

## Practical Paper

# Characteristics of natural organic matter and formation of chlorination by-products at Masaka waterworks

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### ABSTRACT

To minimise the formation of chlorination by-products (CBPs) it is imperative that attention is directed towards the structure and occurrence of natural organic matter (NOM) in raw water sources, and its flow and fate during water treatment processes. In this study, an assessment of the characteristics and flow of NOM along the treatment train at the full scale treatment plant at Masaka, Uganda, was made. Results indicated that 79% of the NOM, determined as total organic carbon, was in the dissolved form (DOC) with 83% of the DOC being hydrophilic in character. The insignificant amount of hydrophobic fraction in the raw water implies that the contributing fraction to THMs formation was mainly the hydrophilic component which subsequently was poorly removed along all units except clarification. The treated water from all unit processes provided specific ultraviolet absorbance values greater than 2 L/mg-m at 254 nm wavelength, indicating that it still had a high potential of reacting with chlorine to form CBPs. This renders water from Nabajjuzi River as unsuitable for chlorination in early stages of treatment and necessitating modification of the processes to reduce or avoid formation of unwanted by-products.

**Key words** | chlorination by-products, drinking water, natural organic matter

### INTRODUCTION

The drinking water industry is required to minimise disinfection by-products (DBPs) formation while ensuring adequate disinfection. Given the inevitable occurrence of natural organic matter (NOM) in all natural water sources, more attention should be directed towards the systematic consideration of NOM – its structure and occurrence in raw water sources, and its flow and fate during water treatment processes. NOM influences the availability and migration of nutrients and pollutants in the environment and largely controls drinking water purification processes (Wong *et al.* 2002). It reacts with chlorine to form CBPs such as trihalomethanes (THMs). DBPs formed as a result of such reactions have been associated with potential health effects that include carcinogenicity, adverse reproductive and developmental effects, and immunotoxic and neurotoxic effects (Amy *et al.* 1988; Arruda & Fromm 1989; Dodds *et al.* 1999; Barrett *et al.*

2000; Yang *et al.* 2000; Gunten *et al.* 2001; Ivancev *et al.* 2002; Cedergren *et al.* 2002; Westerhoff *et al.* 2004). Additionally, NOM is responsible for colour, undesirable taste and odour in natural waters; is a source of nutrients for heterotrophic bacteria; promotes bacterial re-growth and deposition of particles in the distribution system (Escobar & Randall 2000; Lehtola *et al.* 2001; Liu *et al.* 2002) which compromises water quality and increases turbidity at the consumer. The amount and nature of DBPs formed depend on the type of oxidant in use and the characteristics of NOM in a given water source. Therefore, characterisation of NOM is essential in understanding how best to remove it (Barrett *et al.* 2000), though its characterisation is made difficult by the heterogeneous size, structure and functional chemistry of its constituent compounds and by the variation in NOM with origin, climate and season (Wong *et al.* 2002).

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Traditionally, NOM characterisation at most water utilities has focused on surrogate or general organic matter measurements such as total organic carbon (TOC). However, over the last decades, the importance of the size, structure and functionality of NOM has been recognised. The ratio of ultraviolet (UV) and dissolved organic carbon (DOC) – SUVA – is a good indicator of the humic content of water and has been correlated with DBP formation potential. Conventional coagulation removes a portion of NOM (Barrett *et al.* 2000). The nonpolar NOM (humic substances or hydrophobic NOM) has been well characterised and is more readily removed by coagulation than polar (nonhumic) NOM (Dickenson & Amy 2000). Concerns regarding the potential health effects of these by-products have prompted several developed and industrialised countries to develop a number of regulations. The maximum contaminant level (MCL) of THMs and halo acetic acids (HAAs) was set to 80 and 60 µg/L, respectively, by the Environmental Protection Agency (EPA) (Uyak *et al.* 2008). On the other hand, the European Union regulation limit for total THM concentration in drinking water is 100 µg/L (Uyak *et al.* 2008). The World Health Organization guidelines are 200 µg/L for chloroform, 60 µg/L for bromodichloromethane, 100 µg/L for dibromochloromethane, 90 µg/L for dichloroacetonitrile and 100 µg/L for dibromoacetonitrile (WHO 2004). In South Africa, the

water sector is understandably concerned about the levels of NOM in drinking water and set the DOC guideline limit of 5 mg/L and a maximum of 10 mg/L, this culminated in a number of studies on the flow and fate of NOM in treatment plants (Haarhoff *et al.* 2010). The TTHM limit in the same country is 200 µg/L.

In the developing world, swamp waters are a common source of drinking water and are known to contain high concentrations of NOM and metals such as iron. With the most common processes for removing iron from such water being aeration and oxidation using chlorine that reacts with NOM to form chlorination by-products, unlike elsewhere in the world, the water sector in East and Central Africa has not yet taken the effects arising from reactions of chlorine and NOM in drinking water treatment seriously. Therefore, the aim of this study was to assess the characteristics and levels of NOM at Masaka raw water sources and along the water treatment train. Examples of studies that have been carried out at different water treatment plants elsewhere are given in Table 1.

## STUDY AREA

The Masaka waterworks are located 5 km from Masaka Municipal Town in southern Uganda, approximately

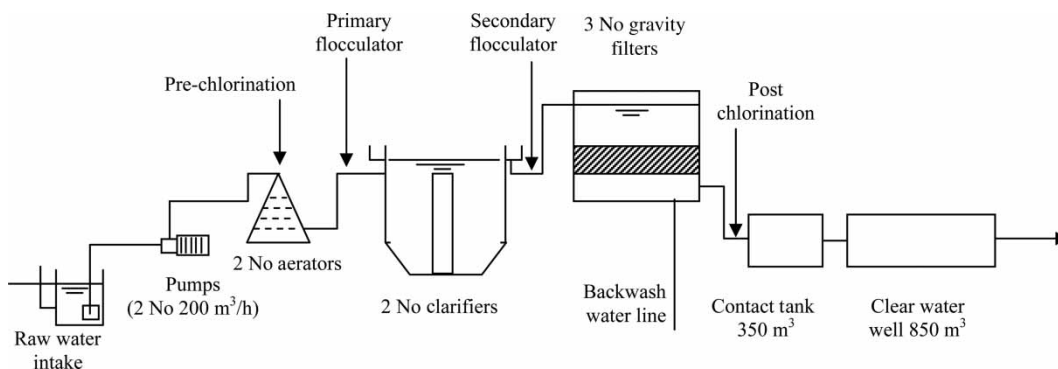
**Table 1** | Similar studies that have been carried out at various water treatment plants

Location	Plant	Unit processes	Characterisation
South Africa	Vaalkop	EC, ozonation, granular activated carbon and chloramination	Hydrophobic and hydrophilic fractions using XAD resins (Nkambule <i>et al.</i> 2009) DOC (Haarhoff <i>et al.</i> 2010)
	Vereenignig Balkfontein	EC, sedimentation tank and chloramination	DOC (Haarhoff <i>et al.</i> 2010)
	Stilfontein	EC, sedimentation tank, rapid sand filtration and free chlorination	DOC (Haarhoff <i>et al.</i> 2010)
Namibia	Stilfontein	Dissolved air flotation, sedimentation tank, ozonation, rapid sand filtration and free chlorination	DOC (Haarhoff <i>et al.</i> 2010)
	Von Bach	Sedimentation tank, rapid sand filtration and free chlorination	DOC (Haarhoff <i>et al.</i> 2010)
Thailand	Goreangab	Pre-ozonation, EC, dissolved air flotation, rapid sand filtration, ozonation, biological activated carbon, granular activated carbon, ultra filtration and free chlorination	DOC (Haarhoff <i>et al.</i> 2010) BDOC & NBD (Haarhoff <i>et al.</i> 2010) Molecular weight distribution using HLSEC technique (Haarhoff <i>et al.</i> 2010)
	Takua Pa	Coagulation, sedimentation tank, filtration and free chlorination	TOC, THMs and Algae (Collivignarelli <i>et al.</i> 2008)

130 km southwest of Kampala. The water treatment works extract raw water from the River Nabajjuzi swamp dominated by *Cyperus papyrus*, L, where the water contains relatively high levels of both natural organic materials and iron. The waterworks comprise of two plants, Boma plant built in 1997 with a capacity of 5,000 m<sup>3</sup>/day and Bwala plant built in 1959. The Bwala plant was improved to restore the design capacity to 3,000 m<sup>3</sup>/day and it supplies water to some parts of Masaka town though it still has inherent structural problems. The treatment processes run from pre-chlorination, aeration, coagulation/flocculation, sedimentation, filtration to disinfection/chlorination. The pre-chlorination stage is mainly applied for the oxidation of iron in the raw water. Currently, only about 44% of the total production capacity of the waterworks (8,000 m<sup>3</sup>/day) is utilised. This is partly attributed to the inadequate distribution system and the available demand from the populace. It serves a population of 49,551 with the target population being 63,527. The study was carried out at Boma water treatment plant (BWTP), a schematic layout of which is indicated

in Figure 1. From January 2008 to December 2009, the BWTP abstracted raw water at a daily average rate of 2,170 m<sup>3</sup>. The production of BWTP alone is not known since part of the treated water is diverted to the clear-well of the Bwala water treatment plant and this is not metered. However, during the same period, the BWTP reservoir received treated water at a daily average rate of 1,730 m<sup>3</sup>/day while the supply from the Bwala clear-well was at a daily average rate of 1,807 m<sup>3</sup> higher than the raw water abstraction of 1,768 m<sup>3</sup>/day. Therefore, production at the BWTP is slightly higher than 1,730 m<sup>3</sup>/day. This indicates that over 10% of the water abstracted goes to waste at the waterworks.

The main focus of chemical treatment at the waterworks is reduction of colour and iron from the swamp water using calcium hypochlorite (HTH) and alum. Removal of colour, which is known to be caused by the presence of natural organic matter, and iron are the major challenges at the waterworks. The average raw water quality is indicated in Table 2. The maximum values are normally experienced during the dry season and it is during this season that



**Figure 1** | Schematic layout of the unit treatment processes at Masaka (Boma) water treatment plant.

**Table 2** | Raw water quality at Masaka water treatment plant

Parameter	Minimum	Maximum	Mean	± Standard deviation	± Standard error
DOC (mg C/L)	6.24	19.90	11.37	7.44	
pH ( <i>n</i> = 339)	5.06	6.71	6.15	0.18	0.17
Turbidity (NTU) ( <i>n</i> = 339)	16.00	84.00	33.65	9.90	1.96
Colour (PtCo) ( <i>n</i> = 339)	88.00	440.00	182.25	53.08	53.15
Conductivity (μS/cm) ( <i>n</i> = 339)	19.30	52.90	27.88	5.16	4.81
Alkalinity (mg as CaCO <sub>3</sub> /L) ( <i>n</i> = 48)	8.00	24.00	16.58	3.87	3.89
Total iron (mg Fe/L) ( <i>n</i> = 67)	1.87	11.66	5.09	2.05	2.03

there are significant problems in operation of the plant. Therefore, the pre-chlorination process is mainly used for the oxidation of iron, and soda ash is mainly used in the correction of pH. Treatment starts by passing raw water to aeration towers where at the same time a solution of HTH is dosed to oxidise iron. This is followed by coagulation/flocculation, sedimentation, filtration and post chlorination processes. Filtration takes place in rapid gravity sand filters.

## METHODS AND MATERIALS

Raw water and the treated water from each process were sampled once a day per week. Samples for the characterisation of NOM were collected in 40-mL glass bottles sealed with Teflon-lined septa caps. The bottles were filled slowly to overflowing so that no air was trapped with the sample and sealed tightly. The samples were kept at 4 °C and transported to the laboratory. Characterisation of NOM was performed with a size exclusion chromatography (LC-OCD) system (DOC-LABOR, Germany). In the system, a column TSK HW-50S is connected to a Graentzel thin-film reactor in which NOM is oxidised to CO<sub>2</sub> by UV before it is measured by infrared detection. A sample of up to 3 mL is injected into the instrument and filtered in-line with a 0.45 µm filter. The deposit on the filter is backwashed after 5 min and directly analysed with the TOC analyser to determine the particulate organic carbon (POC) content. The DOC concentration of samples was also measured by filtering the samples through a 0.45 µm filter before injection into the DOC detector. The column, which separates according to molecular size/weight, is able to fractionate NOM (that is, chromatographable fraction of DOC (CDOC)) 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). In addition to the organic carbon detector (OCD), the system also incorporates a UV detector (UVD) which may be used to assess the aromaticity of the sample as well as of the humic fraction by computing the respective SUVA values. Fractional composition was determined by integration of the area under each chromatogram using FIFFIKUS (DOC-

LABOR) software. HOC is the hydrophobic fraction. The humic substances peak was used for molecular weight determination by fitting a symmetrical Poisson distribution to the peak, which allows determination of average-weight MW ( $M_w$ ) and average number MW ( $M_n$ ). The  $M_w/M_n$  ratio gives an indication of the width of the size distribution characteristics. Samples for the analysis of bulk TOC and DOC were collected in 1-L amber-coloured glass bottles. No preservative was added to these bottles. Analysis was carried out using a Shimadzu TOC 5000A analyser. The TOC concentration was obtained by subtracting the inorganic carbon (IC) concentration from the total carbon (TC) concentration. To measure the TC, the sample was injected into a TC combustion tube filled with an oxidation catalyst heated to 680 °C. The TC component in the sample (composed of inorganic carbon and organic carbon), when combusted and decomposed, produced CO<sub>2</sub> that was detected by a non-dispersive infrared gas analyser (NDIR). The detection signal, in the form of a peak, was integrated into the peak area which is proportional to the TC concentration in the sample. For IC analysis, the sample was injected into an IC reaction vessel where the carrier gas was flowing in the form of gas bubbles in the acidified IC reagent. Only inorganic carbon-containing compounds are decomposed here to form CO<sub>2</sub> that is detected by the NDIR. Once again, the detector signal was converted into the peak area which is proportional to the IC concentration in the sample. A similar procedure was followed for DOC. pH and conductivity were measured on site using an Orion pH-meter and an Orion conductivity metre, respectively. Alkalinity was analysed using a HACH 2010 spectrophotometer. Colour and turbidity were measured using a HACH DR 4000 spectrophotometer. Samples for total iron were collected in glass bottles and preserved using 0.5 mL of nitric acid. Analysis was then carried out using an Atomic Absorption Spectrometer Perkin Elmer 2380 after digesting the samples with nitric acid. UV absorbance at 280 nm was measured using a Shimadzu UV-VIS 1601 spectrophotometer.

## RESULTS AND DISCUSSION

Results from the characterisation experiments of NOM indicated that 79% of the TOC was in the dissolved form (DOC)

while 83% of the DOC was hydrophilic in character. The hydrophobic organic carbon fraction was not detectable in the raw water. The hydrophilic acids and hydrophilic neutrals formed 51 and 14% of the total organic carbon, respectively. The different fractions obtained along the water treatment train are presented in Table 3. In some natural water sources, the hydrophobic fraction, which is much easier to remove by conventional treatment, has been reported to be the major component while in others the hydrophilic fraction dominates (Liang & Singer 2003). Lim *et al.* (2009) found the hydrophobic acids (40%) to be the most dominant followed by hydrophilic neutrals (22%) in the Semenyih River, Malaysia. Elsewhere, hydrophobic acids were reported to make up approximately 50% of the DOC (Thurman 1985; Owen *et al.* 1993). This indicates how NOM characteristics can vary from one location to another.

There was no variation observed in the characteristics of NOM along the train as indicated by the chromatographs in Figure 2. Over 97% removal of the particulate organic carbon and about 43% removal of the hydrophilic fractions were observed at the pre-treatment stage. The hydrophilic fraction was poorly removed (Figure 3) and there was no hydrophobic fraction in the raw water, implying that the major contributing fraction to THMs formation (Figure 4) was the hydrophilic component of NOM, which is not easy to remove by conventional processes. However, an increase in the hydrophobic fraction was noted in the pre-chlorinated and clarified water. Although Dickenson *et al.* (2000) made a similar observation on clarified water that had been pre-treated with ozone, which may indicate the production of soluble microbial products in the treatment train, the increase at the study plant was probably due to the build-up of slime observed on the walls of the collection basins of treated water in the aerators and clarifiers due to irregular cleaning of these units. Growth of slimes on the walls of the clarifiers due to irregular cleaning can increase the levels of dissolved organic matter that the plant must contend with (Ministry of Health 2005). This is further evidenced by the reduction of the hydrophobic fraction after disinfection. Whilst the relative reactivity of the hydrophobic fraction is typically higher than the hydrophilic fraction, there are a number of examples where this relationship does not always fit. For example, Owen *et al.* (1993) showed that hydrophilic material is the main cause for concern with regard to its THM formation

potential. It was reported that 65% of the TOC and 56% of the THMFP from the Colorado river was contributed by hydrophilic compounds and that these fractions were exerting the largest chlorine demand when compared to the hydrophobic material (2.4 mg Cl<sub>2</sub>/mg hydrophilic versus 0.32 mg Cl<sub>2</sub>/mg hydrophobic), which consequently led to a higher concentration of THMs.

Treated water from all the unit processes provided relatively high SUVA values (Figure 5). Related to the organic carbon, SUVA of a given water can give a good estimation of its reactivity against chlorine (Frimmel 2000). However, SUVA value obtained at wavelength of 254 nm (SUVA<sub>254</sub>) for raw water (3.97 L/mg-m) is inconsistent with the rest of the values in Table 3 because the hydrophilic fraction of NOM was the found to be the major component. Natural waters with high SUVA<sub>254</sub> values  $\geq 4$  L/mg-m have a relatively high content of hydrophobic, aromatic and high molecular weight NOM fractions, whereas waters with SUVA<sub>254</sub> of  $\leq 3$  L/mg-m contain largely non-humic, hydrophilic and low molecular weight materials (Świetlik & Sikorska 2005). This was probably due to the interference of other UV absorbing substances such as ferrous iron. The source water had an average total iron concentration of 5.09 mg/L. SUVA values were again determined at 280 nm (SUVA<sub>280</sub>) to minimise the interference. SUVA<sub>280</sub> values varied from 2.27 L/mg-m for raw water to 0.77 L/mg-m for final water. The results indicate the hydrophilic nature of NOM and imply that water from the various stages of the treatment still had a potential of reacting with chlorine to form DBPs. In their study, Rostad *et al.* (2000) reported SUVA of five water fulvic acids (the most similar to the hydrophilic acids isolated) to range from 2.86 to 4.28 L/mg-m, whereas SUVA of surface water humic acids, the most similar to colloids isolated, to range from 4.86 to 7.36 L/mg-m.

The hydrophilic fraction of the organic carbon was further fractionated into biopolymers (MW >20,000 g/mol), humic substances (approx. 1,000 g/mol), building blocks (300–500 g/mol), neutrals (<350 g/mol) and acids (<350 g/mol). The different components or fractions of the hydrophilic organic carbon are indicated in Figure 6. The hydrophilic component was mainly composed of biopolymers with low DON, humic substances, building blocks and low molecular weight neutral compounds. All the

**Table 3** | NOM characteristics along the Boma water treatment plant unit processes

	Partitioning of organic carbon (OC)						Chromatographic fractionation of organic carbon (CDOC)									
	Approx. molecular weights in g/mol:						~1000 (see separate HS-Diagram)									
	TOC	DOC	POC	HOC	CDOC	Bio-	DON	Humic	DON	Aromaticity	Mol-	Building	<350	<350	(UV@254 nm)	SUVA
	Total OC	Dissolved	Particul.	Hydrophob.	Hydrophil.	Polymers	(Norg)	Subst.	(Norg)	(SUVA-HS)	Weight	Blocks	Neutrals	Acids	Inorg.	(SAC/OC)
	ppb-C	ppb-C	ppb-C	ppb-C	ppb-C	ppb-C	ppb-N	(HS)	(ppb-N)	L/(mg*m)	g/mol	ppb-C	ppb-C	ppb-C	SAC	L/(mg*m)
Raw water	10,117	7981	2136	-436	8,417	174	26	5,198	207	4.85	581	1631	1,414	0	0.38	3.97
% TOC	100	78.9	21.1	-4.3	83.2	1.7	-	51.4	-	-	-	16.1	14.0	0.0	-	-
Prechlorinated water	5,230	5,171	60	365	4,806	67	8	2,320	87	3.48	533	1,405	1,014	0	0.01	2.98
% TOC	100	98.9	1.1	7.0	91.9	1.3	-	44.4	-	-	-	26.9	19.4	0.0	-	-
Clarified water	5,122	5123	-1	557	4,566	52	7	2,247	77	3.16	523	1,274	993	0	0.01	2.68
% TOC	100	100.0	0.0	10.9	89.1	1.0	-	43.9	-	-	-	24.9	19.4	0.0	-	-
Filtered water	4,022	3,968	54	321	3,647	55	6	2,027	59	1.91	425	849	715	0	0.00	2.11
% TOC	100	98.7	1.3	8.0	90.7	1.4	-	50.4	-	-	-	21.1	17.8	0.0	-	-
Final water	4,743	4,570	173	51	4,519	48	1	2,728	81	2.14	519	1,083	659	0	0.03	2.15
% TOC	100	96.4	3.6	1.1	95.3	1.0	-	57.5	-	-	-	22.8	13.9	0.0	-	-

DON, Dissolved organic nitrogen.

TOC = DOC + POC, DOC = CDOC + HOC.

Note: POC, hence TOC may be too low.



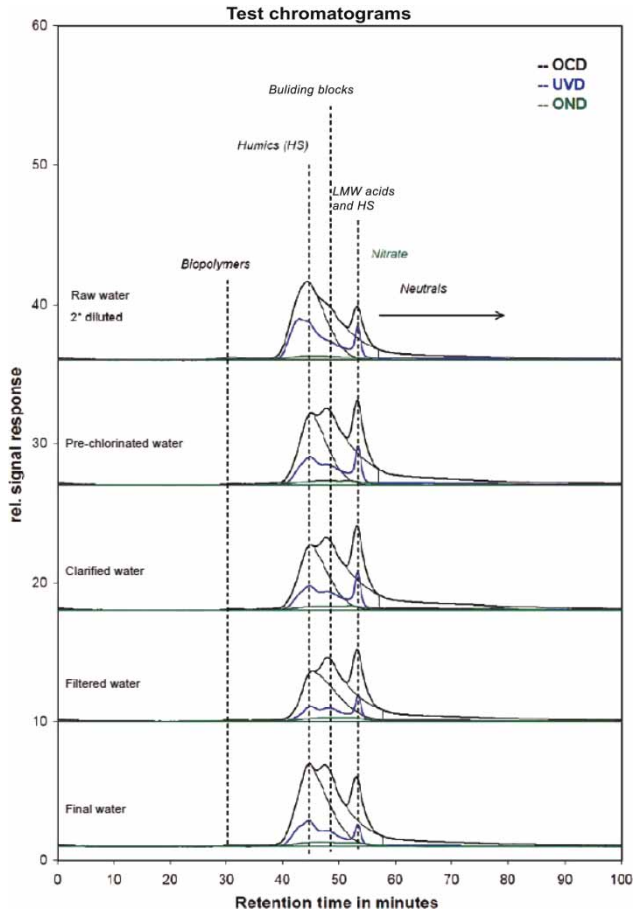


Figure 2 | Chromatograms of NOM along the water treatment train.

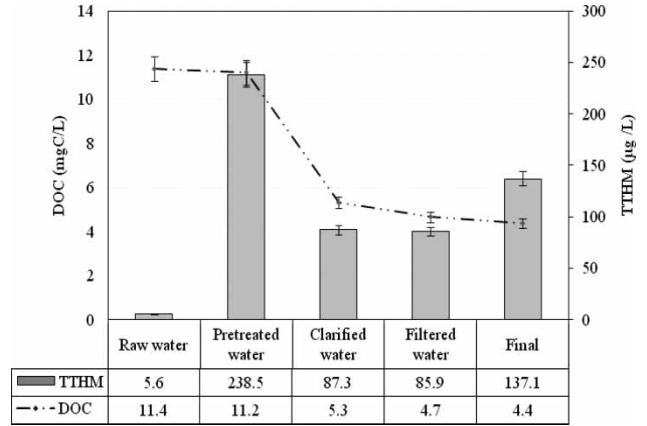


Figure 4 | Total trihalomethanes (TTHM) and DOC levels along the treatment train at Boma plant.

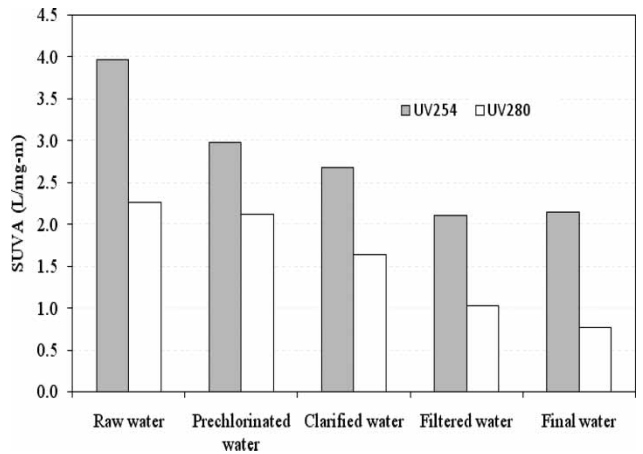


Figure 5 | SUVA of treated water after each unit process.

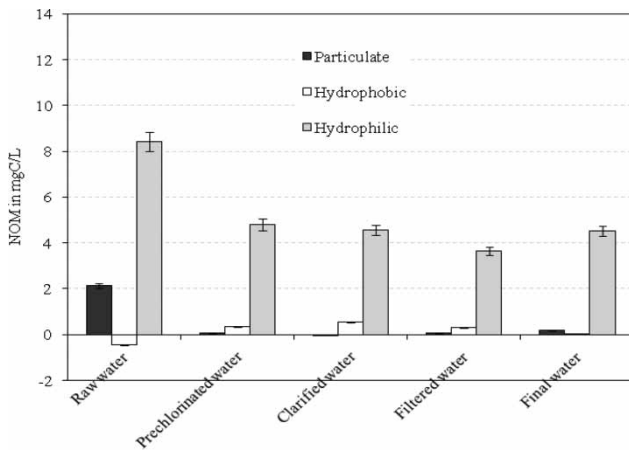


Figure 3 | NOM fractions along the treatment train at Boma plant for the period 2009 (n = 3).

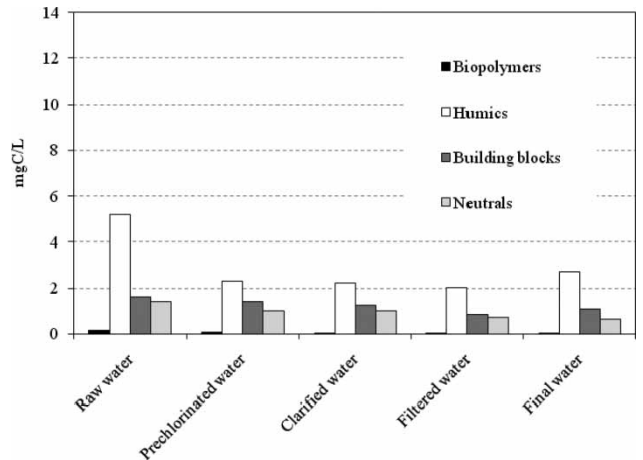


Figure 6 | Fractions of the hydrophilic NOM along the treatment train.

fractions apart from the biopolymers were poorly removed along the treatment train.

## CONCLUSIONS

The hydrophilic NOM formed the majority fraction of NOM at the Masaka raw water source and was poorly removed. Structural changes of NOM only occurred at the pre-chlorination stage, where most of the trihalomethanes are formed. This renders water from Nabajjuzi River unsuitable for chlorination in early stages of treatment.

The clarification (coagulation, flocculation and settling) process reduced the level of trihalomethanes formed which later increased on post chlorination, while the filtration stage had no impact on the by-products. Therefore, the existing treatment train is insufficient for the effective reduction of natural organic matter and control of formation of unwanted treatment by-products like trihalomethanes.

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