

Application of a fractionation technique for better understanding of the removal of natural organic matter by alum coagulation

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Abstract To gain an improved understanding of the types of organic compounds that are recalcitrant to water treatment, natural organic matter (NOM) isolates from two drinking water sources (Mt. Zero and Moorabool reservoirs, Victoria, Australia) were separated into fractions of distinct chemical behaviour using resins. Four fractions were obtained from each water source and were organics absorbed to: (1) XAD-8 (very hydrophobic acids, VHA); (2) DAX-4 (slightly hydrophobic acids, SHA); (3) bound to an anion exchange resin (charged organics, CHAR); and (4) not absorbed or bound to resins (neutrals, NEUT). These fractions were then tested to determine the capacity of alum to remove them from water and to correlate this with the character of each isolate. The fractions were characterised by the application of high performance size exclusion chromatography (HPSEC), bacterial regrowth potential (BRP), trihalomethane formation potential (THMFP), pyrolysis gas-chromatography mass spectrometry (Py-GC-MS) and thermochemolysis. The highest removals of dissolved organic carbon (DOC) by alum treatment were in waters spiked with the CHAR fractions while the NEUT fractions were the most recalcitrant. The number average molecular weights (M_n) of DOC of the CHAR fractions before treatment were the highest, whilst those of the NEUT fractions were the lowest. After alum treatment, the M_n of the NEUT fractions were only slightly reduced. Results from Py-GC-MS and thermochemolysis indicate that the NEUT fractions had the highest relative proportion of saccharide derived organic material. Nonetheless, the BRP of waters spiked with the NEUT fractions differed markedly, indicating that organics recalcitrant to alum treatment can vary substantially in their chemical composition and capacity to support microbial growth.

Keywords BRP; coagulation; HPSEC; NOM fractions; Py-GC-MS; thermochemolysis; THMFP

Introduction

The conventional treatment of raw surface waters for drinking purposes involves removal of turbidity and colour to levels that make the water aesthetically acceptable to consumers. However, the issue of water quality goes beyond the physical appearance of water and community expectations include that water for drinking purposes is both chemically and microbiologically safe. The presence of natural organic matter (NOM) in raw and treated drinking waters is of concern to the drinking water industry as it can cause water to be brown-coloured, it may include compounds that cause taste and odours and is a substrate for microbial growth. NOM that is not removed by the treatment process can react with disinfectants such as chlorine, reducing the concentration of the disinfectant and can be a precursor in the formation of disinfection by-products (Simpson and Hayes, 1996; Arora *et al.*, 1997; Chen and Weisel, 1998).

With the growing awareness of the impacts of NOM on water quality, there has been a general trend by water treatment operators towards treatment processes that maximise the removal of NOM from drinking waters. One such treatment, enhanced coagulation, involves using higher coagulant doses for this purpose.

NOM in raw drinking waters can comprise a range of compounds that may or may not be removed by application of inorganic coagulants such as aluminium and iron-based compounds. Generally, large molecular weight hydrophobic compounds are more easily removed than smaller molecular weight hydrophilic compounds (Krasner and Amy, 1995;

Owen *et al.*, 1995). Studies have been conducted to characterise components of NOM that can be removed or are recalcitrant to treatment with inorganic coagulants (Bolto *et al.*, 1999; Chow *et al.*, 2000). The efficiency of a coagulant in removing NOM is also dependent on the optimum pH for that particular coagulant. Therefore, the buffering capacity or alkalinity of raw water can impact on the removal of NOM when using inorganic coagulants. These factors have been incorporated into models for prediction of treatment conditions that enable enhanced coagulation to be achieved (Stanley *et al.*, 2000; van Leeuwen *et al.*, 2001). Although there is generally a good understanding of the impact of the nature of organic compounds (hydrophobic or hydrophilic and molecular size) on their removal through coagulation, the information available on the types and structures of organic compounds that comprise NOM is limited.

In this study, NOM from two drinking water sources in Victoria, Australia, were fractionated using resins to obtain components of distinct chemical behaviour. These fractions were then tested under laboratory conditions to assess the capacity of alum to remove them from the source water. Characterisation of the fractions was conducted using techniques such as high performance size exclusion chromatography (HPSEC), pyrolysis gas-chromatography mass spectrometry (Py-GC-MS) and bacterial regrowth potential (BRP) in order to compare the different and same type of fractions from the two water sources.

Materials and methods

Waters. Samples were taken to the laboratory as collected from Mt. Zero and Moorabool reservoirs and also after concentration of the organic material using reverse osmosis. The raw waters were treated with alum at 80 and 100 mg/L, respectively. After removal of the flocculated material, the treated waters were used as diluents for NOM fractions. NOM fractions were prepared from the concentrated NOM samples.

Chemicals. Aluminium sulphate stock solution (20,000 mg/L) was prepared in Milli-Q® (Millipore Corporation, USA) water from liquid aluminium sulphate (approximately 7.5% Al₂O₃) used for commercial water treatment. Sodium hydroxide and hydrochloric acid were analytical grade chemicals.

Analytical techniques. Dissolved organic carbon (DOC), colour, turbidity, alkalinity, number average molecular weights (*M_n*), and BRP were determined as previously detailed (Withers *et al.*, 1998; Chow *et al.*, 2000). BRP is expressed as acetate carbon equivalents/mg DOC. Trihalomethane formation potential (THMFP) was determined by measuring trihalomethanes formed after dosing samples with chlorine (~20 mg/L) and after a reaction time of 4 hours, at 35°C.

Pyrolysis gas-chromatography mass spectrometry (Py-GC-MS). This was performed as previously described (van Leeuwen *et al.*, 1999) with the pyrolysis temperature targeted at 650°C.

Thermochemistry. This was performed on-line using a CDS flash pyrolysis unit. Briefly, tetramethylammonium hydroxide (TMAH) was added to freeze-dried material (about 5–15 mg) in a 2 mm diameter quartz tube, plugged at both ends with quartz wool. This was dried at 50°C for 3–4 hours and then analysed in the same manner as by Py-GC-MS.

NOM fractions. The fractionation procedure used has been previously detailed by Chow *et al.*, 2000). This procedure resulted in four fractions, with the organic contents assigned as follows: (1) very hydrophobic acids (VHA, adsorbed by DAX-8); (2) slightly hydrophobic

acids (SHA, adsorbed by XAD-4); (3) charged (CHAR, bound to the anion exchange resin Amberlite IRA-958), ascribed to proteins, amino acids and anionic polysaccharides; and (4) neutral (NEUT, the fraction that passed through all columns, ascribed to carbohydrates, aldehydes, ketones and alcohols).

Jar tests. The DOC concentration of each fraction was determined and the amount equivalent to about 3.5 mg/L DOC was added back to the respective diluent water. The resultant waters were then tested using a jar test procedure as previously described (Chow *et al.*, 2000).

Results and discussion

Water quality data of the two raw waters and following alum treatment are shown in Table 1. The relative abundances of each NOM fraction in raw water and their characterisation are given in Table 2. Organic compounds that comprised the neutral fractions had the lowest SUVA values and of the UV absorbing compounds, the lowest molecular weights (AMW). The bacterial regrowth potential, expressed as ACE/DOC (mg/mg) differed markedly between the two neutral fractions with the Mt. Zero fraction being much higher than the other three fractions from the same water source and the fractions from Moorabool. The BRP of the Moorabool neutral fraction was the lowest or equivalent to the other three fractions from the same water source.

The THMFP/DOC differed between the four fractions of each water and between the same fractions of the two waters. No trend was evident and it appears that the THMFP/DOC varied on the basis of the different chemical compositions of these fractions.

The effects of aluminium hydroxo complexes in removing organics that comprise the various fractions are shown in Figure 1. Trends in DOC removals with alum treatment were similar between the two water sources, with the greatest removals occurring from the waters spiked with the CHAR fractions and the least, spiked with the NEUT fractions. The

Table 1 Summary of the raw and treated water quality parameters of the two waters used in fractionation experiments

Parameter	Mt. Zero (raw)	Mt. Zero (treated ^a)	Moorabool (raw)	Moorabool (treated ^b)
DOC (mg/L)	9.0	4.1	6.9	3.4
UV at 254 nm (cm ⁻¹)	0.265	0.060	0.178	0.052
SUVA (m ⁻¹ mg ⁻¹ L)	2.9	1.5	2.7	1.5
Colour (HU)	54	1	17	1
Average molecular weight (<i>Mn</i>)	1,000	640	1,000	570
Turbidity (NTU)	7.3	0.1	1.70	0.05
Alkalinity (mg/L as CaCO ₃)	7	2	100	32
pH	6.4	5.9	7.6	6.0

^a alum at 80 mg/L ^b alum at 100 mg/L at pH 6

Table 2 Descriptions of NOM fractions isolated from Mt. Zero and Moorabool reservoirs

Water source Parameter	Mt. Zero				Moorabool			
	VHA	SHA	CHAR	NEUT	VHA	SHA	CHAR	NEUT
Organic carbon mass balance (%)	58	14	11	17	34	18	33	15
SUVA (m ⁻¹ mg ⁻¹ L)	2.5	2.1	2.8	0.3	2.4	1.8	2.1	1.0
Average molecular weight (<i>Mn</i>).	1,100	1,200	1,200	580	1,200	1,100	1,200	630
BRP as ACE/DOC (µg/mg)	75	61	106	583	26	22	149	22
THMFP/DOC (µg/mg)	27	28	54	10	13	11	21	21

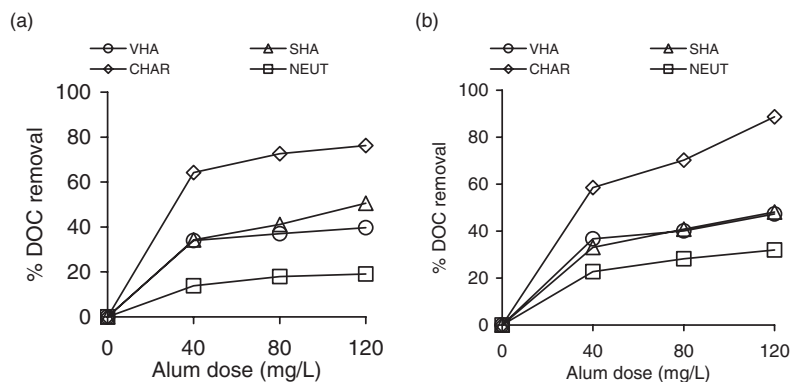


Figure 1 Percentage removals of DOC attributed to the fractions from: (a) Mt. Zero, and (b) Moorabool waters following alum treatment at pH 6

percentage removals of DOC from the four fractions were similar between the two water sources.

Molecular weight (M_n) changes of UV absorbing organic compounds from the four fractions spiked into waters and treated with alum are shown in Figure 2. The neutral fraction, being the most recalcitrant to removal, showed the least change in M_n with alum treatment. However, from this study no information was obtained in relation to changes in the molecular weights of organics that do not absorb UV light.

The BRP of waters spiked with the fractions and after alum treatment are shown in Figure 3. These values correlate with BRP of the fractions (Table 2) with the highest BRP (as ACE/DOC $\mu\text{g}/\text{mg}$) occurring in the NEUT fraction from Mt. Zero, followed by the CHAR fraction from Moorabool. Despite the similarity of the percentage removals of the NEUT fraction with alum treatment between the two water sources, the BRP results indicate markedly different assimilable organic carbon compositions in the two neutral fractions.

The lower BRP values of the VHA and SHA fractions from both waters is consistent with these fractions being of hydrophobic acids formed through humification processes and subsequently being more resistant to further microbial degradation. This resistance can be attributed to the size of the macromolecules, which limits diffusion through microbial cell walls, and the non-specific heterogeneity in chemical composition and structures. Nonetheless, readily assimilable organics may be enmeshed or bound to these macromolecules. With alum treatment there is a preferential removal of large molecular weight hydrophobic material, with smaller molecular weight compounds remaining in the

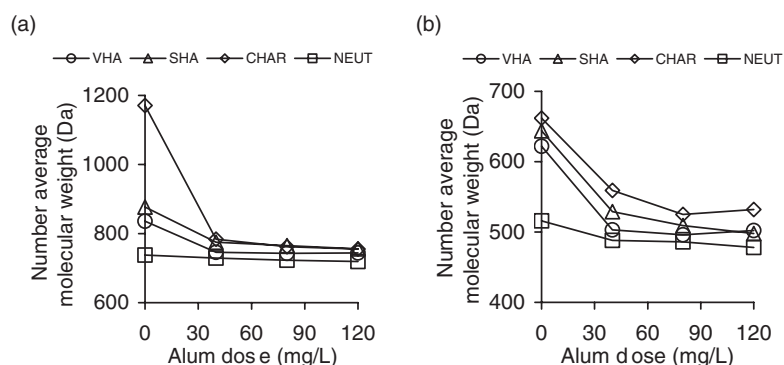


Figure 2 Molecular weights (M_n) of DOC in: (a) Mt. Zero, and (b) Moorabool reservoir waters spiked with NOM fractions and treated with alum at pH 6

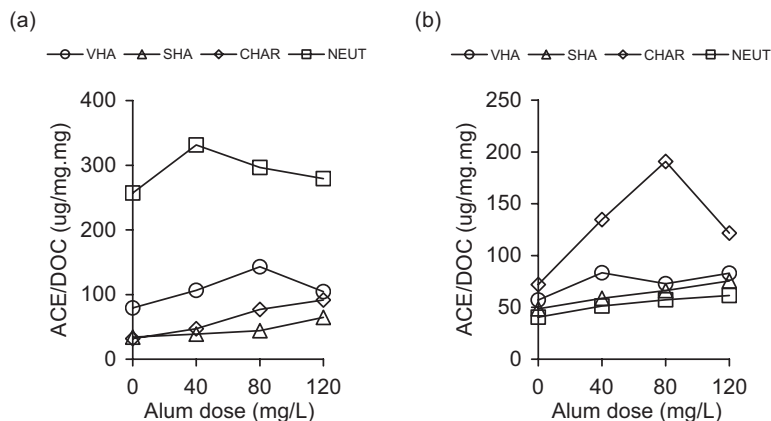


Figure 3 Bacterial regrowth potential of: (a) Mt. Zero, and (b) Moorabool reservoir waters spiked with NOM fractions and treated with alum at pH 6

water. Those organics remaining in the water may then be relatively more assimilable by microorganisms.

The results of pyrolysis gas-chromatography mass spectrometry performed on the various fractions from Mt. Zero and Moorabool are shown in Table 3. Large numbers of pyrolysis products were detected from each analysis and many were of little or no value in terms of indicators of potential macromolecular sources. The relative abundances based on total ion current of selected groups of compounds are given.

Distinctive features of the NEUT fractions when compared with the others, were the low relative abundances of phenolic compounds and high abundances of compounds indicative of saccharide sources. The NEUT fractions from Mt. Zero and Moorabool also differed with a higher relative abundance of saccharide-derived compounds in the Mt. Zero fraction.

The results of thermochemolysis performed on the four fractions from the two raw waters are shown in Table 4. The application of this technique results in the better preservation and detection of chemical functionality through the *in situ* derivatisation of hydroxyl and carboxyl groups than by flash pyrolysis. However, semi-quantification of thermochemolysis products was found to be less consistent than from pyrolysis. Consequently, only the relative frequencies of compounds, grouped according to structure or potential macromolecular source, is given. Using thermochemolysis, aliphatic and fatty acids were detected in most fraction types. The results of the application of this technique also indicate differences in the chemical compositions of the two neutral fractions, with a higher frequency of saccharide-derived products from Mt. Zero water.

Both Py-GC-MS and thermochemolysis indicate a higher relative abundance of saccharide-derived compounds in the neutral fraction from Mt. Zero than from Moorabool. This appears consistent with the BRP values of the two waters spiked with the neutral fractions,

Table 3 Relative percentage abundances (total ion current) of selected pyrolysis products from NOM fractions from Mt. Zero and Moorabool reservoir raw waters

Compounds	Mt. Zero				Moorabool			
	VHA	SHA	CHAR	NEUT	VHA	SHA	CHAR	NEUT
Phenolics	75.8	57.4	54.9	15.9	58.6	65.6	45.3	28.0
Saccharide deriv.	24.2	40.8	45.3	84.1	41.4	30.2	52.9	55.9
N-compounds	N.D.	1.8	1.2	N.D.	N.D.	4.2	1.8	16.1

N.D., not detected

Table 4 Relative frequencies (as percentages) of thermochemolysis products from fractions from Mt. Zero and Moorabool raw waters, grouped according to potential origin or chemical structure

Fractions	Mt. Zero					Moorabool				
	S	Arom	N-c	AHC	FA/AIA	S	Arom	N-c	AHC	FA/AIA
VHA	13.5	51	5.5	19	11	6	50	ND	19	25
SHA	10.5	58	ND	5	26.5	29	64	ND	7	ND
CHARG	11.5	50	6	20.5	12	11	50	5	29	5
NEUT	33	43	5	9.5	9.5	15	54	31	ND	ND

S, compounds derived from saccharides; Arom, aromatic; N-c, nitrogen containing compounds; AHC, aliphatic hydrocarbons; FA, fatty acids; AIA, aliphatic acids

i.e. the Mt. Zero water had the much higher ACE/DOC value. The low SUVA values of the NEUT fractions compared with the others (Table 2) and their differences is also consistent with them having higher saccharide contents and with Mt. Zero having the highest content.

These results are further supported by ^{13}C CPMAS NMR data (Wong *et al.*, in press). ^{13}C CPMAS NMR spectra of the two neutral fractions differed markedly with the Mt. Zero fraction having a well resolved band at 70 ppm, indicative of carbon functionality as ether and alcohol of carbohydrates with a small band at about 180 ppm indicative of carbonyl functionality of carboxyl groups. The NMR spectrum of the Mt. Zero neutral fraction indicated that this fraction had low aromaticity. In contrast to this, the neutral fraction from Moorabool had relatively strong aromatic signals at about 120–140 ppm and 155 ppm (phenols and aryl ethers) and at 160–175 ppm (amides and esters). This Moorabool fraction had a minor signal for carbohydrates compared to these other signals.

The neutral fractions of the two waters were the most recalcitrant to removal with alum treatment with similar levels of about 20–30% at the high alum dose of 120 mg/L.

However, the various techniques applied for chemical structural characterisation of the organics that comprise these fractions indicate that the Mt. Zero water had a higher relative abundance of carbohydrates. Carbohydrates are readily assimilable by microorganisms and hence their higher presence in the Mt. Zero water is the likely basis for the high BRP of its neutral fraction.

The compounds detected by Py-GC-MS and thermochemolysis and the ^{13}C NMR data demonstrate the variation in organic composition of each of four fractions and between the same type of fraction. Although these fractions had been isolated on the basis of obtaining different organics that comprise the raw water NOM, it is likely that there was no discrete separation of these fractions based on organic composition. Different types of organics may have been associated with each other through enmeshment in macromolecular structures and through various types of chemical bonds. Their separation and isolation was then more a function of their overall behaviour in relation to the resins used. Although the results indicate that the composition of organics from the same type of fractions were different, their removals with alum treatment were similar.

Conclusions

The results of this study indicate that organic components recalcitrant to alum treatment can vary in their chemical composition. Although these components behave similarly in relation to treatment with alum, the differences in chemical composition can lead to differences in them supporting microbial growth and in the formation of disinfection by-products. Hence, although enhanced coagulation should minimise problems such as bacterial regrowth in a distribution system and disinfection by-product formation, it appears that variation in chemical compositions of recalcitrant fractions could lead to variation in these potential problems.

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