

Investigation of natural organic matter (NOM) character and its removal in a chlorinated and chloraminated system at Rand Water, South Africa

S. S. Marais, E. J. Ncube, T. A. M. Msagati, B. B. Mamba and T. I. Nkambule

ABSTRACT

In its natural environment, natural organic matter (NOM) is not problematic. However, during water treatment NOM does affect water quality specifically during the disinfection step, where if NOM is present it reacts with disinfectants resulting in the formation of disinfection by-products. To emphasize the importance of NOM monitoring during potable water treatment this study aimed to characterize NOM and evaluate NOM removal by a conventional water treatment plant considering seasonal trends. NOM was characterized by making use of NOM polarity and specific ultraviolet absorbance. NOM removal was monitored with high-performance size exclusion chromatography, dissolved organic carbon (DOC) and UV_{254} analyses. The polarity rapid assessment method indicated that the hydrophobic and hydrophilic NOM fractions within the surface water increased during a period of heavy rain when floods occurred, but conversely decreased during an average rain season. Although NOM character showed variability during the 5-year study period, seasonal relationship during high and low flow seasons between aromatic NOM and total trihalomethane (TTHM) formation was not evident. Aromatic NOM was not the only precursor to TTHM formation, which stresses the need to implement advanced NOM characterization techniques during NOM monitoring to study reactivity of the individual NOM fraction with the disinfectant used at the water treatment plant.

Key words | disinfection by-products, natural organic matter, polarity, specific ultraviolet absorbance

S. S. Marais
E. J. Ncube
Process Technology Department,
Rand Water,
Vereeniging 1939,
South Africa

T. A. M. Msagati
B. B. Mamba
T. I. Nkambule (corresponding author)
Nanotechnology and Water Sustainability
(NanoWS) Research Unit,
University of South Africa,
Florida 1709,
Johannesburg,
South Africa
E-mail: nkambtt@unisa.ac.za

INTRODUCTION

Owing to allochthonous (terrestrial organic carbon input) or autochthonous (phytoplankton and macrophyte activity within a water source) origin, natural organic matter (NOM) abundantly occurs in all water sources in the environment (Carpenter *et al.* 2005; Hanson *et al.* 2014). Even though studies on the assessment of NOM in water supply systems in South Africa are limited, that limited research has highlighted the importance of NOM monitoring and removal during potable water treatment. In addition to the limited data on NOM composition, the drinking water standard for organic carbon is regulated by

the World Health Organization as 5 mg/L, opposed to 10 mg/L by the South African National Standard (SANS241-1:2015). This identifies NOM as a key concern during potable water treatment and is often associated with poor decision-making which impacts on chemical budgets and water treatment options. Although NOM monitoring (characterization and removal) by South African water treatment plants is limited it is known that NOM composition of surface water throughout South Africa differs, resulting in high variability in water treatment plants utilizing these source waters (Nkambule *et al.* 2012).

Although NOM is not problematic in its natural environment the key concern with NOM during drinking water treatment is that NOM acts as a precursor to trihalomethane (THM) formation (Hua & Reckhow 2007; Chowdhury 2013). The regulated disinfection by-products (DBPs) according to SANS241-1:2015 for South African water supply systems are THMs and consist of the compounds bromoform (CHBr_3), chloroform (CHCl_3), dibromochloromethane (CHBr_2Cl) and bromodichloromethane (CHBrCl_2).

Furthermore, although NOM characterization during drinking water treatment is being extensively studied globally, the characterization of NOM has various limitations due to:

- a variety of characterization techniques is needed to ensure all of its functional and structural properties within the heterogeneous NOM pool are quantified;
- NOM structure and character changes seasonally (Sharp *et al.* 2006; Bazrafshan *et al.* 2012);
- change in molecular weight distribution of NOM due to bacterial activity (Khodse & Bhosle 2011);
- NOM composition throughout different geographical areas that varies (Nkambule *et al.* 2012).

Rand Water is the bulk water service provider in South Africa providing an average of 4.2 million m^3/d potable water to 13 million people in South Africa. Rand Water primarily abstracts its source water from the Vaal Dam, a surface impoundment having a storage capacity of 2,536 million m^3 . It is therefore essential to investigate not only the character of NOM within this source but also the seasonal NOM variation. This study aimed to characterize the NOM in Vaal Dam surface water (currently having limited historical NOM character data) and also to monitor NOM removal by Rand Water's full-scale conventional water treatment plant. The outcome of the study would thus assist in underpinning the nature, occurrence and concentration of NOM in Vaal Dam surface water, especially since the character of NOM greatly influences its removal during water treatment (Hu *et al.* 2003; Sharp *et al.* 2006). Ultimately the study aims to provide insight into the nature of NOM within the source water, the efficiency of the treatment process for NOM removal as well as seasonal influences on organic loading and NOM removal.

MATERIALS AND METHODS

Materials

Chemicals used during this study were ascorbic acid (Merck), NaOH (Merck), sodium acetate (Sigma-Aldrich) and were all of analytical grade. All standard solutions were prepared in deionized water (Milli-Q system, Millipore).

Sampling

Samples were collected from the Vaal Dam, which is the source of raw water for the conventional water treatment plant. The catchment area of this water treatment plant receives seasonal rain within the summer months, which is referred to as the high flow season, the low flow season being winter and spring with minimal rainfall. At Rand Water the treatment steps consist of screening, coagulation, flocculation, sedimentation, carbonation, and sand filtration followed by primary (chlorination) and secondary disinfection by addition of ammonia (chloramination). Treated water samples were also collected after the filtration and disinfection steps from the full-scale plant over a period of 5 years on a fortnightly basis, concentrating on the low flow (June–October) and high flow (November–February) seasons. Samples were preserved and kept at 4 °C during transport to the laboratory.

NOM characterization

The pH and conductivity were measured by a Mettler Toledo (DL-53), and turbidity and colour determined by a photometer (HACH 2100AN). All these parameters were measured in the laboratory after being kept at 4 °C.

The change in NOM polarity of NOM in a water sample can be determined through the use of polar, non-polar or anion exchange solid-phase extraction (SPE) cartridges, by evaluating the amount of material adsorbed onto each cartridge through ultraviolet absorbance measurement at 254 nm (UV_{254}) (Rosario-Ortiz *et al.* 2004). This NOM characterization technique is known as the polarity rapid assessment method (PRAM) and was modified by Nkambule

et al. (2012) producing three NOM fractions instead of the original six fractions, resulting in a less time-consuming method. The modified PRAM was used to fractionate NOM into hydrophobic (HPO), hydrophilic (HPI) and transphilic (TPI) fractions as these three fractions best represent the composition of the NOM with respect to its aromaticity (Nkambule *et al.* 2012). The fractionation was performed during the months of October to February to monitor the change in polarity within the surface water due to rainfall (low flow season vs high flow season). Water samples were passed through a non-polar SPE sorbent C18 and a polar sorbent CN, thus extracting the HPO and HPI analytes, respectively, by eluting each fraction with 0.1 M NaOH. To extract the TPI fraction (a mixture of HPO and HPI fractions), the sample was filtered through a NH₂ anion exchange resin. The supernatant from each SPE cartridge was then analyzed by UV₂₅₄.

Organic loading and NOM removal

After filtering the sample through a 0.45 µm membrane filter, dissolved organic carbon (DOC) and UV₂₅₄ were measured to determine the overall organic loading in the surface water during the low and high flow seasons. UV₂₅₄ was measured using a spectrophotometer (Agilent Technologies Cary 60 UV-Vis) and DOC was determined with a Shimadzu TOC-L analyser. Owing to the double bonds between carbon atoms within the organic matter structure that absorbs UV light at a wavelength of 254 nm, a measurement is available indicative of the aromatic character of NOM (Edzwald & Tobiason 2010). Specific ultraviolet absorbance (SUVA) values were calculated by dividing the UV₂₅₄ value by the DOC of the same sample to indicate the presence of humic substances and non-humic substances in a sample (Weishaar *et al.* 2003). The removal efficiency of NOM by the water treatment plant was also quantified as the percentage UV₂₅₄ and DOC removal after the treatment process (rapid gravity sand filtration).

The change in molecular size distribution (MSD) of organic matter is a fast and consistent method to demonstrate performance of the treatment process with regards to NOM removal (Pelekani *et al.* 1999; Myllykangas *et al.* 2002). The MSD was determined by means of high-performance size exclusion chromatography (HPSEC) as described

by Nissinen *et al.* (2001). A water sample was filtered through a 0.45 µm syringe filter whereafter 20 µl was injected into a Hewlett Packard 1100 HPLC system. Humic molecular fractions were separated on a TSK G3000SW column (7.5 mm × 300 mm) at a flow rate of 0.7 ml/min and 0.01 M sodium acetate as the mobile phase. A 70 mm guard column of the same phase was used to protect the analytical column. The peak area of each fraction was measured after detection at 254 nm.

Analytical procedure for THM detection

The halogenated DBPs formed after chlorination are mainly THMs (Knight *et al.* 2011; Kristiana *et al.* 2011). After sampling the chlorinated water for THM analysis, ascorbic acid was immediately added to quench the disinfectant residual. Samples were analysed using a headspace sampler (Agilent 7697A) coupled to a gas chromatograph (Agilent 6890N). After the separation of the THMs on the capillary gas chromatography column (J & W Scientific, 30 mm × 0.530 mm × 0.5 µm) detection was carried out with an electron capture detector. The four THMs determined in the final water samples were: bromoform, chloroform, dibromochloromethane (DBCM) and bromodichloromethane (BDCM). As well as their individual concentrations, their sum was also reported as total trihalomethane (TTHM) in µg/L. The detection limits were as follows: bromoform 0.36 µg/L, chloroform 0.21 µg/L, DBCM 0.33 µg/L and BDCM 0.27 µg/L.

RESULTS AND DISCUSSION

NOM characterization

Water from the Vaal Dam typically has a medium colour (19–168 CU), high turbidity (34–100 NTU), high pH (6.5–8.8) and a conductivity between 16 and 25 mS/m. The SUVA value of a water sample can be used to indicate whether the composition of NOM in a water sample is mainly humic matter, non-humic matter or a mixture of the two (Edzwald & Tobiason 2010). The SUVA of the raw water feeding into the plant is within the range of 2 to 4 L/mg m. This is an indication that the source water is a

mixture of humic and non-humic matter, containing NOM of low and high molecular weights and has both a HPO and HPI character (Edzwald & Tobiasson 2010).

NOM was fractionated by the modified PRAM technique resulting in three fractions, with results of the first 3 years presented in Figure 1. The fractionation was performed between October and February to monitor the change in polarity within the surface water due to rainfall. Results from Figure 1 indicate the average NOM fraction distribution during the various seasons as $TPI > HPO > HPI$ with the exception of the high flow season of year 1 (2010–2011) where the TPI fraction decreased from 78.2 m^{-1} to 34.4 m^{-1} . Also, an increase in the HPO and HPI fractions was observed during the high flow season of year 1 (2010–2011) when terrestrial run-off into the dam and rivers upstream of the Vaal Dam was high. The TPI fraction extracted using the SPE NH_2 anion exchange resin represents the negative charges associated with organic matter (Rosario-Ortiz *et al.* 2007). Vaal Dam source water generally has a high anion exchange capacity and a high negative charge as indicated by the TPI fraction being the dominant fraction. The TPI fraction also

showed high variation throughout the study period with a UV_{254} of 78.2 m^{-1} in year 1 to 13.8 m^{-1} in year 3 indicating the variable structure of NOM during the 3 years (Figure 1).

During a typical rain season (year 2, 2011–2012) the HPO and HPI fractions decreased, as opposed to the fractions that stayed unchanged during the third high flow season (year 3, 2012–2013). Distribution of the three NOM fractions, HPO, HPI and TPI in the low and high flow seasons had almost the same distribution in the third year. A possible reason for the unchanged HPO, HPI and TPI fractions during the low and high flow seasons of year 3 could be attributed to rainfall that had already started in October during the low flow season as indicated by an average rainfall of 234.0 mm in the low flow season (year 3) compared to 62.0 mm and 135.8 mm in year 1 and year 2, respectively (Table 1). Results from the PRAM technique indicate that not only do seasonal changes in NOM character occur, but NOM hydrophobicity also changes yearly, which coincides with a study performed by Bazrafshan *et al.* (2012) suggesting that seasonal variation in NOM does not follow a particular pattern.

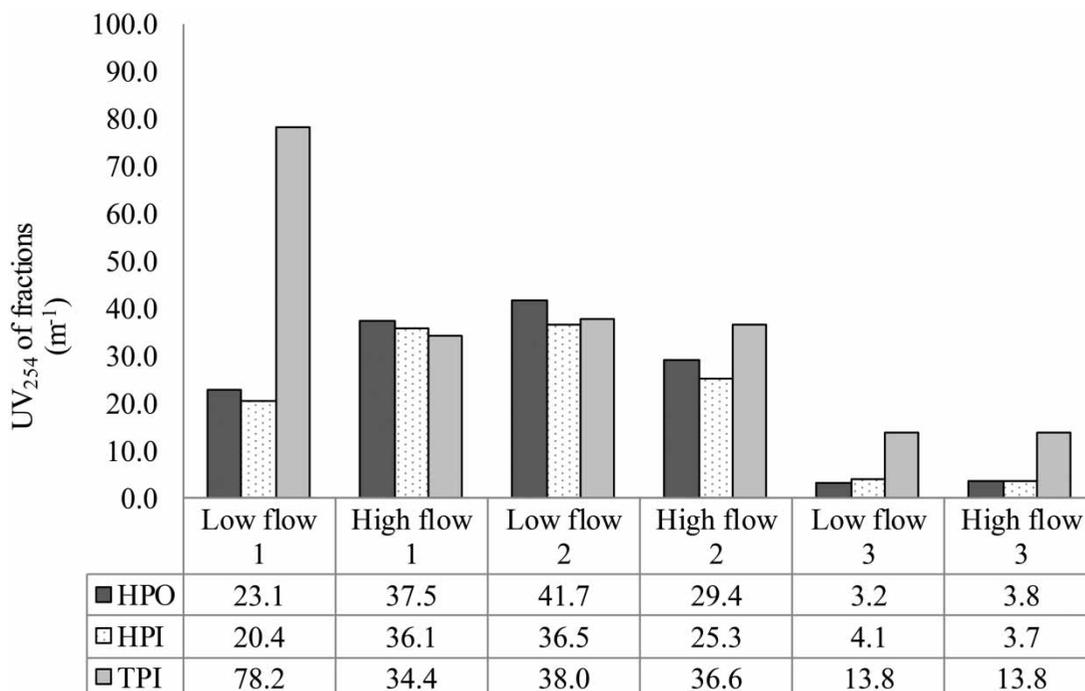


Figure 1 | Annual and seasonal variation of the fractions eluted by modified PRAM.

Table 1 | Mean values of organic loading in the surface water and mean percentage removal in brackets

Period	Parameter			
	DOC (mg/L)	UV ₂₅₄ (m ⁻¹)	SUVA (mg/L m)	Rainfall (mm)
Year 1: 2010–2011	6.1	98.3	–	65.1
Low flow	5.9 (22.1)	99.3 (87.3)	–	62.0
High flow	6.4 (22.0)	96.8 (85.4)	–	524.0
Year 2: 2011–2012	6.1	40.2	4.3	50.2
Low flow	5.7 (24.2)	74.0 (80.2)	5.2	135.8
High flow	6.4 (28.4)	28.0 (68.4)	4.2	316.0
Year 3: 2012–2013	4.7	15.4	3.2	65.8
Low flow	4.5 (20.1)	15.5 (51.2)	3.3	234.0
High flow	4.9 (25.3)	15.3 (62.1)	3.0	358.0
Year 4: 2013–2014	4.8	17.5	3.4	40.8
Low flow	4.4 (23.4)	16.3 (53.7)	3.5	85.0
High flow	4.8 (24.4)	18.5 (61.4)	3.4	282.0
Year 5: 2014–2015	5.8	24.0	4.4	31.9
Low flow	6.4 (21.7)	29.6 (56.8)	5.3	46.0
High flow	4.4 (15.7)	12.0 (34.2)	2.8	241.0

Mean of each year was calculated for June–February (2014–2015, i.e. June 2014–February 2015); low flow season: June–October; high flow season: November–February.

Organic loading and NOM removal

During the 5-year period the average DOC in the source water increased during the first four high flow seasons (Table 1). The mean DOC removal percentages during the first four high flow seasons (year 1 to year 4) also increased. An increase in DOC during different seasons was also documented by Sharp *et al.* (2006) which resulted in increased formation of DBPs. Mean raw water DOC values of year 5 followed a similar trend of smaller raw water DOC values during the high flow season accompanied by a decrease in the DOC removal percentage (Table 1). It has been documented that higher DOC levels result in higher DOC removal percentages (Parsons *et al.* 2004).

Not only is SUVA an indication of the amount of humic substances within a sample but it can also be used to predict NOM removal by the coagulation process (Parsons *et al.* 2004; Edzwald & Tobiason 2010). The raw water SUVA values decreased in all 5 years during the high flow season (Table 1). Since SUVA and UV₂₅₄ are a measure of the

aromaticity of NOM in a sample, a decrease in SUVA and UV₂₅₄ is indicative that NOM is less aromatic and less HPO (Kitis *et al.* 2002), and hence NOM will be more difficult to remove by the treatment process (Matilainen *et al.* 2005). Higher SUVA values imply that the NOM is dominated by humic substances and higher DOC removal can be expected by coagulation (Edzwald & Tobiason 2010). This was supported by the data where, though not strong, positive correlations were found between raw water UV₂₅₄ and UV₂₅₄ removal and also between raw water SUVA and UV₂₅₄ removal (Figure 2). This predicts that high SUVA values in the raw water will result in high UV₂₅₄ removal, which was also documented in other water treatment plants (White *et al.* 1997; Parsons *et al.* 2004). Greater UV₂₅₄ readings are indicative of NOM that is more aromatic and more HPO in nature (Kitis *et al.* 2002; Hassouna *et al.* 2014). Similar studies confirmed that HPO NOM had higher SUVA values indicated by a positive correlation between SUVA and HPO NOM (White *et al.* 1997; Chowdhury 2013). The prediction that NOM (UV₂₅₄) removal will increase when high UV₂₅₄ levels are observed in the raw water indicates that the coagulation process shows preference for removal of the HPO NOM fractions above the HPI fractions.

Furthermore, NOM (measured as UV₂₅₄) removal percentages decreased as predicted, during years 1, 2 and 5 (Table 1). UV₂₅₄ removal decreased from 87.3% to 85.4% in year 1, 80.2% to 68.4% in year 2 and decreased from 56.8% to 34.2% in the high flow season of year 5. SUVA values during the high flow and low flow seasons of year 3 (2012–2013) and year 4 (2013–2014) showed small variation decreasing from 3.3 L/mg m to 3.0 L/mg m (year 3) and 3.5 L/mg m to 3.4 L/mg m in year 4 (Table 1). According to the results in Table 1 during year 3 no change was also observed in the raw UV₂₅₄ values indicated by an average UV₂₅₄ of 15.5 m⁻¹ and 15.3 m⁻¹ during the low flow and high flow season, respectively. This minimal change in SUVA and UV₂₅₄ within the raw water resulted in an increase in the UV₂₅₄ removal percentages, increasing from 51.2% to 62.1% in the high flow season of year 3 and increasing from 53.7% to 61.4% in year 4. This confirms that SUVA and UV₂₅₄ of the raw water can be used as an indication of process performance in terms of NOM removal. The SUVA value of the final water in year 3 decreased from

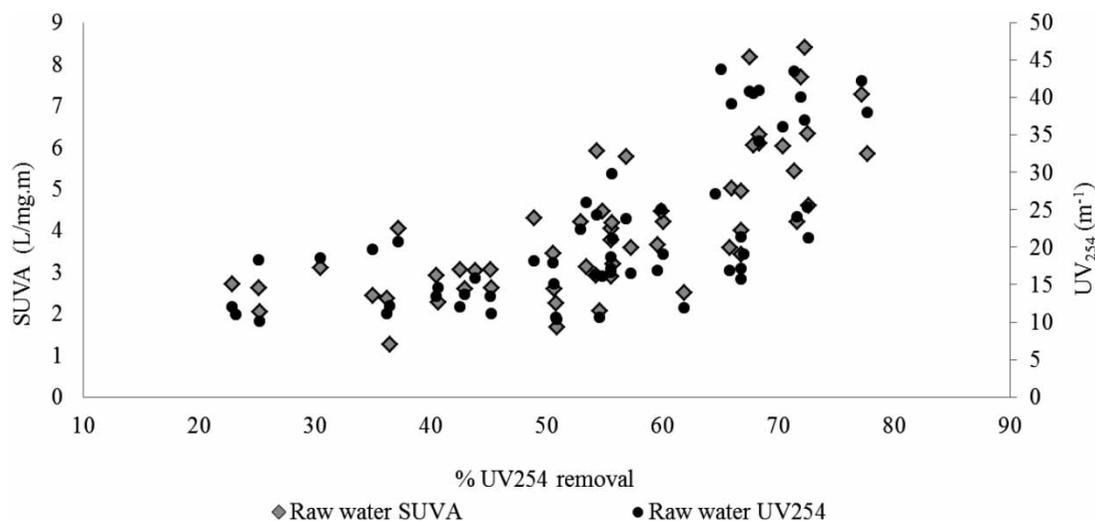


Figure 2 | Positive correlations between raw water SUVA and UV_{254} removal and between UV_{254} of the raw water and UV_{254} removal in the final water.

1.8 L/mg m in the low flow season to 1.5 L/mg m in the high flow season, this being the only year that the final water SUVA value was below 2 L/mg m. In a study done by [Kitis *et al.* \(2001\)](#) the SUVA of the treated water could not be reduced below 1.5 L/mg m using coagulation. It can be concluded that the final water SUVA value can be used to assess the plants' performance for NOM removal.

Using SUVA as an indicator of NOM treatability by coagulation, good NOM removal was achieved by the water treatment process as the more aromatic HPO NOM fraction was removed. This was evident over the 5-year period with an average NOM (UV_{254}) removal of 65%. NOM removal by other water treatment plants after sand filtration and granular activated carbon (GAC) filtration was documented as 83% and 19%, respectively ([Nkambule *et al.* 2012](#)), 20% by coagulation and 36% by GAC in a study done by [Chen *et al.* \(2007\)](#).

Correlations between low and high flow season and aromatic NOM characteristics (UV_{254} and SUVA) and DOC are not presented, due to their poor correlations ($R^2 < 0.5$). Although a decreasing trend in source water UV_{254} , lower SUVA values and increased TTHM was measured in the final water during the high flow seasons (summer), no clear seasonal relationship in NOM character was evident.

NOM characterization by HPSEC is based on the differential separation of molecules of different molecular sizes flowing through a porous matrix. During this separation

technique molecules larger than the gel pores are eluted first due to rapid movement through the column, while smaller molecules penetrate into the gel pores ([Pelekani *et al.* 1999](#); [Nissinen *et al.* 2001](#)). HPSEC analyses have extensively been used to determine the removal efficiency of NOM by water treatment plants specifically after the various treatment steps when comparing the MSD before and after treatment ([Nissinen *et al.* 2001](#); [Matilainen *et al.* 2002](#)). Five NOM fractions (five peaks) were eluted by HPSEC with peaks I–II being the high molecular weight (HMW) fraction and peaks III–IV the intermediate molecular weight (IMW) fraction. Peak V represents the low molecular weight (LMW) fraction ([Vuorio *et al.* 1998](#); [Nissinen *et al.* 2001](#)). [Figure 3](#) is a typical example of the chromatographs produced by HPSEC plotting peak profiles against retention time, which represents the molecular weight fractions eluted in each sample. The peak height of each fraction was measured in milli-absorbance units and retention time ranged between 0 and 20 minutes.

The HMW fraction accounted for up to 51% of the total NOM fractions. Results of the NOM MSD showed that on average 45% of the HMW fraction was removed from the final water; however, the LMW fraction (peak V) stayed unchanged in the final water indicating that this fraction was not removed by conventional water treatment ([Figure 3](#)). These results coincided with other studies indicating that conventional water treatment removes mostly the

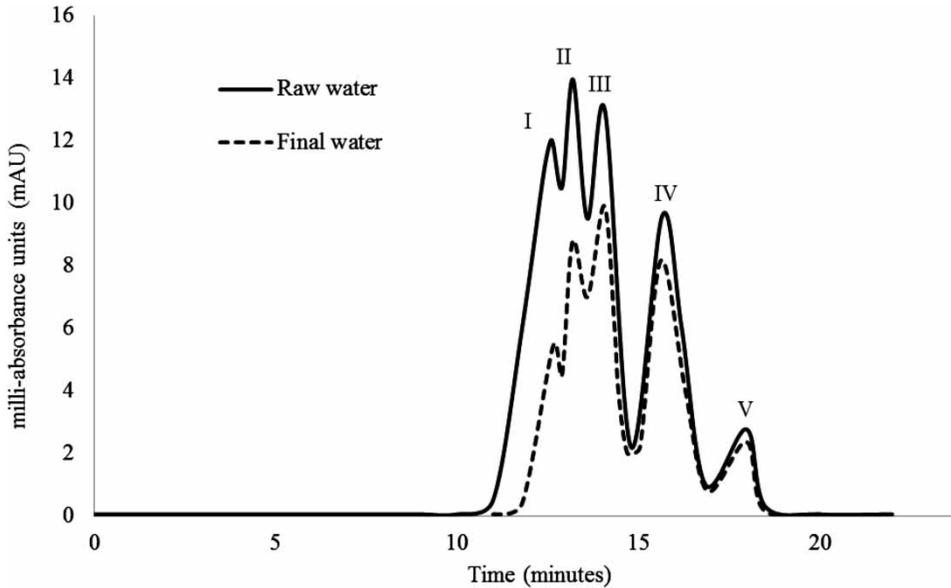


Figure 3 | Typical HPSEC chromatograph of humic fractions of the raw and final water indicating the change in molecular size after treatment.

HMW NOM and that the LMW are not easily removed (White *et al.* 1997; Chiang *et al.* 2002; Matilainen *et al.* 2005). It is recognized that the HMW fraction represents the humic- and fulvic-type compounds that leach from the soil and the LMW fraction represents the non-humic fractions (Szabó & Tuhkanen 2007).

The change in MSD throughout the water treatment process is presented in Figure 4 and displays NOM removal based on molecular size after the various treatment steps. Figure 4 is a summative graph of the peak profiles from the HPSEC chromatographs and compares the removal of

the NOM molecular sizes in a bar graph after sedimentation, filtration, and primary and secondary disinfection by the full-scale water treatment plant. A greater reduction of the HMW NOM (peaks I and II) and IMW (peak III) in the water after sedimentation is observed and was also observed in other conventional water treatment plants (Vuorio *et al.* 1998; Matilainen *et al.* 2002). These LMW non-humic fractions are more highly charged than the humic HMW NOM fractions and are therefore more difficult to destabilize during precipitation and coagulation in conventional water treatment. Additional removal after

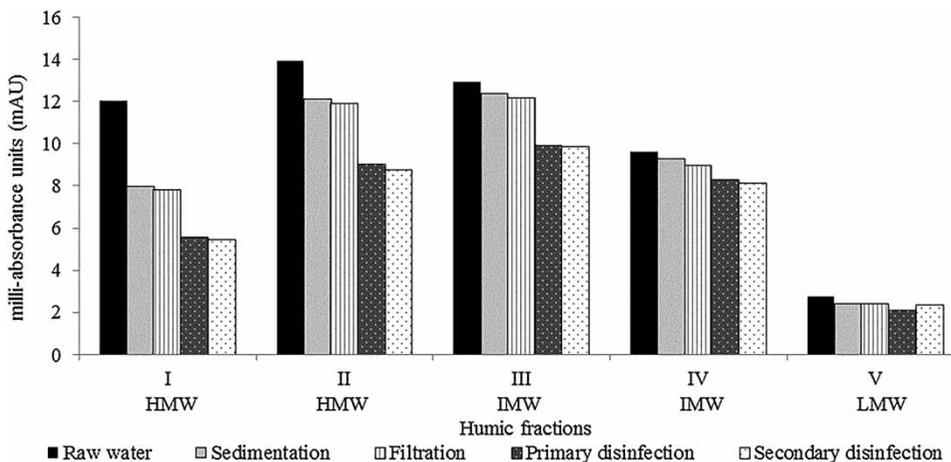


Figure 4 | MSD of the humic fractions indicated by the average peak heights after the various treatment steps.

filtration (rapid gravity sand filtration) was not observed, indicating that coagulation primarily removes the HMW NOM. After primary disinfection (chlorination) further removal of the HMW and IMW NOM is evident (Figure 4).

THM detection

The THMs measured in the final water after chlorination consisted of bromoform, chloroform, DBCM and BDCM. Since bromoform and DBCM were always under the detection limits of 0.36 µg/L and 0.33 µg/L, respectively, during this study, the results are presented as the sum of the four THMs measured (TTHM). Chloroform constituted on average 85% of the total TTHM concentration. Chowdhury (2013) demonstrated that HMW NOM forms up to 75% more chloroform than LMW NOM and that NOM of LMW is mostly responsible for the formation of DBCM and BDCM. Since the formation of DBCM was below the detection limit during this study period and because brominated THM (DBCM) was not the major THM constituent it can be concluded that the THM formed during this study was mostly due to the HMW NOM fraction not being removed. This is supported by Chowdhury (2013) illustrating that brominated THM formation decreases with an increase in molecular weight and that LMW NOM is a precursor for brominated THMs (Hua & Reckhow 2007). The LMW NOM fractions are also strongly associated with *N*-nitrosodimethylamine formation after chloramination as indicated

by a correlation of $R^2 = 0.898$ (Qi *et al.* 2014). It is clear that not only is NOM hydrophobicity substantial in determining treatability of organic matter (Hu *et al.* 2003) but also that the molecular weight of NOM strongly correlates to specific DBP classes during chlorination and chloramination (Hua *et al.* 2015). In a study performed by Chiang *et al.* (2002) the HPO group was mostly associated with the formation of THMs indicated by a trihalomethane formation potential (THMFP) of 194 µg/mg. Świetlik *et al.* (2004) also demonstrated that organics with larger molecular weights are more reactive to disinfectants, causing decomposition of the HMW fractions, illustrating that THM formation is highly influenced by this HPO fraction.

Figure 5 summarizes the distribution of the TTHM data during the low and high flow seasons. A seasonal increase of TTHM formation during the high flow seasons of year 1 to year 4 is illustrated. An increase in the average TTHM concentration as well as greater variation in the data were observed during the high flow seasons of year 1 (high flow 1) and year 4 (high flow 4), when floods were evident in the catchment area of the Vaal Dam. Although the mean TTHM was well below 100 µg/L during the entire study period, its formation was also the highest during year 1 and year 4 in the high flow season. Opposite to the average TTHM during the first two years, which increased during a high flow season, a small seasonal increase in the TTHM concentration was observed during the high flow season of year 3 (high flow 3). TTHM formation in year 3 increased

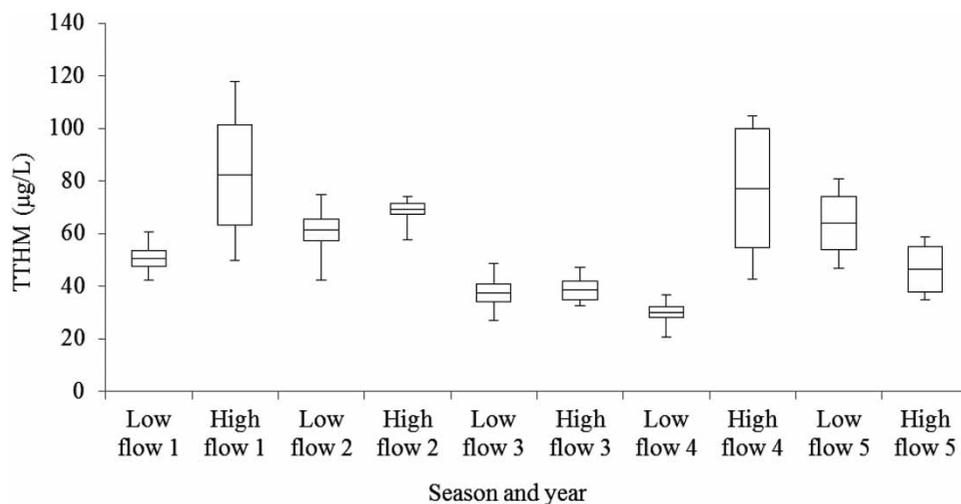


Figure 5 | TTHM formation in the final water during the low and high flow seasons.

on average from 37.1 $\mu\text{g/L}$ to 38.2 $\mu\text{g/L}$. These increased TTHM levels during the high flow seasons (summer months) coincided with results from a study done by Knight *et al.* (2011) where an increase in TTHM was also observed during summer. However, TTHM decreased in year 5 from 60.8 $\mu\text{g/L}$ in the low flow season to 42.9 $\mu\text{g/L}$ in the high flow season (Figure 5). It was also noted that year 5 (June 2014–February 2015) was the only period where raw water DOC and mean DOC removal decreased during the high flow season (Table 1). In addition to smaller DOC values, year 5 received the lowest rainfall during the high flow season (241.0 mm) compared to the previous 4 years average rainfall during the high flow (rain) seasons.

Controversially, studies have demonstrated the use of SUVA and UV_{254} as surrogate parameters for DBP formation by demonstrating positive regression coefficients between UV_{254} or SUVA and TTHM formation potential (Kitis *et al.* 2002; Parsons *et al.* 2004). Although an increase in TTHM formation and accompanying decrease in UV_{254} removal (Table 1) by the water treatment plant during high flow seasons 1 and 2 were experienced, poor correlations between raw water UV_{254} and TTHM ($R^2 = 0.1874$) and between SUVA and TTHM ($R^2 = 0.1117$) in the final water were evident (Figure 6). These small regression coefficients between UV_{254} and TTHM suggest that aromatic compounds are not the only precursors to the THMs formed. Similar results suggesting nonaromatic compounds contribute to the formation of THMs were reported by Weishaar *et al.* (2003) and the total SUVA of the source water was not strongly correlated to THM formation potential. Hua

et al. (2015) studied the relationship between SUVA and the different chlorinated and chloraminated DBP classes based on the hydrophobicity and molecular weight of NOM fractions and also observed weak correlations between SUVA and TTHM during chlorination, and observed no correlation between SUVA and chloramination THMs.

CONCLUSIONS

The novelty of this study is that it demonstrates variability in NOM character in Vaal Dam surface water during a 5-year study period and shows that a definite seasonal pattern could not be predicted. A low and high flow NOM seasonal relationship based on the aromatic character of NOM was not evident since the results did not show a strong correlation using Pearson's correlation. Seasonal influence on organic loading and NOM removal did however exist as indicated by an increase in DOC and less-aromatic NOM (reduced source water SUVA) which resulted in an increase in the average TTHM formation during high flow (summer) seasons. Conventional water treatment is more prone to removal of HMW aromatic humic matter compared with LMW less-aromatic NOM. Average NOM removal achieved by the water treatment plant was 65% and correlated well with the treatability prediction (SUVA) made based on raw water NOM composition. Decreased UV_{254} removal percentages were noted when raw water SUVA was low during the high flow seasons.

NOM removal was not affected by seasonal influence but rather by organic loading, as high NOM removal can

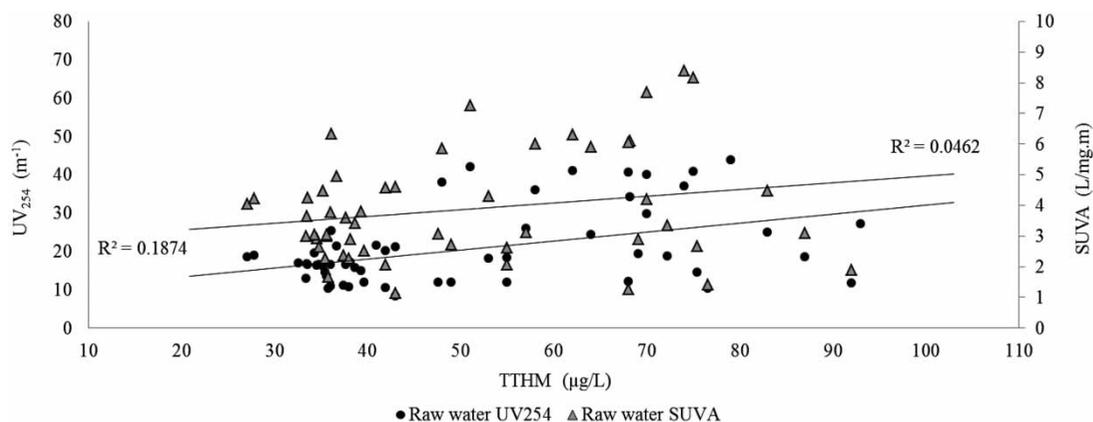


Figure 6 | Weak positive correlation between aromatic NOM (UV_{254} and SUVA) in the source water and TTHM measured in the final water.

be expected during times of increased DOC or UV₂₅₄ absorbancies. Measuring the aromatic carbon content of NOM could not be used as an indicator of NOM reactivity with chlorine since SUVA did not correlate well with TTHM formation in the final treated water. This indicates that aromatic humic compounds were not the only precursors to the TTHMs formed and the reactivity of non-humic substances with the disinfectant should in future also be investigated. Also, THMFP and not TTHM formed in the final treated water should be considered when investigating the influence of individual NOM fractions and their reactivity with chlorine and chloramine.

The change in NOM polarity over the years and also during the different seasons necessitates NOM characterization and monitoring of NOM removal on a continuous basis. This study stresses the need to implement advanced NOM characterization techniques during NOM monitoring to provide insight into NOM character and reactivity of the individual NOM fractions with the disinfectants used at the Rand Water treatment plant.

ACKNOWLEDGEMENTS

This study was financed by Rand Water and the University of South Africa (UNISA). The authors wish to express gratitude towards the Analytical Services Department at Rand Water and also to Mr Johan Hendriks from North West University, South Africa for their analytical assistance. The authors are also grateful for funding and support received from the Water Research Commission (WRC) of South Africa.

REFERENCES

- Bazrafshan, E., Biglari, H. & Mostafapour, F. K. 2012 Determination of hydrophobic and hydrophilic fractions of natural organic matter in raw water of Zahedan water treatment plant. *Journal of Health Scope* **1** (1), 25–28.
- Carpenter, S. R., Cole, J. J., Pace, M. L., Van de Bogert, M., Bade, D. L., Bastviken, D., Gille, C. M., Hodgson, J. R., Kitchell, J. F. & Kritzberg, E. S. 2005 Ecosystem subsidies: terrestrial support of aquatic food webs from ¹⁵C addition to contrasting lakes. *Ecology* **86** (10), 2737–2750.
- Chen, C., Zhang, X., He, W., Lu, W. & Han, H. 2007 Comparison of seven kinds of drinking water treatment processes to enhance organic material removal: a pilot test. *Science of the Total Environment* **382**, 93–102.
- Chiang, P. C., Chang, E. E. & Liang, C. H. 2002 NOM characteristics and treatabilities of ozonation processes. *Chemosphere* **46**, 929–936.
- Chowdhury, S. 2013 Trihalomethanes in drinking water: effect of natural organic matter distribution. *Water SA* **39** (1), 1–8.
- Edzwald, J. K. & Tobiason, J. E. 2010 Chemical principles, source water composition, and watershed protection. In: *Water Quality and Treatment – A Handbook on Drinking Water*, 6th edn (J. K. Edzwald, ed.). AWWA and McGraw-Hill, New York, USA, pp. 2222–2223.
- Hanson, P. C., Buffam, I., Rusak, J. A., Stanley, E. H. & Watras, C. 2014 Quantifying lake allochthonous organic carbon budgets using a simple equilibrium model. *Limnol. Oceanogr.* **59** (1), 167–181.
- Hassouna, M. E. M., Badawy, M. I., Gad-Allah, T. A. & Said, M. H. 2014 Fate of natural organic matter for raw and conventionally treated waters of El-Fayoum Governorate, Egypt. *International Journal of Advanced Research* **2** (3), 787–794.
- Hu, J. Y., Ong, S. L., Shan, J. H., Kang, J. B. & Ng, W. J. 2003 Treatability of organic fractions derived from secondary effluent by reverse osmosis membrane. *Water Research* **37**, 4801–4809.
- Hua, G. & Reckhow, D. A. 2007 Characterization of disinfection byproduct precursors based on hydrophobicity and molecular size. *Environmental Science and Technology* **41** (9), 3309–3315.
- Hua, G., Reckhow, D. A. & Abusallout, I. 2015 Correlation between SUVA and DBP formation during chlorination and chloramination of NOM fractions from different sources. *Chemosphere* **130**, 82–89.
- Khodse, V. B. & Bhosle, N. B. 2011 Bacterial utilization of size fractionated dissolved organic matter. *Aquatic Microbial Ecology* **64**, 299–309.
- Kitis, M., Karanfil, T., Kilduff, J. E. & Wigton, A. 2001 The reactivity of natural organic matter to disinfection byproducts formation and its relation to specific ultraviolet absorbance. *Water Science and Technology* **43** (2), 9–16.
- Kitis, M., Karanfil, T., Wigton, A. & Kilduff, J. E. 2002 Probing reactivity of dissolved organic matter for disinfection by-product formation using XAD-8 resin adsorption and ultrafiltration fractionation. *Water Research* **36**, 3834–3848.
- Knight, N., Watson, K., Carswell, S., Comino, E. & Shaw, G. 2011 Temporal and spatial variation of trihalomethanes and haloacetic acids concentration in drinking water: a case study of Queensland, Australia. *Air, Soil and Water Research* **4**, 1–17.
- Kristiana, I., Joll, C. & Heitz, A. 2011 Powdered activated carbon coupled with enhanced coagulation for natural organic matter removal and disinfection by-product control: application in a Western Australian water treatment plant. *Chemosphere* **83** (5), 661–667.

- Matilainen, A., Lindqvist, N., Korhonen, S. & Tuhkanen, T. 2002 Removal of NOM in the different stages of the water treatment process. *Environment International* **28**, 457–465.
- Matilainen, A., Lindqvist, N. & Tuhkanen, T. 2005 Comparison of the efficiency of aluminium and ferric sulphate in the removal of natural organic matter during drinking water treatment process. *Environmental Technology* **26**, 867–876.
- Myllykangas, T., Nissinen, T. K., Rantakokko, P., Martikainen, P. J. & Vartiainen, T. 2002 Molecular size fractions of treated aquatic humus. *Water Research* **36**, 3045–3053.
- Nissinen, T. K., Miettinen, I. T., Martikainen, P. J. & Vartiainen, T. 2001 Molecular size distribution of natural organic matter in raw and drinking waters. *Chemosphere* **45**, 865–873.
- Nkambule, T. I., Krause, R. W. M., Mamba, B. B. & Haarhoff, J. 2012 Natural organic matter (NOM) in South African waters: NOM characterisation using combined assessment techniques. *Water SA* **38** (5), 697–706.
- Parsons, S. A., Jefferson, B., Goslan, E. H., Jarvis, P. R. & Fearing, D. A. 2004 Natural organic matter – the relationship between character and treatability. *Water Science and Technology: Water Supply* **4** (5–6), 43–48.
- Pelekani, C., Newcombe, G., Snoeyink, V. L., Hepplewhite, C., Assemi, S. & Beckett, R. 1999 Characterization of natural organic matter using high performance size exclusion chromatography. *Environmental Science and Technology* **33** (16), 2807–2813.
- Qi, W., Fang Yee, L. & Jiangyong, H. 2014 Relationship between organic precursors and *N*-nitrosodimethylamine (NDMA) formation in tropical water sources. *Journal of Water and Health* **12** (4), 736–746.
- Rosario-Ortiz, F. L., Kozawa, K., Al-Samarrai, H. N., Gerringer, F. W., Gabelich, C. J. & Suffet, I. H. 2004 Characterisation of the changes in polarity of natural organic matter using solid-phase extraction: introducing the NOM polarity rapid assessment method (NOM-PRAM). *Water Science and Technology: Water Supply* **4**, 11–18.
- Rosario-Ortiz, F. L., Snyder, S. A. & Suffet, I. H. 2007 Characterization of dissolved organic matter in drinking water sources impacted by multiple tributaries. *Water Research* **41**, 4115–4128.
- Sharp, E. L., Parsons, S. A. & Jefferson, B. 2006 Seasonal variations in natural organic matter and its impact on coagulation in water treatment. *Science of the Total Environment* **363**, 183–194.
- South African National Standard (SANS241-1:2015) *Drinking Water. Part 1: Microbiological, Physical, Aesthetic and Chemical Determinants*. South African Bureau of Standards (SABS) Division, Pretoria, South Africa. www.sabs.co.za/standards/index.asp (accessed 18 April 2016).
- Świetlik, J., Dąbrowska, A., Raczek-Stanisławiak, U. & Nawrocki, J. 2004 Reactivity of natural organic matter fractions with chlorine dioxide and ozone. *Water Research* **38**, 547–558.
- Szabó, H. M. & Tuhkanen, T. 2007 Deterioration of drinking water sources through leaching of organic matter – development of a method to identify the source of leaching. In: *International Symposium on New Directions in Urban Water Management*. 12–14 September 2007, UNESCO, Paris, France.
- Vuorio, E., Vahala, R., Rintala, J. & Laukkanen, R. 1998 The evaluation of drinking water treatment performed with HPSEC. *Environment International* **24** (5/6), 617–623.
- Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R. & Mopper, K. 2003 Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environmental Science and Technology* **37** (20), 4702–4708.
- White, M. C., Thompson, J. D. & Singer, P. C. 1997 Evaluating criteria for enhanced coagulation compliance. *J. Am. Water Works Assoc.* **89** (5), 64–77.

First received 27 July 2016; accepted in revised form 17 February 2017. Available online 9 March 2017