The characterisation of natural organic matter (NOM) in South African waters
T. I. Nkambule, R. W. M. Krause, J. Haarhoff and B. B. Mamba

ABSTRACT

The removal of natural organic matter (NOM) from water is becoming increasingly important in order to prevent the formation of carcinogenic disinfection by-products (DBPs). The inadequate removal of NOM has a bearing on the capacity of other treatment processes to remove organic micro-pollutants or inorganic species that may be present in water. In order to effectively study the nature of South African water sources in terms of their NOM composition, water samples were collected from drinking water treatment plants in the five geographic water regions of South Africa. A raw water sample, an intermediate sample taken before sand filtration and a final sample after sand filtration were collected three times from these water treatment plants at two-month intervals and over three different seasons. Fluorescence excitation-emission matrices (FEEM), biodegradable dissolved organic carbon (BDOC), ultraviolet (UV) characterisation (200–900 nm) and dissolved organic carbon (DOC) analyses were used to characterise the NOM in the water samples. The FEEM and UV results revealed that the samples were composed mainly of non-humic substances with low UV-254 absorbance, while some samples had high humic substances with high UV-254 values. The samples’ DOC results were within the range of 3.25–21.44 mg/L carbon, which was indicative of the varying nature of the NOM composition in the regions where samples were collected. The BDOC fraction of the NOM, on the other hand, ranged from 20 to 65%, depending on the geographical location of the sampling site.

Key words | biodegradable dissolved organic carbon, disinfection by-products, fluorescence excitation-emission matrices, humic substances, natural organic matter

INTRODUCTION

Natural organic matter (NOM) is a mixture of organic compounds, having diverse chemical properties, that occurs in all natural water sources when animal and plant material breaks down (Kim & Yu 2005). NOM affects water quality in the following ways:

- It could be responsible for the colour, undesirable taste and odour of natural waters.
- It inhibits precipitative processes which form the backbone of drinking water treatment.
- It is a major membrane foulant and causes high disinfectant demand.
- It promotes bacterial re-growth in the distribution system and could be a source of nutrients for heterotrophic bacteria, which compromises water quality.
- It accelerates corrosion of the distribution network while increasing turbidity at the consumer end.
- It causes high disinfectant demand.
- In addition, it has recently become obvious that the interaction of NOM with disinfectants can form carcinogenic and mutagenic disinfection by-products (DBPs) (Kim et al. 2006).

All these problems, combined or individually, negatively affect human life and that of other aquatic organisms.

Since NOM emanates from many different sources, it can be predicted that the composition of NOM in different water sources may not be uniform and characterisation studies are therefore necessary. Many authors have suggested that the character of NOM varies per geographic location of the
water source. Indiana (2011) even suggests that the character
of NOM is also dependent on the climatic conditions of that
particular locality while Wong et al. (2007) suggested that the
character of NOM per water source is dependent on the type
of agricultural/industrial activities occurring in the surround-
ing catchment area. It is therefore crucial to understand the
composition of the NOM in the source water, especially as
applied to local NOM conditions. Once the character of
the NOM in the water source has been understood, methods
aimed at effectively removing the NOM from the water
source can then be developed. The need to characterise the
NOM before attempting to remove it is based on the fact
that that its aromaticity, functional group distribution, mole-
cular weight and elemental composition have a great
fluence on how NOM can be effectively removed from
water (Nkambule et al. 2009).
A review of NOM characterisation at water treatment
plants in South Africa has revealed attempts to try and
characterise the NOM occurring at individual plants, but
that it has not been possible to conclusively determine the
nature of NOM occurring in the country (Haarhoff et al.
2010). The primary objective of this study is thus to character-
ise the NOM occurring in South Africa through an extensive
sampling of different water types, both as raw water and fol-
lowing certain treatment steps. Herein, we thus report
NOM characterisation results of samples obtained from
five different water treatment plants in South Africa, representing
the five major source water types. Understanding the charac-
ter of NOM within a short period of time would help inform
water treatment engineers of necessary adjustments to be
carried out within a water treatment plant, since the com-
position of NOM changes during the process or as a result of
external factors like the weather or season.

**EXPERIMENTAL PROCEDURE**

**Sample collection**

Samples were collected from five different water treatment
plants three times, at 2 month intervals. The sampling
times are referred to as Round 1, Round 2 and Round 3 for
the first, second and third samplings respectively. Round 1
was done in spring, Round 2 in summer and Round 3 in
winter. The five different water treatment plants selected
are: Olifantsvlei (O) Wastewater Treatment Plant north of
Johannesburg (Johannesburg Water); the Plettenberg Bay
(P) Water Treatment Plant in the Southern Cape; the Rietvlei
(R) Water Treatment Plant of the Tshwane Metropolitan
Municipality; the Stilfontein (M) Water Treatment Plant of
Midvaal Water; and the Wiggins (W) Water Treatment
Plant of Umgeni Water. Figure 1 shows the general water
treatment train employed in South Africa for the production
of drinking water. These processes vary per water treatment
company and per type of raw water source used.

At each water treatment plant, two to four samples were
collected depending on the particular water treatment train
used. These were a raw water sample, an intermediate
sample before sand filtration and a final sample after sand
filtration where appropriate. The Olifantsvlei is a waste-
water treatment plant and hence here only two samples
were taken, i.e. before and after the maturation pond.

**Bulk water characterisation**

On site, the pH, turbidity, conductivity and temperature of
all samples taken were determined using a Hanna 98129
multi-meter, in order to establish the NOM characteristics
in the samples.

**Organic carbon analysis**

The dissolved organic carbon (DOC) analyses were carried
out using a total organic carbon (TOC) analyser (Teledyne
Tekmar, TOC fusion). Prior to analysis all samples were
filtered through 0.45 μm filter paper. DOC is the organic
constituent that can pass through 0.45 μm filter paper,
while TOC is the measure of all organic molecules present
in a water sample. Standards of 1, 5, 10, 20 and 30 mg/L
carbon were prepared with potassium hydrogen phthalate
(KHP) and de-ionised water, and were then run prior to
analysis of samples to calibrate the instrument.

**Ultraviolet-visible (UV-Vis) spectrophotometric analysis**

A Shimadzu UV-2450 Spectrophotometer was used to ana-
lyse the samples in the UV range over the following four
wavelengths: 214 nm (indicative of nitrites and nitrates;
Narayana & Sunil 2009); 254 nm (indicative of humic substances and aromatics); 272 nm (reported in the literature to be the best predictor of Trihalomethane (THM) formation; Liu et al. 2006); and 300 nm (used by Rand Water and other treatment plants as a measure of DOC). A full wavelength spectrum (200–900 nm) of each sample was also obtained to further study the NOM characteristics in the samples.

Specific ultraviolet absorbance analysis

The specific ultraviolet absorbance (SUVA) gives an indication of the amount of humic substances vs. non-humic substances in the NOM (Weishaar et al. 2003). SUVA can also be used to indicate the treatability of the water. The SUVA calculation requires both DOC and UV measurement. The UV_{254} and DOC values were used to calculate the SUVA using Equation (1):

\[
SUVA = \frac{UV_{254} (\text{Cm}^{-1})}{DOC (\text{mg L}^{-1})} \times 100
\]

Fluorescence excitation-emission matrices (FEEM) characterisation

The FEEM method is used as a technique for classifying and distinguishing between humic substances of various origins and natures (Chen et al. 2003). FEEM attempts to give the structural information of NOM based on the UV absorption of the molecular group. A Perkin Elmer LS 45 Fluorescence spectrometer was used in combination with the UV-Vis spectrophotometer to try and study the character of the NOM. ‘FEEM regions’ were chosen as per grouping by Chen et al.
These regions were chosen only as estimates and values slightly higher or lower than them can be chosen. These regions were:

<table>
<thead>
<tr>
<th>FEEM region</th>
<th>Excitation (nm)</th>
<th>Emission (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>≤250</td>
<td>&lt;350</td>
</tr>
<tr>
<td>II</td>
<td>≤250</td>
<td>340–380</td>
</tr>
<tr>
<td>III</td>
<td>≤250</td>
<td>380–540</td>
</tr>
<tr>
<td>IV</td>
<td>260–300</td>
<td>280–380</td>
</tr>
<tr>
<td>V</td>
<td>250–300</td>
<td>380–540</td>
</tr>
</tbody>
</table>

Biodegradable dissolved organic carbon (BDOC) analysis

BDOC in drinking water is an indicator of bacterial re-growth potential in the distribution network. The method of analysis chosen is based on measuring the reduction of DOC over 6 days by bacteria fixed on biologically active sand (BAS). The BDOC measurements were only carried out on the raw water samples. An inoculum of BAS, obtained from the Rietvlei water treatment plant, was washed until there was no further release of DOC. This was achieved by washing the BAS ten times or more with 500 mL rinsing solution (10 mL sodium thiosulphate solution, 0.1 M: 490 mL deionised). The DOC and UV content of the last washing were then measured, to study the background DOC and UV due to the sand. The inoculums was then rinsed with 100 mL of the raw water sample to be analysed, after which the solution was left to stand for 20 minutes to allow an acclimation of biomass to the water before gently pouring it out.

A fixed weight of sample (300 mL) and inoculated sand (100 g) was then placed together in clean Erlenmeyer flasks, aerated and kept at room temperature for 6 days. Each flask was covered with aluminium foil paper, to prevent any atmospheric interference in the condition of the bacteria and samples in the flask. The heterotrophic bacteria in the sand digest the carbon in the sample to get energy, while at the same time biologically degrading the sample. Daily measurements of the DOC concentration were made until no further changes in DOC were observed. BDOC is calculated as the difference between the initial DOC and the minimum DOC value reached. Sodium acetate was used as a control. Three different solutions (5, 8 and 10 mg/L) of sodium acetate were prepared as controls and run at the same time as the samples (under similar conditions as those of the samples) as controls in order to monitor the activity of the bacteria in known concentrations of substrate. Sodium acetate was chosen because it is organic and has been widely used in many bacterial decay studies (Takundwa & Mvula 2007).

RESULTS AND DISCUSSION

Bulk water characterisation of samples

The five water treatment plants were selected based on the various source water supply regions in South Africa. Table 1 and Table 2 show the bulk characterisation of the water samples collected during the three sampling times.

According to Tan (2003), the type of soil and vegetation in the surrounding catchment area and seasonal variations influence the NOM in water bodies. It has been found that there is a strong relationship between the intensity of precipitation and the NOM concentration, since run-off leads to higher NOM discharge from the upper part of the soil profile or percolation through the soil column. This was

Table 1 | DOC and turbidity values for the three rounds of sampling

<table>
<thead>
<tr>
<th>Sample</th>
<th>DOC (mg/L)</th>
<th>Turbidity (NTU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>7.94</td>
<td>11.62</td>
</tr>
<tr>
<td>R2</td>
<td>6.79</td>
<td>11.02</td>
</tr>
<tr>
<td>R3</td>
<td>6.35</td>
<td>7.65</td>
</tr>
<tr>
<td>R4</td>
<td>5.89</td>
<td>5.93</td>
</tr>
<tr>
<td>O1</td>
<td>9.91</td>
<td>9.51</td>
</tr>
<tr>
<td>O2</td>
<td>8.78</td>
<td>9.80</td>
</tr>
<tr>
<td>M1</td>
<td>7.60</td>
<td>9.06</td>
</tr>
<tr>
<td>M2</td>
<td>7.29</td>
<td>8.05</td>
</tr>
<tr>
<td>M3</td>
<td>6.78</td>
<td>9.30</td>
</tr>
<tr>
<td>M4</td>
<td>6.40</td>
<td>7.03</td>
</tr>
<tr>
<td>M5</td>
<td>–</td>
<td>4.42</td>
</tr>
<tr>
<td>W1</td>
<td>4.64</td>
<td>3.20</td>
</tr>
<tr>
<td>W2</td>
<td>3.75</td>
<td>2.64</td>
</tr>
<tr>
<td>W3</td>
<td>3.30</td>
<td>2.51</td>
</tr>
<tr>
<td>P1</td>
<td>21.44</td>
<td>9.98</td>
</tr>
<tr>
<td>P2</td>
<td>3.85</td>
<td>5.01</td>
</tr>
<tr>
<td>P3</td>
<td>3.25</td>
<td>3.68</td>
</tr>
</tbody>
</table>
The P sample water is characteristic of the organically coloured surface water found on the south-west coast in South Africa; its brownish colour is usually due to humic and fulvic substances. This is evidenced by the high DOC values of the raw water (P1) samples (21.44, 9.98 and 11.37 mg/L for the first, second and third sampling, respectively). The turbidity of the raw water samples is also high (ranging from 1.34 to 1.93 NTU), indicative of a high content of colloids and clay particles in these samples.

The W sample is characterised by Montaigne water flowing eastwards from the Drakensberg and Amatola escarpments. This water is generally low in colour as evidenced by the low DOC values of the raw water from this treatment plant (DOC = 3.75, 3.20, and 3.19 mg/L for first, second and third sampling, respectively). The DOCs were higher after rainfall (Round 3), with a few exceptions, for all the samples. These findings correlate well with a study by Krasner (1999), who also demonstrated that seasonal variation would lead to increased DOC and UV values after rainfall. They attributed these increases to the leaching of soil organic matter during river discharge.

The O samples are treated sewage effluent, which dominates the NOM character in many streams and rivers in South Africa. These are thus very high in DOC as evidenced by an average concentration of 9.00 mg/L DOC for all these samples. They also have the highest turbidity values, indicative of high concentrations of colloids and clay particles. During the sampling periods, turbidity ranged from 0.56 NTU to as high as 114 NTU, indicative of the varying nature of the NOM character within South African waters. The turbidity governs the coagulation process in raw waters. Pernitsky (2003) pointed out that coagulant dosages increase where raw water turbidity rises, but the relationship is not linear.

The M and R samples are characteristic of oligotrophic waters, supplemented by the Lesotho Highlands Water Project (LHWP). These samples had relatively similar amounts of DOC and turbidity throughout the sampling period, as can be seen from Table 1 and Table 2. It is interesting to note that DOC removal efficiencies for all the water treatment plants are relatively high, as can be seen with an 85% DOC removal efficiency at Plattenberg Bay. It is also noteworthy

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity (mS/m)</th>
<th>pH</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>0.42 0.43 0.39</td>
<td>8.07</td>
<td>12.4 21.3 21.2</td>
</tr>
<tr>
<td>R2</td>
<td>0.40 0.40 0.41</td>
<td>8.08</td>
<td>11.9 22.3 21.3</td>
</tr>
<tr>
<td>R3</td>
<td>0.40 0.41 0.42</td>
<td>8.05</td>
<td>9.18 9.47 11.7</td>
</tr>
<tr>
<td>R4</td>
<td>0.41 – 0.40</td>
<td>7.99</td>
<td>– 9.14 –</td>
</tr>
<tr>
<td>O1</td>
<td>0.46 0.42 0.51</td>
<td>7.49</td>
<td>11.7 22.9 26.0</td>
</tr>
<tr>
<td>O2</td>
<td>0.47 0.43 0.53</td>
<td>8.10</td>
<td>15.9 22.5 23.7</td>
</tr>
<tr>
<td>M1</td>
<td>0.49 0.62 0.20</td>
<td>9.50</td>
<td>13.4 23.7 25.7</td>
</tr>
<tr>
<td>M2</td>
<td>0.51 0.64 0.29</td>
<td>9.53</td>
<td>16.9 23.4 26.4</td>
</tr>
<tr>
<td>M3</td>
<td>0.53 0.63 0.26</td>
<td>9.51</td>
<td>16.2 23.9 25.0</td>
</tr>
<tr>
<td>M4</td>
<td>0.51 0.64 0.22</td>
<td>9.46</td>
<td>16.2 23.8 25.7</td>
</tr>
<tr>
<td>M5</td>
<td>– – 0.26</td>
<td>– 9.48</td>
<td>16.2 – 27.0</td>
</tr>
<tr>
<td>W1</td>
<td>0.23 0.22 0.29</td>
<td>7.96</td>
<td>17.1 23.4 26.1</td>
</tr>
<tr>
<td>W2</td>
<td>0.22 0.22 0.29</td>
<td>7.90</td>
<td>17.1 23.1 26.4</td>
</tr>
<tr>
<td>W3</td>
<td>0.22 0.22 0.29</td>
<td>7.91</td>
<td>17.0 23.0 28.1</td>
</tr>
<tr>
<td>P1</td>
<td>0.12 0.07 0.10</td>
<td>6.73</td>
<td>13.7 21.3 26.0</td>
</tr>
<tr>
<td>P2</td>
<td>0.12 0.11 0.22</td>
<td>6.73</td>
<td>13.6 21.3 25.5</td>
</tr>
<tr>
<td>P3</td>
<td>0.12 0.11 0.22</td>
<td>6.39</td>
<td>13.6 20.5 25.2</td>
</tr>
</tbody>
</table>
that all the water treatment plants distribute water to consumers that meets South African National Standards (SANS), and in some instances the water supply meets even the stringent World Health Organization (WHO) standards.

Coagulation and flocculation processes are not efficient in low temperatures because the viscosity of the water is high, shifting the coagulant stability and reducing the kinetics of the hydrolysis reactions and particulate flocculation. As can be seen in Table 2, the temperature range of the water in all sampling rounds and samples is not low (11.7–28.1 °C), thus enabling DOC removal by coagulation and flocculation.

Ultraviolet-visible (UV-Vis) spectrophotometric analysis

UV absorbance is usually measured at a wavelength of 254 nm (and reported in cm⁻¹), which is the wavelength used as an industrial standard for the maximum UV absorption of NOM samples. Absorption at this wavelength has been reported to represent the aromatic character of the organic species. An increase in UV absorbance at 254 nm indicates that NOM is increasing in aromaticity and unsaturated carbon bonds (Kiwa 2006). UV was also measured at 214, 272 and 300 nm for a more in-depth analysis of the NOM character in this study. As already discussed above, UV214 nm is indicative of nitrates and nitrates, UV272 nm and DOC removal of up to 85%, indicating the effectiveness of the water treatment techniques employed for NOM removal.

Specific ultraviolet absorbance analysis

SUVA is calculated by dividing the UV-absorbance of the sample at 254 nm (in cm⁻¹) by the DOC of the sample (in mg/L) and then multiplying by 100 mg m. It is a method used to determine the relative aromaticity of the humic fraction (Weishaar et al. 2005). Generally a SUVA value of above 4 is considered to represent high aromatic content, i.e. humic substances, while a SUVA value of below 2 represents low aromatic content, i.e. non-humic substances. Table 4 gives the various SUVA values for all the samples analysed during the different sampling periods.

Only the P samples exhibited SUVA >4 L/mg m, implying that these were the only samples that were predominantly composed of highly aromatic humic substances. The other samples (R, M, O and W) had SUVA <2 L/mg m, for the first and second round of sampling, implying that these samples contained non-humic substances. However, during the third round of sampling, these samples had SUVA values greater than 2 L/mg m but still less than 4 L/mg m, which meant that the samples had slightly aromatic NOM but were still not as highly aromatic as the P samples.

SUVA values can also be used to indicate treatability. Edzwald & Tobiason (1999) presented guidelines for interpretation of SUVA, proposing that water with a higher SUVA (>4) has an expected TOC removal of above 50%. This assertion was found to hold true in this study as the P samples had high SUVA values and thus had a % DOC removal of up to 85%.

Fluorescence excitation-emission matrices (FEEM) characterisation

The FEEM method is used as a technique for classifying and distinguishing between humic substances of various origins and natures. It is often used as a ‘discrimination technique’, i.e. it gives a distinction between humic-like (fulvic acids, humic acids and humin) or other NOM components (Weishaar et al. 2005). The principle of fluorescence is the ability of a molecule to absorb light of a certain wavelength...
and to emit light of another wavelength depending on specific molecular bonds (Hua et al. 2007). Usually, the absorption/emission wavelength pair is different for different groups of molecules, and hence aromatics can be differentiated from carbohydrates. FEEM attempts to give the structural information of NOM based on the UV absorption of the molecular group.

Figures 2–5 show the results obtained for the P samples at different excitation-emission wavelengths (guided by the FEEM regions given in section 2.6). As can be seen from Figures 2–5, the P samples have a very broad peak occurring at 420–500 nm with a maximum intensity occurring at 600 intensity units. This peak is symbolic of hydrophobic acids, humic and humic acid-like material. At a different excitation, again the P sample has a broad peak occurring at 580–680 nm (Figure 5). This peak is symbolic of microbial by-products such as tryptophan-like and fulvic acid material. The intensity here is approximately 200 intensity units.

The results obtained for the other samples indicate that the samples had very low aromatic content, i.e. low humic substances, as evidenced by very narrow peaks or no peaks at all where peaks for humic substances were expected. The results are also in agreement with the SUVA values, which suggest that only the P samples contain a high hydrophobic NOM. The different spectrum displays the extent of the varying composition of NOM from place to place and season to season. The spectrum also displays the difference in the character of NOM as evidenced by the varying peak intensities. The results obtained after the second and third sampling indicate characteristic features of NOM (with different concentrations) similar to the ones from the first sampling. Even though FEEM analysis is not entirely conclusive, by comparing the data against standard literature fluorescence emission-excitation data, important inferences of NOM characteristics can be drawn.

### Table 3 | UV values at different wavelengths for the three rounds of sampling (in m⁻¹)

<table>
<thead>
<tr>
<th>Sample</th>
<th>214 nm Round 1</th>
<th>214 nm Round 2</th>
<th>214 nm Round 3</th>
<th>254 nm Round 1</th>
<th>254 nm Round 2</th>
<th>254 nm Round 3</th>
<th>272 nm Round 1</th>
<th>272 nm Round 2</th>
<th>272 nm Round 3</th>
<th>300 nm Round 1</th>
<th>300 nm Round 2</th>
<th>300 nm Round 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>72.9</td>
<td>38.9</td>
<td>75.5</td>
<td>14.1</td>
<td>17.4</td>
<td>29.9</td>
<td>11.7</td>
<td>14.0</td>
<td>24.7</td>
<td>7.6</td>
<td>8.3</td>
<td>18.1</td>
</tr>
<tr>
<td>M2</td>
<td>67.7</td>
<td>35.7</td>
<td>66.5</td>
<td>9.3</td>
<td>14.0</td>
<td>19.8</td>
<td>7.4</td>
<td>10.9</td>
<td>13.8</td>
<td>4.4</td>
<td>6.1</td>
<td>9.4</td>
</tr>
<tr>
<td>M3</td>
<td>65.5</td>
<td>32.6</td>
<td>55.9</td>
<td>15.7</td>
<td>12.0</td>
<td>15.3</td>
<td>14.0</td>
<td>8.8</td>
<td>12.4</td>
<td>11.7</td>
<td>4.7</td>
<td>8.7</td>
</tr>
<tr>
<td>M4</td>
<td>67.7</td>
<td>39.0</td>
<td>85.3</td>
<td>7.1</td>
<td>9.5</td>
<td>30.7</td>
<td>5.0</td>
<td>7.0</td>
<td>25.0</td>
<td>2.7</td>
<td>3.6</td>
<td>17.2</td>
</tr>
<tr>
<td>M5</td>
<td>–</td>
<td>–</td>
<td>60.2</td>
<td>–</td>
<td>–</td>
<td>17.7</td>
<td>–</td>
<td>–</td>
<td>14.3</td>
<td>–</td>
<td>–</td>
<td>10.0</td>
</tr>
<tr>
<td>R1</td>
<td>78.8</td>
<td>41.8</td>
<td>69.2</td>
<td>14.7</td>
<td>17.3</td>
<td>28.5</td>
<td>11.7</td>
<td>133</td>
<td>22.1</td>
<td>6.6</td>
<td>7.4</td>
<td>15.8</td>
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<tr>
<td>R2</td>
<td>78.6</td>
<td>36.6</td>
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<td>9.6</td>
<td>12.2</td>
<td>15.4</td>
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<td>R3</td>
<td>73.8</td>
<td>32.0</td>
<td>78.7</td>
<td>10.2</td>
<td>9.8</td>
<td>19.8</td>
<td>7.8</td>
<td>7.0</td>
<td>14.7</td>
<td>3.9</td>
<td>3.3</td>
<td>10.3</td>
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<tr>
<td>R4</td>
<td>81.0</td>
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<td>63.4</td>
<td>8.3</td>
<td>–</td>
<td>14.6</td>
<td>6.1</td>
<td>–</td>
<td>11.9</td>
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Biodegradable dissolved organic carbon (BDOC) analysis

The BDOC gives a ratio of the BDOC content of any sample vs. the NBDOC content of that sample. Figures 6, 7 and 8 show the BDOC analysis of the samples obtained over the 6 day period. From a microbial perspective, the aim of drinking water treatment is to eliminate all pathogenic bacteria and to minimise the presence and potential regrowth of heterotrophic bacteria in the distribution system. Such regrowth can give rise to biofilm formation in pipelines which in the long run causes operational problems such as bio-fouling and bio-corrosion (Hammes & Egli 2005).

The percentage DOC removal of the samples ranged between 20 and 65% (Table 5). The highest percentage removal was noted for the P sample (65%) and the least for the W and M samples (20%). It has been reported by Volk et al. (2000) that water with high humic substances easily undergoes biological biodegradation as confirmed by the highest % BDOC removal of the P samples, which are highly coloured waters with a high concentration of humic substances. The lower % DOC removal was noted in the water that has low SUVA values (implying low humic substances content).
Eikebrokk (2004) suggested that the BDOC could be improved by about 10% through coagulation optimised for removal of DOC and particles. Generally, Eikebrokk argues that water containing high molecular weight hydrophobic fractions is more amenable to water treatment processes such as coagulation than waters with a low molecular weight fraction. This also explains the question of why water with high BDOC values (the P1 samples) had the highest DOC removal percentages compared to the low DOC removal percentages of the water with least BDOC (W1 and O1).

**CONCLUSIONS**

Characterisation results have given an indication of the character of NOM in all the water samples. UV-Vis and DOC results indicate that most of the samples were not aromatic in nature since they had relatively low UV absorbance at UV$_{254}$ (between 0.01 and 128.2 absorbance units). The various water treatment processes employed at the different treatment plants were able to effectively reduce NOM, as evidenced by a percentage DOC removal of up to 82% for the P samples. The turbidity of the samples was used as an indicator of the amount of clay particles and colloidal NOM. Some raw water samples (e.g. V) had a high turbidity value (114 NTU) indicative of a high amount of colloids in the raw waters. FEEM characterisation of the samples indicated that the P samples had...
hydrophobic acids, humic and humic acid-like material but in varying proportions. The Wiggins (W) sample contained the least amounts of humic substances. For the BDOC analysis, the percentage DOC removal for the samples ranged from 20 to 65%. The highest percentage DOC removal in terms of BDOC was again noted in the P sample, further confirming that the NOM levels of highly coloured waters with high levels of aromatic substances are easy to treat. Knowing the NOM composition of the local water source is an important prerequisite for better understanding NOM and for designing water treatment plants for its optimal removal. The results presented in this paper clearly demonstrate the high variability of NOM in South African water treatment plants.

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REFERENCES


Indiana, G. 2001 Removal of Natural Organic Matter to Reduce the Presence of Trihalomethane’s in Drinking Water, School of Chemical Science and Engineering. Royal Institute of Technology, Sweden.


Kim, H. C., Yu, M. J. & Han, I. 2006 Multi-method study of the characteristic chemical nature of aquatic humic substances isolated from the Han River, Korea. Applied Geochemistry 21, 1226–1239.

Kiwa, N. V. 2006 Selection of anionic resins for NOM removal. BTO 042, 9–16.

Krasner, S. W. 1999 Chemistry of Disinfection By-Products Formation on Formation and Control of Disinfection By-Products in Drinking Water, Chapter 2. AWWA, Denver, CO.


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