Characterization of NOM in a drinking water treatment process train with no disinfectant residual

S. A. Baghoth, M. Dignum, A. Grefte, J. Krosesbergen and G. L. Amy

ABSTRACT

For drinking water treatment plants that do not use disinfectant residual in the distribution system, it is important to limit availability of easily biodegradable natural organic matter (NOM) fractions which could enhance bacterial regrowth in the distribution system. This can be achieved by optimising the removal of those fractions of interest during treatment; however, this requires a better understanding of the physical and chemical properties of these NOM components. Fluorescence excitation-emission matrix (EEM) and liquid chromatography with online organic carbon detection (LC-OCD) were used to characterize NOM in water samples from one of the two water treatment plants serving Amsterdam, The Netherlands. No disinfectant residual is applied in the distribution system. Fluorescence EEM and LC-OCD were used to track NOM fractions. Whereas fluorescence EEM shows the reduction of humic-like as well as protein-like fluorescence signatures, LC-OCD was able to quantify the changes in dissolved organic carbon (DOC) concentrations of five NOM fractions: humic substances, building blocks (hydrolysates of humics), biopolymers, low molecular weight acids and neutrals.

Key words | fluorescence EEM, LC-OCD, NOM

INTRODUCTION

Natural organic matter (NOM) is a major concern in drinking water since it causes adverse aesthetic qualities such as colour, taste and odour. It affects in a negative way the performance of water treatment processes such as granular activated carbon filtration and membrane filtration (Lee et al. 2006). Furthermore, it can decrease the effectiveness of oxidants and disinfectants and it may produce undesirable disinfection by-products during oxidation processes (Owen et al. 1998). The biodegradable fraction of NOM is known to enhance biofilm formation in water distribution networks (Van der Kooij 2003). Thus, it is essential to limit the concentration of specific NOM fractions in treated water. However, the efficiency of water treatment is affected by both the amount and composition of NOM. Therefore, a better understanding of the physical and chemical properties of the various components of NOM would contribute greatly towards optimisation of the design and operation of drinking water treatment processes.

Many studies and reviews have been undertaken on the structural characterization of NOM (Chin et al. 1994; Frimmel 1998; Baker 2001; Abbt-Braun et al. 2004; Leenheer 2004) but its structure and fate in drinking water treatment (individual processes and process trains) are still not fully understood. Because NOM may contain literally thousands of different chemical constituents, it is not realistic to characterize it on the basis of a thorough compilation of the individual compounds (Croué et al. 2000). Therefore, researchers have found it more practical to characterize NOM according to operationally defined chemical groups. They have used many characterization methods involving concentration and fractionation of NOM into groups having similar properties (Frimmel & Abbt-Braun 1999; Peuravuori et al. 2002). However, some of these techniques
have inherent inaccuracies such as may arise as a result of the overlapping of different fractions during fractionation. Furthermore, they are often laborious and time consuming and may involve extensive pre-treatment of samples which could modify the NOM character.

There are other analytical techniques that can be applied to characterize bulk NOM without fractionation and that require minimal sample preparation and these are becoming increasingly popular among researchers. Specific ultraviolet absorbance at a wavelength of 254 nm (SUVA) gives an indication of the aromatic character of NOM (Croué et al. 2000) and is now commonly used. Fluorescence spectroscopy has also been used to characterize dissolved organic matter (Coble et al. 1990). Coble (1996) used fluorescence excitation-emission matrix (EEM) to characterize dissolved organic carbon (DOC) in water samples from different aquatic environments and humic-like, tyrosine-like and tryptophan-like fluorescent signals were observed, each with distinct locations of excitation and emission maxima.

Liquid chromatography with online detectors is also commonly used to characterize NOM. It has been coupled with organic carbon and ultraviolet (UV) detectors (LC-OCD/UV) to separate NOM according to molecular size/weight (MW) (Huber & Frimmel 1994). The DOC and UV at a wavelength of 254 nm (UV254) chromatographic peaks have been used to assign identity to various NOM components and the results demonstrate that this NOM characterization tool is very effective in following changes in the NOM distribution along water treatment trains; it can capture the removal of highly reactive NOM (i.e., humic structures), show a shift from high MW to low MW structures after oxidation processes (i.e., more biodegradable NOM), and show the removal of relatively easily biodegradable NOM such as proteins and polysaccharides.

In this research, fluorescence EEM and LC-OCD were used to characterize NOM in water samples from Loenderveen-Weesperkarspel, a Dutch water treatment train in which no chemical residual is applied in the distribution. These two complementary techniques are useful in tracking NOM fractions that are of interest in such a situation; that is, they can provide information on the fate of biodegradable NOM fractions such as proteins, polysaccharides, and low molecular weight acids during treatment.

**MATERIALS AND METHOD**

**Sample collection**

Water samples were collected from different points along the drinking water treatment train operated by Waternet for water supply of Amsterdam. The treatment train consists of a pre-treatment plant called Loenderveen, comprising coagulation, retention in surface water reservoir for about 100 days and rapid sand (RS) filtration treatment steps. The pretreated water is then transported over about 10 km to a post treatment plant called Weesperkarspel, where the water is further treated by ozonation, pellet softening, biological activated carbon (BAC) filtration and slow sand (SS) filtration. Samples were collected in duplicate and one set for analysis by LC-OCD was transported to Het Waterlaboratorium, Haarlem, Netherlands. The other set was transported to UNESCO-IHE Institute for Water Education for DOC, UV254 absorbance, SUVA and fluorescence analyses. In each case, the samples were stored under refrigeration at 5°C and the analysis performed within one week. Twelve samples were collected once a month over a period of twelve months from January to December, 2007. Samples for LC-OCD analysis were collected in reusable glass bottles which were precleaned by soaking in 0.01 M HCl and then in 0.1 M NaOH, for 24 hours in each case. Samples for analysis at UNESCO-IHE were collected in disposable glass bottles and these samples were prefiltered through 0.45 μm Whatman RC55 regenerated cellulose membrane filters within 24 hours of arrival and then stored at 5°C until required for analysis.

**DOC and UV254 absorbance measurements**

DOC concentrations of all prefiltered samples were determined by the combustion method using a Shimadzu TOC-VCPN organic carbon analyzer. UV absorbance at 254 nm was determined for all prefiltered samples at ambient pH using Shimadzu UV-2501PC UV-VIS spectrophotometer. SUVA was then determined by dividing the UV254 by the corresponding DOC of each sample.

**Fluorescence EEM spectroscopy**

Prior to fluorescence measurements, prefiltered samples were diluted to DOC of 1 mg C/l using 0.01 M KCl solution...
in order to minimize interferences due to high DOC. The pH of the diluted samples were adjusted to 2.8 (± 0.1) using 0.1 M HCl. All sample measurements were performed at room temperature (20 ± 1°C). An EEM of each sample was obtained from fluorescence measurements using a Horiba Jobin Yvon FluoroMax-3 spectrofluorometer. The samples were excited at wavelengths of 240 to 450 nm, at 10 nm intervals and the emission captured at wavelengths of 290 to 500 nm, at 2 nm intervals. An EEM of the 0.01 M KCl solution, with pH 2.8, was measured and this was subtracted from the EEM of each sample in order to minimize Raman scatter peaks. An emission scan of the Raman-scatter band of water was performed and the EEM of each sample was normalized to the area under the water-Raman peak. For plotting of the EEM contours, the first and second order Raleigh scatter were removed and the values in the removed areas interpolated using EEMSCAT (http://www.models.kvl.dk/source/EEM_correction/) and N-Way toolbox (http://www.models.kvl.dk/source/nwaytoolbox/).

In this study, characterisation of NOM by fluorescence will be based on the fluorescence intensities at selected excitation/emission wavelength pairs which are attributable to known fluorophores. Table 1 shows the fluorescence intensity peaks that were selected based on the contour plots obtained from the EEMs in the study. It also shows the corresponding peaks that were identified by Coble (1996) and that have been attributed to known fluorescing compounds: tyrosine-like, tryptophan-like and humic-like.

### Table 1 | Selected fluorescence intensity peaks for bulk water samples

<table>
<thead>
<tr>
<th>Peak</th>
<th>Excitation max (nm)</th>
<th>Emission max (nm)</th>
<th>Fluorophore</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coble (1996)</td>
<td>This work</td>
<td>Coble (1996)</td>
<td>This work</td>
</tr>
<tr>
<td>B</td>
<td>275</td>
<td>280</td>
<td>310</td>
</tr>
<tr>
<td>T</td>
<td>275</td>
<td>280</td>
<td>340</td>
</tr>
<tr>
<td>C</td>
<td>350</td>
<td>330</td>
<td>420–480</td>
</tr>
<tr>
<td>M</td>
<td>312</td>
<td>310</td>
<td>380–420</td>
</tr>
</tbody>
</table>

### Table 2 | The variation of dissolved organic carbon (DOC) across the treatment train

<table>
<thead>
<tr>
<th>Sample</th>
<th>DOC (mgC/l)</th>
<th>UV_{254} (m^-1)</th>
<th>SUVA (L/mg/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>S.D.</td>
<td>Mean</td>
<td>S.D.</td>
</tr>
<tr>
<td>Raw surface water</td>
<td>9.0</td>
<td>0.8</td>
<td>27.1</td>
</tr>
<tr>
<td>Coagulation effluent</td>
<td>7.1</td>
<td>0.6</td>
<td>19.1</td>
</tr>
<tr>
<td>Surface reservoir effluent</td>
<td>6.5</td>
<td>0.2</td>
<td>16.1</td>
</tr>
<tr>
<td>Rapid sand filtration effluent</td>
<td>6.0</td>
<td>0.3</td>
<td>15.1</td>
</tr>
<tr>
<td>Ozonation effluent</td>
<td>5.7</td>
<td>0.3</td>
<td>9.0</td>
</tr>
<tr>
<td>Pellet softening effluent</td>
<td>5.4</td>
<td>0.3</td>
<td>8.7</td>
</tr>
<tr>
<td>Biological activated carbon filter effluent</td>
<td>3.0</td>
<td>0.5</td>
<td>3.9</td>
</tr>
<tr>
<td>Treated water</td>
<td>2.7</td>
<td>0.3</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Size exclusion chromatography (LC-OCD)

At Het Waterlaboratorium, size exclusion chromatographic separation of NOM was performed with a LC-OCD system (DOC-LABOR, Germany). In the system, a column TSK HW-50S is connected to a Graentzel thin-film reactor (Huber & Frimmel 1992) in which NOM is oxidized to CO₂ by UV before it is measured by infrared detection. The column, which separates according to molecular size/weight, is able to fractionate NOM into five fractions: biopolymers (such as polysaccharides, polypeptides, proteins and amino sugars), humic substances, building blocks (hydrolysates of humics), low molecular weight (LMW)
acids and low molecular weight neutrals (such as alcohols, aldehydes, ketones and amino acids). Besides the organic carbon detector, the system also incorporates a UV detector which may be used to assess the aromaticity of the sample as well as of the humic fraction by computing the respective SUVA values. The DOC concentration of samples was also measured by filtering the samples through a 0.45 μm filter before injection into the DOC detector. Fractional composition was determined by integration of the area under each chromatogram using FIFFIKUS (DOC-LABOR) software.

RESULTS AND DISCUSSION

Bulk water characteristics

Table 2 shows a summary of DOC, UV254 and SUVA results that were obtained and used to characterize bulk NOM of water samples. The DOC of the raw surface water at the pretreatment plant at Loenderveen varied from a minimum of 7.6 mg C/l to a maximum of 9.8 mg C/l and the annual mean DOC was 9.0 mg C/l. The annual mean DOC is reduced by 33% to 6.0 mg C/l before final treatment at Weesperkarspel, where it is further reduced by 55% to 2.7 mg C/l. Whereas the mean percentage removal of DOC during final treatment is nearly twice as much as during pre-treatment, the actual mean DOC removal is nearly the same: 3.0 mg C/l during the latter and 3.3 mg C/l during the former.

Figure 1 shows the temporal variation of DOC of the raw water as well as at different points of water treatment train. The variation is more pronounced in the raw water and during pre-treatment by coagulation, showing generally higher levels during summer than during winter. However, this seasonality is effectively dampened after about three months of storage in the surface reservoir. During post treatment, it is mainly BAC filtrated and finished waters that show a similar seasonal variation but with slightly less DOC in summer than in winter, an indication of the better performance of BAC filtration during warmer periods.

Figure 2 shows that the bulk DOC is mainly removed by two treatment processes: by coagulation during pre-treatment, which removes about 22% of the influent DOC; and by biological activated carbon (BAC) filtration during post treatment, which removes about 45% of the BAC filter influent DOC.

Table 2 shows that the raw water has a mean SUVA of 3.5 L/mg/m, an indication of NOM of moderate aromaticity, while treated water has a mean of 1.5 L/mg/m, typical
of NOM with low aromaticity (SUVA < 2 L/mg/m). Figure 3 shows the mean percentage reduction in SUVA by different treatment processes across the treatment train; most of the reduction occurs during coagulation, during ozonation and during BAC filtration. Coagulation achieves nearly as much percentage reduction of SUVA as of DOC. The percentage reduction of DOC by BAC filtration is about twice that of SUVA, indicating that a significant fraction of the DOC removed by BAC filtration is of lower aromaticity. In contrast, the percentage reduction of SUVA by ozonation is almost twice that of DOC. This can be ascribed to the transformation of larger and more aromatic humic substances to smaller and less aromatic humics, hydrolysates of humics and LMW acids, rather than to the reduction of DOC by ozonation.

Fluorescence EEM

Figure 4 is a typical EEM contour plot for raw samples and it shows the locations of the fluorescence intensity peaks B, T, C and C2. The intensities of the two humic-like peaks C and C2 are much higher than of the protein-like peaks B and T. This is an indication that the NOM in the raw water as well as the treated water is predominantly humic in character. Figure 5 shows the variation of the mean intensities of the four peaks across the treatment train. Whereas there is a marked difference between the intensities of the humic-like peaks (C and C2) and the protein-like peaks (B and T), there is no significant difference between the mean intensity of peak C and C2, which could be as a result of the overlapping of the two peaks.

Figure 6 shows the mean percentage reduction in the peak fluorescence intensities, clearly illustrating that by far, the biggest changes in the fluorescence properties of the fluorophores occur during ozonation and during BAC filtration. In both cases, the intensities of all the peaks except peak B are reduced by over 50%. Peak B is reduced by over 50% by ozonation but it is not significantly reduced by BAC filtration. The reduction in intensities of all the four peaks by ozonation could be explained by the fact that proteins as well as humic substances consist of unsaturated bonds which could be broken through oxidation by ozonation. The removal/creation of peak B by softening, BAC filtration or by SS filtration is not statistically significant at 95% confidence.
NOM characterization by LC-OCD

LC-OCD was used to separate NOM into five fractions and Figure 7 shows the average percentage contribution of each fraction across the treatment train. In agreement with the results obtained from fluorescence measurements, humic substances dominate NOM in the water samples across the treatment train, ranging from a minimum of 66% after coagulation, to a maximum of 73%; however, the mean percentage contribution of humic substances to the pool of DOC is more or less the same in the treated water as in the raw water. While the mean percentage contribution of both the biopolymers and the neutrals decreases after treatment, that of building blocks increases, probably as a result of the combined effect of the preferential removal of the humic fraction by coagulation and the slight increase of the building blocks after ozonation. The results indicate that there are no LMW acids in the raw water and that these are created during ozonation, making their mean percentage contribution about 1%. Their absence, as ascertained from the results of LC-OCD, is unexpected since LMW dicarboxylic acids are known to contribute 0.5–1% of DOC in natural waters (Thurman 1985). One possibility could be...
that building blocks (hydrolysates of humics) and LMW humics elute in the same fraction as the LMW acids and accounting for the contribution of each of these may be difficult using LC-OCD. Indeed, FIFIKUSS calculates the amount of LMW acids on the premise that all aliphatic LMW acids co-elute in the same fraction as LMW humics and the fraction of each is computed on the basis of their UV254/DOC ratios. There is, therefore, a need for further investigation of how the contribution of each of the co-eluting fractions can be accurately determined.

**Figure 8** shows the removals of the five NOM fractions by different treatment processes across the treatment train. The humic fraction, which contributes about 70% of the total DOC, is mainly removed by coagulation (30%) and by BAC filtration (42%). This suggests that a significant fraction of the humic fraction is readily biodegradable. The biopolymers are significantly removed (>40%) by all the three filtration processes. The LMW acids, which are created by ozonation, are largely removed by softening, BAC filtration and SS filtration.

**CONCLUSIONS**

Fluorescence EEM and LC-OCD were able to identify NOM fractions that are of concern in a drinking water treatment that does not use disinfectant residual in the distribution. The former was able to give an indication of the relative contribution of protein-like components across the treatment train but it is still not possible to use this technique to quantify the actual concentrations of the responsible fluorophores. LC-OCD was able to separate NOM into five fractions and the respective quantities were quantified using FIFIKUSS. It was possible to track not only the humic substances, but also the relatively more biodegradable fractions such as the polysaccharides and the low molecular weight acids. However, more research is needed to evaluate the detection and quantification of the latter fraction using LC-OCD, particularly for water samples taken prior to the oxidation step.

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REFERENCES


