transferred into 60 mL extraction vials and adjusted to pH 3.5 with 0.2 N sulphuric acid. Samples were then extracted using 3

mL of MtBE containing 200 µg/L of 1,2-dibromopropane as an internal standard. After the addition of ~10 g pre-baked (at 500 °C) sodium sulphate, the samples were vortexed for 1 min and left to settle for 5 min. The extract was transferred into 2 × 2 mL autosampler vials for injection into an Agilent 7890A GC-ECD (Forest Hill, Australia), with the chromatographic separation performed on a dual column system using Agilent columns (DB-5; 30 m length × 0.25 mm inner diameter × 1.0 µm film thickness and DB-1; 30 m length × 0.25 mm inner diameter × 1.0 µm film thickness). Pulsed splitless injection was used at a temperature of 200 °C. The oven temperature program was as follows: 40 °C for 25 min, ramp to 145 °C at 5 °C/min and held for 2 min and then ramp to 260 °C at 20 °C/min and held for 10 min. The ECD temperature was 290 °C. The relative percent differences for duplicate samples were in all instances lower than 10%. The reporting limit for all DBPs was 0.1 µg/L and the recovery was between 80% and 120%. The following DBPs were analysed: TCM, BDCM, DBCM, TBM, DCAN, BCAN, DBAN, CH, 1,1-DCP and 1,1,1-TCP.

2.8 Bromide analysis

Bromide analysis was conducted using a Dionex ICS-5000 ion chromatography system, run in one-dimensional mode with an IonPac AS19 analytical column (4 mm internal diameter × 250 mm length) using a previously published method (Watson et al. 2014). The method reporting limit was 20 µg/L. Calibration standards, duplicate samples, blank-matrix and spiked-matrix standards were run with each batch as quality controls.

2.9 DOC, alkalinity, and UV₂₅₄

DOC and alkalinity (inorganic carbon) were measured using a Shimadzu TOC-VCSH TOC analyser using a high temperature catalytic oxidation method (Standard Method 5310B) (Clesceri et al. 1998). UV₂₅₄ was measured using a Bio-Rad SmartSpec Plus spectrophotometer and quartz cuvette with 1 cm path length.

2.10 Elemental microanalysis for C, H, N, S, O

C, H, N, S and O elemental analysis was performed on a FLASH 2000 CHNS/O Analyzer in duplicate by the modified Pregl-Dumas technique (dynamic flash combustion) [13].

2.11 Excitation emission matrix (EEMs) fluorescence spectroscopy

EEMs measurements of NOM were performed at room temperature using a PerkinElmer LS-55 luminescence spectrometer (PerkinElmer, Australia) and a quartz cuvette with 1 cm path length. The spectrometer displayed a maximum emission intensity of 1000 arbitrary units (AU). Excitation wavelengths were monitored from 200 nm to 400 nm at steps of 5 nm, and emission wavelengths were monitored from 280 nm to 500 nm with a 0.5 nm step. A 290 nm emission wavelength cut-off was used to limit second-order Raleigh scattering. Excitation and emission scan slits were set at 7 nm and the scan speed was 1200 nm/min. Samples were diluted prior to analysis to give an absorbance maximum of 0.05 at 220 nm, and a MilliQ water blank was subtracted. In order to quantify differences between NOM isolates and relative changes in the EEM spectra after adsorptive treatments, percent fluorescence response ($P_{i,n}$) was calculated using the integration method proposed by Chen et al. (Chen et al. 2003) (Figure SI 2).

3. Results and discussion

3.1 Raw water characteristics

Tables 1 and SI 2 summarise water quality parameters and DBP formation potentials for the raw SEQ drinking water sources studied. TR had a high organic carbon load compared to the other two sites, however, BR had a higher salt load (inorganic carbon, and bromide) than AL and TR. BR raw water had the highest $SUVA_{254}$, consistent with mostly aquatic humic acids and high molecular weight NOM (Gheraout 2014). TR and AL raw water had slightly lower

SUVA₂₅₄, indicating NOM was a mixture of aquatic humic and other NOM substances, with varying molecular weights (Gheraout 2014). EEMs and P_{i,n} show that humic substances (fulvic and humic acids) were major components of NOM in all source waters. Although DBP formation potential varies widely between sources, it cannot be determined from these experiments whether these variations are a result of differences in overall concentrations of NOM, alkalinity, halides, and other relevant water quality parameters, or differences in the DBP reactive NOM components in these individual NOM sources. Since water quality characteristics (such as NOM and bromide concentration) vary between the raw source waters, in order to study differences in NOM reactivity, a standardised synthetic water matrix was required in order to control for variables other than NOM source.

3.2 NOM Isolate characteristics

3.2.1 Comparison of raw waters with their reconstituted NOM isolates

NOM was isolated from the three major surface water sources in SEQ; TR, BR and AL. EEMs for raw source waters and reconstituted isolate samples were analysed for percent fluorescence response ($P_{i,n}$), to assess how the isolates compared to the original source water (Table SI 3). For each sample site, raw water and reconstituted NOM isolate samples had EEM $P_{i,n}$ within 8% of each other for each EEM region, except for the humic acid-like region for BR for which the EEM $P_{i,n}$ between source water and reconstituted NOM isolate was within 15%. The EEM $P_{i,n}$ analysis shows that the NOM isolates are representative of the natural source waters. The IHSS whole NOM from the Suwannee River is isolated using a RO/cation exchange resin method similar to what we describe here (Serkiz and Perdue 1990).

3.2.2 Elemental composition and atomic ratio

Elemental analysis along with elemental ratios, including C/H, C/N and C/O, can provide information on the possible composition of NOM isolates (Rice and MacCarthy 1991). The elemental analysis results for each NOM isolate is shown (Table 2). SR contained the highest content of carbon, hydrogen, and oxygen and lowest content of sulphur and nitrogen when compared to the Australian isolates. Australian isolates had a higher ash content than SR, which will affect the accuracy of elemental analysis. Although our NOM isolation process was shown to give excellent cation removal (Table SI 4), we were unable to adequately remove silica, which we believe contributed to the much higher ash content observed in our isolates compared to the SR NOM.

The C/H ratio indicates relative saturation of the carbon atom within the NOM (Perdue and Ritchie 2005). The high C/H ratio of SR indicates significant portions of aromatic functional groups, while the lower C/H ratio of the three Australian isolates suggests they are more

aliphatic in character. Leenheer (Leenheer 1994) found Suwannee River NOM was characterised by a high aromatic carbon content from (allochthonous) terrestrially-derived lignin organic matter, while McKnight et al., (McKnight et al. 1994) found that (autochthonous) microbial-derived NOM had a higher content of aliphatic carbon and more organic nitrogen than terrestrially-derived NOM. The high C/N ratio of SR further reflects the greater allochthonous character of the SR, when compared to the Australian isolates. The more microbial-derived NOM character of the Australian isolates may be due to significant anthropogenic modification of all three Australian reservoir catchments leading to increased flows, erosion and delivery of both nutrients and sediments from the catchments to the waterways, facilitating microbial degradation (Abal et al. 2006, Burford et al. 2007).

The C/O ratio relates to oxygenation of NOM, that is, it indicates the content of oxygen-containing functional groups, such as carboxylic acid, carbonyl, hydroxyl, and methoxyl moieties, and degree of humification (Senesi et al. 2009, Tsutsuki and Kuwatsuka 1978). The lower C/O ratio of the three Australian isolates implies lower humification than SR. The C/H, C/N and C/O ratios decrease as the hydrophilic character of NOM increases (Beckett and Ranville 2006). Therefore, the SR isolate indicates significant hydrophobic character, while the Australian isolates exhibit more hydrophilic character. Similarly, Croue et al. (Croue et al. 2000) found SR NOM fractions were more hydrophobic than South Platte River fractions.

Although the three Australian isolates are similar to each other, there are notable differences in their composition and elemental ratio. BR had a notably lower C/N ratio than the other two Australian isolates, indicating a higher proportion of autochthonous derived carbon than both TR and AL. The increased proportion of microbial-derived NOM in BR may be due to the increased availability of light caused by depth differences between reservoirs (Cooke et al. 2005). BR reservoir is a shallow weir, while TR is a larger and deeper dam. The higher C/H, C/N and C/O ratios of TR isolate than BR isolate indicates a more hydrophobic character.

AL had the lowest C/O ratio of all samples, indicating this NOM source had a lower proportion of O-containing functional groups and was less humified than TR and BR. These results are also reflected in the EEM Pi_n data (Table SI 3). That is, TR had the highest proportion of humic substances and the lowest proportion of microbial-derived substances, while BR had the highest proportion of microbial-derived substances and the lowest proportion of humic substances and AL humic and microbial-derived substances proportions were intermediate.

3.3 DOC and bromide removal

Regardless of NOM source, EC combined with any secondary treatment was more effective at removing DOC than EC alone, with EC averaging 83% (SD 1, CV 0.01) DOC removal (Table 3, Figure 1a). EC has been previously reported to preferentially remove the higher molecular weight NOM compounds (Stanley 2000). DOC removal was similar whether by EC/GAC or EC/SIAC in all cases (91.3%, SD 6.9, CV 0.08), however, DOC removal by EC/GAC and EC/SIAC was greatest for the three Australian isolates (94.7%, SD 0.5, CV 0.01). In all cases DOC removals were higher for EC/GAC and EC/SIAC than for other treatment methods. The mechanism used by both GAC and SIAC to remove DOC has been previously shown to be by adsorption onto surface functional groups of the activated carbon by hydrogen bonding and van der Waals forces (Loganathan et al. 2013). EC/MIEX and EC/PAC also behaved in a similar manner to each other, with an average DOC removal of 82% (SD 7.5, CV 0.09).

DOC removal behaviour was clearly different between samples of different origins, with treatment methods generally trending from highest to lowest DOC removal efficiency in the order; TR>BR>AL>SR. The exception to this was EC/GAC and EC/SIAC treatments, which remained similar in DOC removal efficiency for the three Australian isolates; TR~BR~AL

before trending down to 81.1% (SD 2.1, CV 0.03) for SR-NOM isolate samples. Although SR had lower percent DOC removal for all treatments compared to the other isolates, the lower removal efficiencies were due to the low DOC removal by EC, rather than secondary treatment removal efficiency. Similarly, Dubrawski *et al.* (Dubrawski *et al.* 2013) observed higher DOC removal after electrocoagulation in a natural drinking water source than in a reconstituted Suwannee river NOM synthetic water. The differences in DOC removal between these NOM sources were attributed to the greater proportion of high molecular weight NOM present in the natural water (Dubrawski *et al.* 2013).

The additional DOC removal attained after EC by MIEX® secondary treatment averaged 7% (SD 3, CV 0.43) (Table 3). AL had the highest additional DOC removal attained by MIEX® of all isolates, at 11% (SD 2, CV 0.18). MIEX® treatment increased removal of BR isolate DOC by an additional 7% (SD 5, CV 0.71) beyond what was achieved with EC alone. TR and SR additional DOC removals by MIEX® were similar and averaged 5% (SD 1.5, CV 0.3). Drikas *et al.*'s (Drikas 2003) previous study combining EC with MIEX® secondary treatment in two natural waters found that DOC removal was approximately double for combined EC/MIEX® treatment than for EC alone. This large disparity in NOM removal capacity of the combined treatment is likely due to differences in experimental conditions explored (such as MIEX® dose), NOM character and competing ion concentrations (Boyer and Singer 2006, Hsu and Singer 2010).

The additional DOC removal attained after EC by PAC secondary treatment was modest and similar between sources, averaging 6% (SD 0.4, CV 0.07) removal. The lower molecular weight NOM remaining after EC treatment appeared to be similarly susceptible to PAC treatment, regardless of source. Previous studies on EC/PAC treatment have documented large variations in additional DOC removal capacity of PAC between studies (7 – 31% DOC removal) (Alvarez-Uriarte *et al.* , Carrière *et al.* 2009, Kristiana *et al.* 2011, Uyak *et al.* 2007).

Kristiana *et al.* [53] found the use of PAC after EC treatment did not result in preferential removal of a specific molecular weight fraction of NOM, rather, all NOM fractions were similarly treatable.

Finally, the additional DOC removals attained after EC by GAC and SIAC secondary treatments were very similar, with low variance between sources, averaging 16.01% (SD 4.9, CV 0.31). TR had the lowest DOC removals attained by GAC and SIAC, with only 11% (SD 2, CV 0.18) and 11% (SD 1, CV 0.09) greater removal than what was achieved with EC, respectively. AL had the highest percent DOC removals attained by GAC and SIAC, with 22% (SD 1, CV 0.05) and 23% (SD 1, CV 0.04) greater removal than from EC alone, respectively. DOC removals from BR and SR waters after EC by GAC and SIAC were intermediate (BR: 16% (SD 2, CV 0.13) and 15% (SD 2, CV 0.13) and SR: 13% (SD 2, CV 0.15) and 17% (SD 2, CV 0.12) respectively).

Bromide concentration strongly influences DBP speciation during disinfection (Richardson *et al.* 2007). Bromide concentrations were decreased considerably by EC/SIAC, by an average of 99% (SD 1, CV 0.01) irrespective of NOM isolate source (Figure 1b, Table 4). It should be noted that the SIAC studied was a fresh, unused product, so the silver binding-sites on the activated carbon were unsaturated. All isolates from Australian sources treated by EC/MIEX® had similar bromide reductions (45%, SD 7, CV 0.16). Notably, EC/MIEX® treatment only reduced bromide concentration in the SR sample by 35%, (SD 3, CV 0.09). The large difference between SR and other isolates is likely due to the lower NOM removals by EC in the SR isolate and consequential competition between bromide and NOM for exchange sites during MIEX® treatment (Hsu and Singer 2010). Conversely, the lower DOC concentrations in TR, BR and AL samples after EC allowed both DOC and bromide to be removed effectively during the MIEX® step.

Figure 1: (a) Percentage DOC removal for each NOM source and treatment method combination, and (b) Percentage bromide removal for each NOM source and treatment method combination.

EC/GAC showed some variation in bromide removal capacity depending on NOM isolate source, although all samples derived from Australian isolates had substantially greater bromide treatability than SR NOM isolate samples. Again, the lower bromide adsorption capacity of GAC for SR samples was likely to be due to the presence of a higher concentration of competing NOM after EC compared to the other samples. EC and EC/PAC did not decrease bromide concentration in any case, and this is consistent with previous reports (Kristiana et al. 2011). The aluminium coagulation of bromide is inhibited by the presence of organic matter and anions in treated waters (Watson et al. 2012), and it has been suggested that the kinetics of bromide adsorption onto PAC may be inhibited by the PAC batch mode of application, as compared to a column mode (Gary L. Amy 1999). The adsorption of bromide by the various treatments did not appear to be dependent on the origin of the NOM component of the samples. Rather, higher concentrations of competing NOM appeared to have the greatest effect on the bromide adsorption capacity of EC/MIEX®, and EC/GAC treatment. EC/SIAC remained highly efficient for bromide adsorption regardless of NOM source or concentration. A recent study of bromide adsorption onto silver-impregnated PAC found that bromide removal efficiency was affected by water composition (NOM and chloride concentration) as well as silver content and surface area of the SIAC (Chen et al. 2017).

3.4 DBP concentration and speciation after treatment

DBP formation potential tests were undertaken using untreated synthetic water samples for all NOM isolates, and results were compared to DBP formation potential tests conducted

after EC, and after EC combined with a secondary treatment (Figures 2-5, Table SI 5). DBP formation potential tests were also performed on blank synthetic water samples made without NOM and bromide addition, that were subjected to all treatment protocols (including no treatment). No DBP formation was observed in these blank samples, ruling out the possibility of contribution to DBP formation from the treatment itself by leaching of DBP precursors. While the DOC and bromide concentrations of synthetic water samples before treatment were similar, the DBP concentrations formed by chlorination of untreated samples varied widely between sources. EC combined with a secondary treatment was more effective at reducing overall DBP formation than EC alone, and this was directly correlated to the percentage of DOC removed and corresponding reduction in chlorine demand, as expected (Figure SI 3).

The speciation of DBPs varied greatly across treatments due to the DOC and bromide removal capacity of treatments and subsequent changes to the Br:DOC ratio favouring the formation of brominated over chlorinated DBPs when bromide removal either 1) did not occur, or 2) was insufficient compared to the NOM removal of the treatment to prevent an unfavourable Br:DOC ratio from occurring (Figure SI 4). Bromine substitution factor (BSF) quantifies the degree of bromine incorporation into individual classes of DBPs. The relationship between Br:DOC ratio and BSF is shown, as it changes across the various NOM isolate/treatment combinations studied here (Figures SI 5). EC and all secondary treatments except SIAC caused an increase in the concentrations of TBM and DBAN due to the increased Br:DOC ratio created by these treatments, although chlorinated DBPs were well controlled in all cases (Figures 2-5, Table SI 5).

EC/SIAC was the only treatment of those studied in which all brominated and chlorinated DBPs decreased in concentration, and this was the most effective DBP controlling treatment of those studied. That is, tTHMs were decreased by 99.6% (SD 0.6, CV 0.01), DHANs were decreased by 90.9% (SD 20, CV .22), CH was decreased by 99.9% (SD 0.1, CV 0.001), CPs

were decreased by 95.5% (SD 7, CV 0.07). This is attributed to the efficient simultaneous NOM and bromide adsorption of the SIAC. Decreases in brominated THMs concentration after SIAC treatment has been observed elsewhere (Chen et al. 2017). EC/PAC, which did not remove bromide at all, was the least effective of the combined treatments for controlling brominated DBP formation, causing large increases in concentrations of the most highly brominated DBPs (Figures 2 and 3, Table SI 5). EC/MIEX® resin and EC/GAC treatments were able to adsorb bromide to some extent (Table 4), as well as NOM (Table 3), however this was not sufficient to prevent an increase in the Br:DOC ratio and subsequent increase in the formation of some highly brominated DBPs upon chlorination (Figures 2 and 3, Table SI 5). DBCM was also increased by EC across all four NOM isolates, while EC/MIEX® treatment led to DBCM increases in SR-NOM derived samples, and EC/PAC treatment led to DBCM increases in AL and SR-NOM derived samples. EC/GAC and EC/SIAC were able to lower the formation of this DBP in all cases examined.

Total trihalomethanes (THMs), defined as the sum concentration of TCM, BDCM, DBCM and TBM, in $\mu\text{g/L}$, and total dihaloacetonitriles (DHANs), defined as the sum concentration of DCAN, DBAN and BCAN, in $\mu\text{g/L}$, show an overall decrease in concentration after EC, and a further decrease with secondary treatment in all cases except total DHAN for AL isolate-derived samples after EC treatment (Figures 2 and 3). The increase in total DHAN for the AL isolate was due to large increases in BCAN and DBAN after EC treatment, resulting from the increased Br:DOC ratio relative to untreated samples.

Figure 2: THMs concentrations ($\mu\text{g/L}$) derived from DBP formation potential test of a synthetic water matrix utilising each NOM isolate, (a) before and after EC treatment, (b) after each secondary treatment.

Figure 3: DHANs concentration ($\mu\text{g/L}$) derived from DBP formation potential test of samples made with each NOM isolate, **(a)** before and after EC treatment, **(b)** after each secondary treatment.

Figure 4: CH concentration ($\mu\text{g/L}$) derived from DBP formation potential test of samples made with each NOM isolate, **(a)** before and after EC treatment, **(b)** after each secondary treatment. *Singlicate DBP concentrations are reported.

Figure 5: Chloropropanone (CP) concentrations ($\mu\text{g/L}$) derived from DBP formation potential test of synthetic water samples made with each NOM isolate, **(a)** before and after EC treatment, **(b)** after each secondary treatment. *DBP concentrations are reported in singlicate.

3.5 Specific chlorine demand (SCD_{72}) and specific DBP formation potential

Specific chlorine demand (SCD_{72}) and specific DBP formation potentials (specific total THM, total DHAN, CH, CP, Cl-DBPs and Br-DBPs) measurements are useful in comparing the effectiveness of different treatments in removing fractions of NOM that cause chlorine decay and DBP formation, when DOC concentrations significantly differ. SCD_{72} was defined as the ratio of 72 h chlorine demand (mg/L) to the initial DOC concentration (mg/L) and the specific DBP formation potentials were defined as the ratio of DBP formation potential to the initial DOC concentration. Also, Br-DBP is defined here as the sum concentration of BDCM, DBCM, TBM, BCAN and DBAN, in μM , and Cl-DBP is defined as the sum concentration of TCM, DCAN, CH, 1,1-DCP and 1,1,1-TCP, in μM . Comparisons of SCD_{72} and specific DBP formation potentials showing which treatments were more able to remove the compounds that were responsible for chlorine reactivity and DBP formation, for each isolate, are shown (Figure 6). Despite having similar initial DOC concentrations across all synthetic water samples, the reactivity of carbon from each source with chlorine to form DBPs was different.

Chlorine demand was significantly reduced after EC treatment (Figure SI 3a), however, SCD_{72} increased after EC for all isolate sources, which indicates that coagulation did not preferentially remove the chlorine reactive components of NOM (Figure 6a). Furthermore, SCD_{72} of EC samples showed that the Australian isolates had a greater proportion of chlorine reactive compounds recalcitrant to EC than SR. EC combined with secondary treatment for SR isolate samples showed a reduction in SCD_{72} after all treatments, indicating that a greater proportion of the chlorine reactive compounds were removed by EC combined with secondary treatments than by coagulation alone.

For AL isolate-containing samples, only EC/PAC treatment showed a reduction in SCD_{72} . All other Australian isolates showed an increase in SCD_{72} after all treatments, indicating that chlorine reactive components of the samples were recalcitrant to removal by EC and EC combined with secondary treatments. In contrast, a previous study comparing the character of NOM in selected Australian and Norwegian drinking waters after DWTP treatments reported increases in SCD_{72} for the two Norwegian water sources, while all Australian sources showed decreases (Fabris et al. 2008). This indicates the variability in reactivity between different NOM sources, even after similar treatments.

SCD_{72} of the Australian isolates were higher in EC/GAC and EC/SIAC than EC, EC/MIEX® and EC/PAC treated samples, showing that the EC/GAC and EC/SIAC processes were not as capable of removing NOM with a high reactivity with chlorine as EC, EC/MIEX® or EC/PAC.

Sohn's (Sohn and Han 2007) study showed that changes in both specific THM and specific haloacetic acids formation potential varied depending on the treatment processes; coagulation and GAC treatment increased specific DBP formation potential, while ozonation decreased specific DBP formation potential.

The order of chlorine reactivity between isolates varied between treatments, indicating the physicochemical characteristics of each isolate led to varying treatment effectiveness, chlorine reactivity and DBP formation after disinfection (Table SI 6). Specific Cl-DBPs formation potentials were reduced in all waters after all treatments, however, specific Br-DBPs formation potentials generally increased for all NOM isolates after each treatment, except for EC/SIAC (Figures 6b and 6c). This is expected to occur as a consequence of the increased Br:DOC ratio created by the treatments, however, in addition to this, a recent study investigating the effect of molecular weight distribution on the reactivity of NOM in surface waters found that chlorine was preferentially incorporated into higher molecular weight fractions of NOM, while bromine and iodine were preferentially incorporated into the lower molecular weight fractions of NOM, some of which may be expected to remain after secondary treatments (Kristiana et al. 2014). Lower molecular weight NOM has been shown to be more reactive than higher molecular weight NOM in forming some DBPs, e.g. THMs and haloacetonitriles (HANs) (Owen et al. 1993). Specific Br-DBPs formation potentials were greater than specific Cl-DBPs formation potentials after all treatments apart from EC/SIAC, reflecting the increased bromine substitution into the low concentrations of reactive NOM remaining after treatments, changing the speciation of THMs and DHANs.

EC/GAC treatment reduced specific Cl-DBPs formation potential to below the method reporting limit for all isolates. Regardless of source, EC combined with secondary treatments were more effective at reducing specific Cl-DBPs formation potential than EC alone. The specific Cl-DBPs formation potential was reduced with NOM removal, while specific Br-DBPs formation potential reduction was dependent on both bromide and NOM removal (Farré et al. 2011).

Figure 6: Effect of each treatment on (a) specific chlorine demand ($\text{mg Cl}_2/\text{mg C}$), (b) specific Cl-DBP formation potential ($\mu\text{M Cl-DBP}/\text{mg C}$) and (c) specific Br-DBP formation

potential ($\mu\text{M Br-DBP/mg C}$) for waters containing TR, BR, AL and SR isolates. Points above the straight line indicate an increase relative to NT samples, and points below the straight line indicate a decrease relative to NT samples.

The specific formation potential of each individual DBP and total class of DBP was also examined (Figure SI 6a-m). For untreated (NT) samples, the three Australian NOM isolates had higher specific total THM formation potential than the Suwannee River NOM standard (Figure SI 6a). All treatment/NOM isolate combinations led to a decrease in specific tTHM formation potential compared to NT samples, apart from EC treatment of BR-containing isolate samples, which experienced a modest increase in specific tTHMs formation potential.

EC/SIAC was the only treatment able to consistently lead to a decrease in specific total DHANs formation potential across the four NOM sources studied. All other treatments led to increased specific total DHANs formation potential for the AL and BR NOM sources, however, SR and TR saw a decrease in specific DHANs formation potential with EC/MIEX® and EC/GAC treatments, respectively. SR-NOM clearly had a lower specific DCAN formation potential after each treatment than the three Australian NOM isolates. Substantial and consistent decreases in specific CH formation potential were observed with EC and all combined treatments. Specific 1,1-DCP formation potential increased in EC/SIAC treated TR and AL-containing samples, as well as in EC/PAC treated SR and BR-containing waters. Specific 1,1,1-TCP formation potential was in general well-mitigated by all treatments across all NOM sources.

The increase in specific DBP formation potential observed after some treatment/NOM source combinations indicates that there are source-specific reactive NOM components that act as DBP precursors and that are not amenable to those treatments. This highlights that even after treatment there can be large variability in physicochemical characteristics between NOM

sources leading to variable reactivity and DBP formation after disinfection. Generally, the specific DBP formation potential for chlorinated DBPs was substantially decreased with treatment of the four NOM isolates, although there were exceptions to this. The brominated DBPs saw frequent increases in specific DBP formation potential across all NOM isolates and after all treatments except combined EC/SIAC, due to the increase in Br:DOC ratio created by many of the other treatments leading to greater bromide incorporation into the organic material remaining (Kulkarni and Chellam 2010, Watson et al. 2014). Increased bromide incorporation into low molecular weight NOM recalcitrant to treatment may also contribute to the observed increase in specific DBP formation for some Br-DBPs (Kristiana et al. 2014, Owen et al. 1993).

4. Conclusions

Bromide concentrations were best mitigated by EC/SIAC treatment (99%, SD ± 1 , CV 0.01, removal) irrespective of NOM isolate source. EC/MIEX® and EC/GAC treatment also provided some bromide removal from samples containing the three Australian NOM isolates, although they were less efficient for samples derived from the Suwannee River NOM isolate, due to higher concentrations of competing NOM in Suwannee River NOM samples at the point of secondary treatment. Importantly, adsorption of bromide did not appear to be dependent on the origin of the NOM component of the samples.

EC/SIAC treatment generally led to decreases in concentration of >92% for brominated and chlorinated DBPs, regardless of NOM source, and this was the most effective method of DBP control studied, due to the efficient simultaneous NOM and bromide adsorption of the SIAC. EC and all secondary treatments other than SIAC caused an increase in the concentrations of TBM and DBAN for all isolates due to the increased Br:DOC ratio created by these treatments, although chlorinated DBPs were well controlled. DBCM was also increased by some isolate/treatment combinations, albeit well-mitigated by others. The applicability of

SIAC technology to large-scale water treatment systems has not been investigated, to the extent of the authors' knowledge, and is an area for future research (Watson et al. 2012).

Regardless of NOM source, combined treatments were more effective at removing DOC than EC alone, and DOC removals were higher for EC/GAC and EC/SIAC than EC/MIEX® and EC/PAC treated samples. Percentage DOC removal for each treatment was dependent on NOM source, and generally decreased in the order TR>BR>AL>SR. DOC removal for Suwannee River NOM isolate-containing samples was substantially lower than for the three Australian isolates due to the poor DOC removal efficiency by EC for samples containing this isolate.

Treatment method was more important than NOM source in determining Br-DBP formation, which was largely correlated to bromide removal capacity of the treatments. Cl-DBPs were well-mitigated by all treatment methods for all NOM sources. So, DOC and bromide removal capacity of each treatment had a greater effect on DBP formation than NOM source.

In general, EC and EC/GAC were not as effective as EC/MIEX®, EC/PAC and EC/SIAC in removing NOM relevant to formation of the targeted DBPs, and EC/SIAC treatment led to the lowest specific DBP formation potential of all treatments. Specific Cl-DBPs formation potentials were reduced in all waters after all treatments, however, specific Br-DBPs formation potentials generally increased for all NOM isolates after each treatment, except for EC/SIAC. The specific Cl-DBPs formation potential was reduced with NOM removal, while specific Br-DBPs formation potential reduction was dependent on both bromide and NOM removal.

SCD₇₂ increased after EC for all isolate sources, indicating some chlorine reactive components of NOM were recalcitrant to removal by EC. This was most pronounced in the

Australian NOM isolates, which frequently also showed an increase in SCD₇₂ after secondary treatments.

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Sample	DOC (mg/L)	Br ⁻ (µg/L)	Alkalinity (mg/L CaCO ₃)	pH	UV ₂₅₄	SUVA ₂₅₄ (L mg ⁻¹ m ⁻¹)	TCM (µg/L)	BDCM (µg/L)	DBCM (µg/L)	TBM (µg/L)	DCAN (µg/L)	BCAN (µg/L)	DBAN (µg/L)	CH (µg/L)	1,1-DCP (µg/L)	1,1,1-TCP (µg/L)
TR	13.7	85.5	25.8	6.72	0.4	3.2	850.9	57.6	2.3	<0.1	20.6	1.6	<0.1	73.9	1.4	10.5
BR	2.4	313.0	198.4	7.23	0.1	4.5	114.0	95.7	49.6	4.9	7.6	6.7	3.7	21.9	0.5	3.4
AL	4.0	38.0	35.1	7.11	0.1	3.5	225.2	22.9	1.3	<0.1	8.0	0.7	<0.1	21.5	0.7	7.9

Table 1. Raw water characteristics for SEQ source waters studied. DBP concentrations shown were determined by DBP formation potential test.

Table 2. Elemental composition and atomic ratios for isolated NOM samples.

Sample	Elemental composition (%)						Atomic ratio		
	C	H	N	O	S	Ash	C/H	C/N	C/O
TR	34.53	4.14	1.16	41.21	0.96	18.00	0.70	34.73	1.12
BR	30.27	3.92	1.33	37.86	1.96	24.66	0.64	26.55	1.07
AL	31.18	3.67	1.10	41.97	3.78	18.30	0.71	33.07	0.99
SR	52.47*	4.19*	1.10*	42.69*	0.65*	0.98	1.04	55.65	1.64

* Elemental analysis obtained from IHSS- sample 1R101N.

Table 3. DOC concentrations and percent removals from synthetic water samples made from all NOM isolates and subjected to all water treatments.

Sample	TR		BR		AL		SR	
	DOC (mg/L)	Percent removal (%)	DOC (mg/L)	Percent removal (%)	DOC (mg/L)	Percent removal (%)	DOC (mg/L)	Percent removal (%)
NT	10.9±0.4	n.a.	9.5±0.3	n.a.	12.3±1.0	n.a.	10.7±0.2	n.a.
EC	1.8±0.1	83.4±1	2.0±0.2	79.0±2.8	3.4±0.3	72.6±0.1	3.6±0.5	66.1±0.5
EC/MIEX [®]	1.2±0.0	88.7±0.2	1.3±0.2	86.0±2.0	2.0±0.4	84.0±2.3	3.1±0.4	71.1±1.0
EC/PAC	1.2±0.2	89.3±3	1.4±0.2	84.9±1.3	2.6±0.4	79.3±1.6	3.0±0.1	72.5±0.2
EC/GAC	0.7±0.1	94.1±0.9	0.5±0.0	95.1±0.4	0.6±0.1	94.9±0.6	2.3±0.1	79.00±2.8
EC/SIAC	0.6±0.0	94.5±0.2	0.6±0.1	94.2±1.3	0.6±0.1	95.2±0.4	1.8±0.5	83.2±1.3

Table 4. Bromide concentrations and percent removals from synthetic water samples made from all NOM isolates and subjected to all water treatments.

Sample	TR		BR		AL		SR	
	Br ⁻ (μM)	Percent removal (%)	Br ⁻ (μM)	Percent removal (%)	Br ⁻ (μM)	Percent removal (%)	Br ⁻ (μM)	Percent removal (%)
NT	5.5±0.1	n.a.	5.3±0.2	n.a.	5.5±0.0	n.a.	5.6±0.1	n.a.
EC	5.4±0.1	0	5.2±0.1	0	5.5±0.1	0	5.6±0.2	0
EC/MIEX®	2.7±0.1	49.8±1.3	2.7±0.2	48.9±1.9	2.9±0.1	47.0±1.3	3.6±0.2	35.5±3.1
EC/PAC	5.4±0.2	0	5.4±0.2	0	5.4±0.1	0	5.6±0.1	0
EC/GAC	4.3±0.4	21.1±5.9	4.4±0.2	16.5±1.2	4.4±0.1	19.7±1.6	5.2±0.1	8.4±1.9
EC/SIAC	<0.13*	99.6±0.1	<0.13*	99.6±0.1	<0.13*	99.3±0.5	<0.13*	100±0.0

*Method reporting limit (0.13 μM).

ACCEPTED MANUSCRIPT

Graphical abstract

Highlights

- Bromide removal capacity was independent of natural organic matter (NOM) source.
- Enhanced coagulation with silver-impregnated activated carbon minimised all DBPs.
- All other treatments caused concentration increases for the most highly brominated DBPs.
- NOM removal capacity was dependent on NOM source and treatment.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Accepted Manuscript

Comparing three Australian natural organic matter isolates to the Suwannee river standard: Reactivity, disinfection by-product yield, and removal by drinking water treatments

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