

Simulation of NOM events in pilot plant evaluation of DAF/Ozone/BAC for drinking water treatment

Y. Yan, M. Carter and A. Mercer

ABSTRACT

Pilot plant testing is invaluable for ascertaining the robustness of water treatment processes against raw water quality events such as turbidity and colour spikes, whether it be for stress testing of an existing process or designing of a new process. Unfortunately, the natural occurrence of such events (particularly colour) can be difficult to predict and commercial humic materials generally fail to closely match the indigenous natural organic matter (NOM) present in the raw water. Therefore, it is highly desirable to be able to simulate NOM event conditions. This paper describes a simple brewing method that we developed and used in our recent pilot plant evaluation of a proposed DAF/Ozone/BAC process for drinking water treatment. Using this method we successfully prepared, by using fallen leaves etc. collected from the local catchment area, large quantities of a concentrated NOM stock solution with its specific ultraviolet absorbance (SUVA), when diluted, very close to the median SUVA of historical NOM events. The brewed solution showed broadly similar NOM characteristics to those of the raw water encountered during the pilot investigation period in terms of molecular weight distribution and fractionation. The coagulation behaviour was also examined for the spiked and non-spiked raw water.

Key words | humic substances, natural organic matter, NOM, pilot testing, SUVA, water treatment

Y. Yan (corresponding author)

M. Carter

Hunter H₂O Holdings Pty Limited,
P.O. Box 5007, HRMC, Mayfield West,
NSW 2310,
Australia
E-mail: yaode.yan@hunterh2o.com.au

A. Mercer

Watercare Services Limited,
Private Bag 92 521, Wellesley Street,
Auckland 1141,
New Zealand

INTRODUCTION

As part of the strategy to upgrade one of its drinking water treatment plants in the North Island of New Zealand, Watercare Services Ltd required that sufficient and reliable pilot plant data be collected so that the suitability of the proposed treatment process utilising dissolved air flotation (DAF) and ozone and biological activated carbon (Ozone/BAC) for the upgrade design could be confirmed, approved and released for design. A key pilot testing objective was to evaluate the performance of the entire pilot plant process comprising coagulation/flocculation, DAF, ozonation and biological filtration under both typical raw water quality conditions and poorest raw water quality conditions.

To enable assessment of the pilot plant process under the historically poorest conditions in terms of turbidity (~40 NTU) and dissolved organic carbon (~8 mg/L) in the source water, it was found that both turbidity and colour

spiking were required due to lack of natural occurrence of such events during the trial period.

It is widely recognised that use of suitable natural organic matter (NOM) for colour spiking is very important since each water source can be different in its organic characteristics which can significantly affect the NOM removal performance through the coagulation and flocculation process (Sharp *et al.* 2006; Matilainen *et al.* 2010; Wang *et al.* 2013a, 2013b; Sillanpää 2014). Apart from the possible negative impact on downstream treatment processes, the recalcitrant NOM is a large contributor to precursors for formation of disinfection by-products such as trihalomethanes upon chlorination (Lu *et al.* 2009; Bond *et al.* 2012).

NOM is a major component of the easily measurable total and dissolved organic carbon (TOC and DOC) in water supply sources. It is usually the result of living or

decaying vegetation, partial bacterial degradation of soil, living organisms and plant detritus (Matilainen *et al.* 2010; Siljanpää 2014). Its composition in water varies from site to site and with time and climatic effects (Sharp *et al.* 2006; Bond *et al.* 2012; Gui *et al.* 2015). It is a complex, heterogeneous mixture of organic compounds of varying structure, molecular weight, functional group and reactivity. Broadly speaking, it is made up of hydrophobic (water hating) and hydrophilic (water loving) components, each of which can be further separated into acids, bases and neutrals. Humic and fulvic acids represent the most significant part of the NOM in surface waters (Maurice & Namjesnik-Dejanovic 1999). Unfortunately, we found during this study that commercially available humic materials failed to provide a match to the indigenous NOM that was of interest to us.

This paper describes a simple NOM brewing method which used fallen leaves etc. collected from the local catchment area and has enabled us to make up a large quantity (~5 kL) of a concentrated NOM stock solution for spiking tests on the pilot plant to simulate natural NOM events. The brewed NOM was characterised and compared with both the historical NOM events (in terms of specific ultraviolet absorbance, or SUVA) and the more typical raw water encountered during the pilot plant trial period (in terms of molecular weight distribution and fractionation).

MATERIAL AND METHODS

Tank and flames method for 'tea' brewing

Large quantities (>10 m³) of leaves, peat and humic material were gathered from the local catchment area. The

peat, punga bark and leaves were sifted through and all rocks, stones and large twigs/sticks removed manually (Figure 1). The mixture was blended with raw water and chopped up using a 30 L capacity industrial blender (Figure 2). The mixture was then poured into a 1 kL brewing tank (Figure 2) and heated to the required temperature and then cooled down.

The general 'tea' brewing procedure used was as follows:

1. Sift through the peat, punga bark and leaves and remove all rocks, stones and large twigs/sticks by hand. The final material consisted of mostly leaves.
2. Add approximately 20 L raw water and 20 L leaves to the blender.
3. Turn the blender on and mix until fully blended.
4. Pour the mixture into the brewing tank.
5. Repeat Steps 1 through 4, until the brewing tank is ~90% full.
6. Start all four gas burners and heat the 'tea' for about 9 hours to reach approximately 80–90 °C and mix as necessary.
7. Remove heat and allow to cool overnight.
8. Collect a small sample of the brewed 'tea'. Dilute and measure the UVA to ensure the NOM concentration is acceptable (targeting 0.39–0.40 cm⁻¹).
9. Once the UVA target is achieved or exceeded, transfer the 'tea' brew to the storage tank. Then collect more raw water ready for the next batch.
10. Repeat Steps 1 through 9 until the required volume of 'tea' has been brewed (~5 kL for this study).

The brewed 'tea' solution had a dark brown colour and is illustrated in Figure 3.



Figure 1 | Peat, punga bark and leaves collected.



Figure 2 | 'Tea' brewing setup with blender, brewing tank and gas burners.



Figure 3 | The final 'tea' solution.

'Tea' characterisation

There are a number of methods for the characterisation of NOM in relation to drinking water treatment (Croue *et al.* 2000; Matilainen *et al.* 2011; Sillanpää 2014). In this study the brewed NOM stock solution was characterised in terms of SUVA, molecular weight distribution using high performance size exclusion chromatography (HPSEC) and four defined organic character fractions using rapid fractionation (RF). UVA (at 254 nm) and DOC were analysed by Watercare Laboratory Services in Auckland according to APHA (online edition) 5910 B and 5310 B, respectively. The HPSEC and RF analyses were performed by Australian Water Quality Centre (AWQC) in South Australia (Chow *et al.* 2004, 2008).

The HPSEC data are primarily plotted as UVA at 260 nm (relating to conjugated organic matter) versus calibrated apparent molecular weight on a logarithmic scale. RF is an analytical method for determination of the concentrations of four defined organic character fractions, based on their

Table 1 | NOM character fraction definitions and description

Code	Definition	Description
VHA	Very Hydrophobic Acids	Adsorbs on DAX-8 resin. High molecular weight & highly coloured. Also known as humic acids.
SHA	Slightly Hydrophobic Acids	Adsorbs on XAD-4 resin. Moderate molecular weight, less coloured. Also known as fulvic acids.
CHA	Charged Hydrophilics	Adsorbs on IRA-958 resin. Higher specific charge. High SUVA.
NEU	Neutral Hydrophilics	Not adsorbed. Lower molecular weight, uncharged, uncoloured. Low SUVA.

selective adsorption to a series of ion exchange resins, as detailed in Table 1.

RESULTS AND DISCUSSION

Historical SUVA

SUVA has been shown to be a good indicator of the composition of NOM (Edzwald & Tobiason 1999). It is a useful parameter for describing the nature of the raw water organic matter (see Table 2). SUVA is the ratio of UV absorbance (at 254 nm) to the DOC concentration of that water. Therefore, strictly speaking, SUVA is not a directly measured parameter but a calculated one. SUVA can be used as an indicator to describe the hydrophobicity of NOM in water and a guide to the treatability of NOM through coagulation methods. Low SUVA fractions are much more difficult to remove via coagulation than high SUVA fractions.

The historical raw water SUVA values for this study are plotted in Figure 4 as a function of the raw water DOC. It shows that the raw water SUVA decreased slightly as the DOC concentration increased, with the median SUVA of the entire data set being $\sim 4.7 \text{ m}^{-1} \cdot \text{L} \cdot \text{mg}^{-1}$. Also shown in Figure 4 is a shaded area of DOC concentrations exceeding

the 75%ile cut-off value (i.e., $\text{DOC} > 5.1 \text{ mg/L}$), above which the raw water was considered to be experiencing NOM event conditions. The median SUVA value based on the NOM event data was $3.69 \text{ m}^{-1} \cdot \text{L} \cdot \text{mg}^{-1}$.

'Tea' brewing

Our initial investigation focused on the use of commercial-grade humic substances. Both humic acid (HA) (Cat# 53680) and humic acid sodium salt (NaHA) (Cat# H16752) were procured from Sigma Aldrich and assessed, as per the methodology outlined by Rodrigues *et al.* (2009), to determine the SUVA value of each substance and hence whether they resembled the SUVA values of the raw water from NOM event conditions. It was found that both the HA and NaHA had a similar SUVA of $\sim 4.8 \text{ m}^{-1} \cdot \text{L} \cdot \text{mg}^{-1}$. This was close to the median SUVA of $4.7 \text{ m}^{-1} \cdot \text{L} \cdot \text{mg}^{-1}$ of the entire raw water data set but at the very high end of the SUVA range (*ca.* $2\text{--}5 \text{ m}^{-1} \cdot \text{L} \cdot \text{mg}^{-1}$) corresponding to the historical NOM events. The relatively high SUVA values of the commercial humic substances would present a lesser challenge for the treatment process and were considered to be not representative of the NOM characteristics in the local catchment. In addition, HA and NaHA were expensive and the available stocks would not be enough for the quantity required for our planned pilot plant trials.

The possibility of preparing an organic blend ('tea') by simply soaking in the raw water of organic material of fallen leaves etc. collected from the local catchment was examined and this method was quickly abandoned as the solution was not concentrated enough to be practical for the purposes of our pilot plant trials. It was concluded that the decay rate of the organic material must be accelerated through, e.g., a brewing (heating) process.

Table 2 | SUVA as a guide to the nature of NOM in water

Raw water SUVA ($\text{m}^{-1} \cdot \text{L} \cdot \text{mg}^{-1}$)	NOM composition
>4	High molecular weight, high hydrophobicity, humic acids
2–4	Mixture of hydrophobics and hydrophilics
<2	Low molecular weight, low hydrophobicity, non-humics

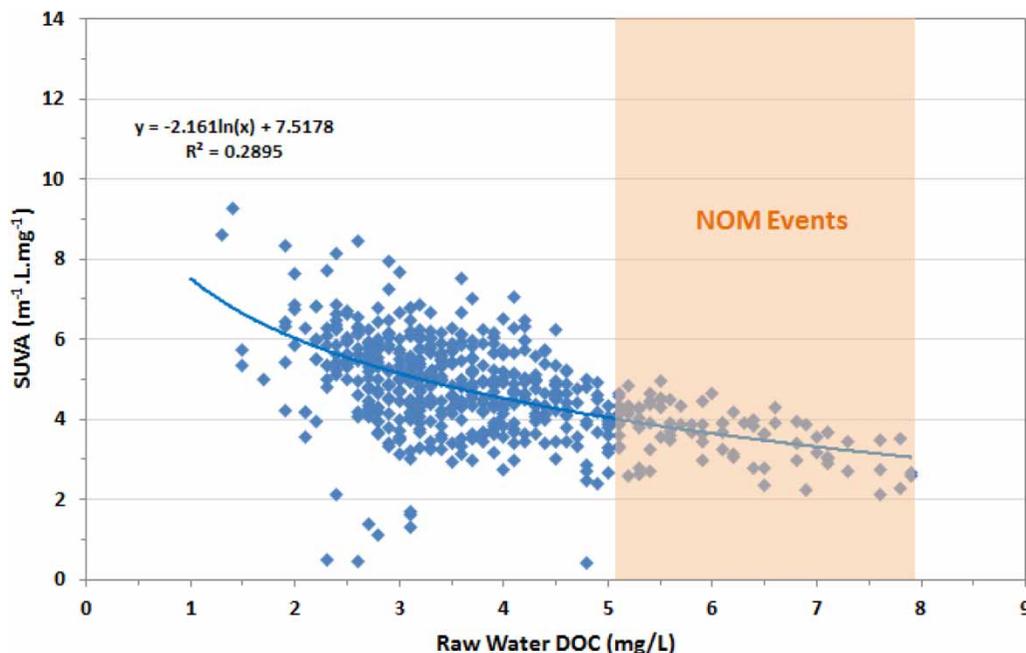


Figure 4 | Historical raw water SUVA versus DOC. Note that the trend line is shown to guide the eye.

A small batch of leaves, peat and humic material gathered from the local catchment area was blended and then brewed in an urn. The urn was brought to the boil and then cooked overnight at approximately 60 °C. The brewed ‘tea’ was then strained and used in dilution tests for UVA analysis. Multiple dilutions were prepared ($\geq 30\times$ dilution). All diluted samples were adjusted to pH 7.2 using a NaOH solution and then sent to an external analytical laboratory for UVA and DOC analysis. The brewed ‘tea’ was found to result in a SUVA value of 3.6–3.9 $\text{m}^{-1}\cdot\text{L}\cdot\text{mg}^{-1}$ (after diluting to DOC concentrations of ≤ 15 mg/L), which is very similar to the median SUVA value of 3.69 $\text{m}^{-1}\cdot\text{L}\cdot\text{mg}^{-1}$ of the raw water corresponding to the historical NOM events and was thus considered to be reasonable for use as a spiking material to simulate raw water NOM event conditions.

It was estimated that ~ 5 kL of the NOM spiking solution would be required for the pilot plant trials based on this initial ‘tea’ solution prepared. This would require a massive up-scaled approach to the ‘tea’ preparation. Various methods of larger-scale brewing were investigated such as the use of electrical drum heaters. It was concluded that the most effective way was to brew the ‘tea’ using a tank and flames method.

‘Tea’ characteristics

The ‘tea’ brewed using the tank and flames method had a DOC of ~ 800 mg/L. Once diluted into distilled water ($\geq 50\times$ dilution) and corrected to the raw water pH (7.2) using a NaOH solution, it resulted in a SUVA value of 3.64 $\text{m}^{-1}\cdot\text{L}\cdot\text{mg}^{-1}$, which nearly equals the median raw water SUVA value under the historical NOM event conditions.

The molecular weight distribution and organic character fractions of the brewed NOM stock solution (i.e., ‘Distilled Tea Spiked’, prepared by diluting the brewed ‘tea’ in distilled water) are shown in Figures 5 and 6, respectively. For comparison, the non-spiked raw water (‘Raw’), the spiked raw water (‘Spiked Raw’), and the DAF subnatant (‘DAF Sub’) following coagulation/flocculation and DAF treatment of the spiked raw water, are also shown. As can be seen from these figures, the key features on the molecular weight distribution curve and the four defined organic character fractions between the diluted NOM stock solution (‘Distilled Tea Spiked’) and the raw water (‘Raw’) encountered at the time of the pilot plant trial matched closely. Figures 5 and 6 also show that the dominant organic fraction of the NOM stock solution (‘Distilled Tea Spiked’) and the raw water (‘Raw’) was the large molecular weight, very

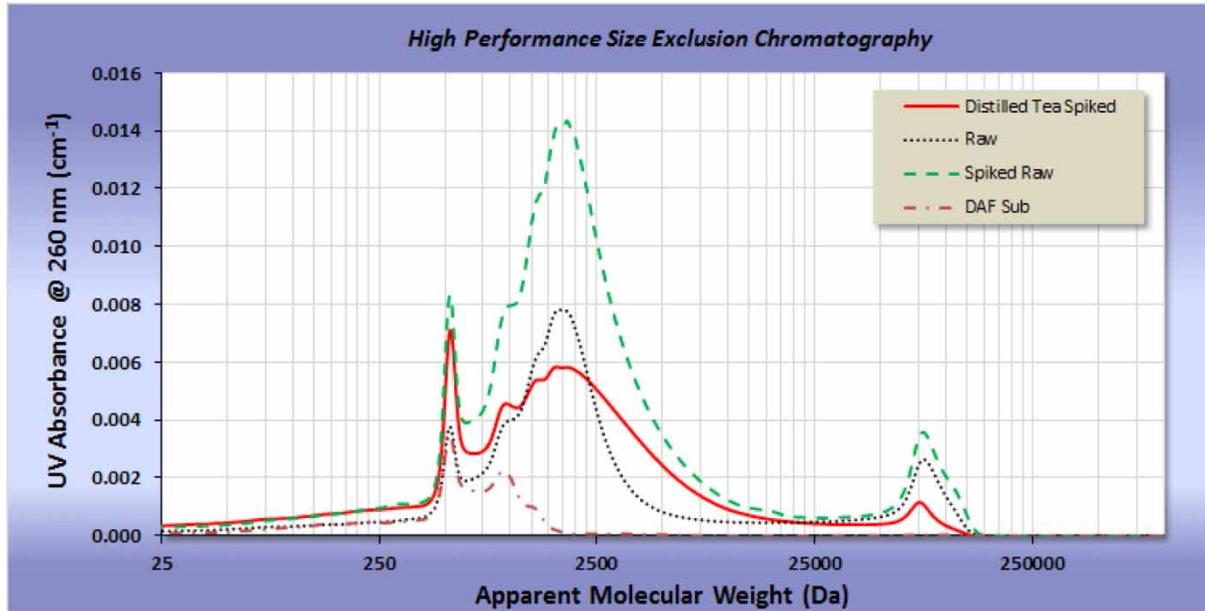


Figure 5 | Comparison of molecular weight distributions between the Distilled Tea Spiked, the Raw, the Spiked Raw and the DAF Sub of the Spiked Raw.

hydrophobic NOM that is generally very amenable to removal through coagulation and flocculation.

Note that it would have been useful to be able to compare the NOM characteristics of the brewed ‘tea’ to that extracted using established techniques (mostly pH

adjustment) such as the standard procedure recommended by the International Humic Substances Society (IHSS). Nevertheless, our objective was to produce a concentrated NOM stock solution of a sufficient quantity to enable us to conduct trials on the pilot scale. It turned out that our

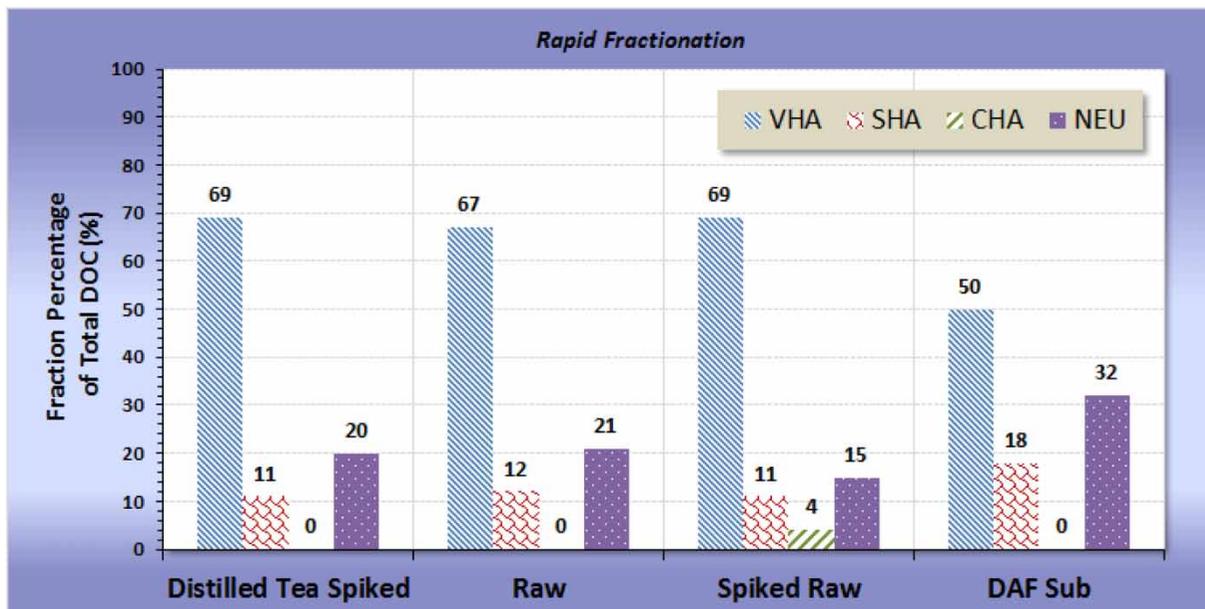


Figure 6 | Organic character fraction compositions of the Distilled Tea Spiked, the Raw, the Spiked Raw and the DAF Sub of the Spiked Raw. Refer to Table 1 for the definition of the four character fractions.

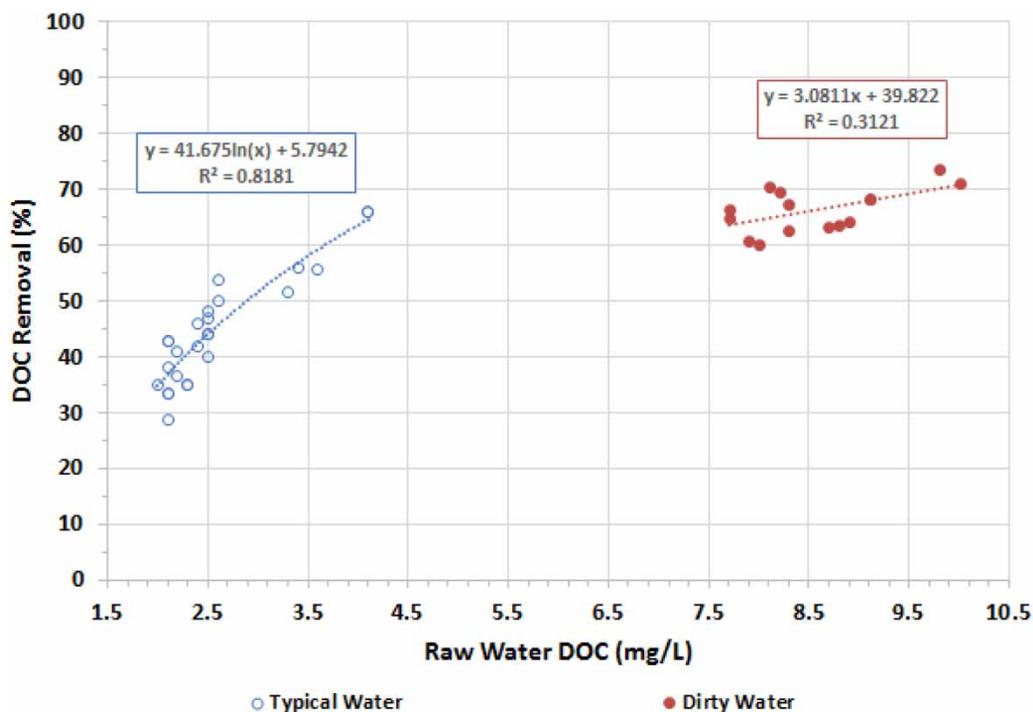


Figure 7 | DOC removal performance through coagulation/flocculation and DAF as a function of the DOC concentration of the spiked ('Dirty Water') and non-spiked raw water ('Typical Water').

simple brewing method was able to meet our needs and yielded, when diluted, a NOM solution with a SUVA that was quite representative of that of the source water. This may be somewhat fortuitous; however, use of organic materials collected from the local catchment must have played a significant role in our success in simulating the indigenous aquatic NOM.

Coagulation behaviour

For the purposes of simulating turbidity and colour events a spiked raw water turbidity of ~ 40 NTU and a DOC concentration of ~ 7.9 mg/L were targeted, which were close to the respective historical maximum values of the raw water. The DOC removal performance of the non-spiked raw water ('Typical Water') and spiked raw water ('Dirty Water'), through coagulation/flocculation (PACl as the coagulant) followed by DAF in the pilot plant (operated at a raw water flow rate of 1,200 L/h), is plotted as a function of the raw water DOC in Figure 7. It can be seen that the spiked raw water exhibited better DOC removal, possibly due to application of larger coagulant doses required for

the higher DOC concentrations of the spiked raw water. As expected, coagulation/flocculation/DAF treatment did not significantly remove the small molecular weight neutral hydrophilics (cf. Figures 5 and 6), which are known to generally have lower SUVA values; coagulation treatment alone is generally not effective in removing this fraction (Matilainen *et al.* 2010; Bond *et al.* 2012).

CONCLUSIONS

A simple but useful brewing method using fallen leaves etc. collected from a local catchment area has been developed for preparing NOM spiking solutions that can be used to evaluate new or stress test existing water treatment processes through pilot testing. The brewed solution was found to closely resemble the indigenous organic matter of the raw water of interest. This method renders a more relevant means for simulating NOM events on the pilot scale.

As NOM composition in water sources can vary from site to site and with time and climatic effects, it is suggested that this brewing method be tested via a small-scale test (urn

test) to assess the viability before upscaling to the brewing method for preparing larger quantities.

ACKNOWLEDGEMENTS

The authors wish to thank Marnie Coates of Hunter H₂O for conducting the preliminary urn tests. Thanks also go to Lukian Harris and his staff at Marine and Civil Solutions Ltd, Auckland, NZ for their kind assistance in brewing the NOM solution using the tank and flames method.

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First received 9 February 2017; accepted in revised form 2 May 2017. Available online 18 May 2017