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Seasonal Variation of Organic Matter Concentration and Characteristics in the Maji ya Chai River (Tanzania): Impact on Treatability by Ultrafiltration

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Abstract

Many waters in Tanzania exhibit high concentrations of organic matter and dissolved contaminants such as fluoride. Due to bacteria and virus removal, ultrafiltration (UF) is an attractive option for drinking water treatment, and when coupled with adsorbents, may compete with other established processes like nanofiltration (NF) for lower contaminant concentrations. The results presented here examine the characteristics and treatability of tropical natural organic matter (NOM) by UF as a function of seasonal variation.

The Tanzanian river Maji ya Chai was sampled monthly during one year. The composition of NOM in Maji ya Chai River is influenced strongly by precipitation. Total organic carbon (TOC), specific ultraviolet absorbance (SUVA) and concentration of allochthonous organics substances (such as humic substances (HS)) are elevated in periods following high precipitation, while TOC is lower and contains more biopolymers in the dry seasons.

UF experiments with two regenerated cellulose membranes of different molecular weight cut-off (MWCO, 5 and 10 kDa) were conducted. UF is able to remove 50-95% of TOC with a seasonal variability of 10-20%. Due to the remaining NOM in the water that would contribute to disinfection by-product formation and bacterial regrowth, the physically disinfected water is more applicable for point of use systems than distribution or storage.

Keywords: organic matter, surface water, ultrafiltration, liquid chromatography organic carbon detection (LC-OCD)

1. Abbreviations

AFM: Atomic force Microscopy

A_M : Membrane surface area

DBP: Disinfection by-products

DOC: Dissolved organic carbon

EC: Electrical conductivity

GCM: Global climate modelling

HPSEC: High-performance size exclusion chromatography

HS: Humic substances

IC: Inorganic carbon

ICP-MS: Inductively coupled plasma mass spectrometry

J/J_0 : Normalized flux

J : Flux

LC-OCD: Liquid chromatography coupled with on-line organic carbon detection

LMW: Low molecular weight

MW: Molecular weight

MWCO: Molecular weight cut-off

NF: Nanofiltration

NMM: Nonhydrostatic meso-scale models

NOM: Natural organic matter

R : Retention

R_W : Recovery

SUVA: Specific UV absorbance

THM: Trihalomethanes

TOC: Total organic carbon

UF: Ultrafiltration

US EPA: US Environmental Protection Agency

UV_{254nm} : Ultraviolet absorbance at 254 nm

ρ_w : Water density

2. Introduction

Maji ya Chai is a river originating at Mt. Meru in Arusha National Park in the North of Tanzania located between Mt. Meru (4,565 m) and Mt. Kilimanjaro (5,895 m) (Figure 1). Its catchment is located in Arumeru district which is a rural, densely populated area (228 inhabitants km⁻²) with an annual population growth rate of 3.1% (Istituto Oikos 2011). The river's name refers to its brownish water color, Maji ya Chai means "water with tea" in Kiswahili. The intensity of this color varies with the seasons as reported in other regions and is indicative of natural organic matter (NOM). During the rainy seasons with high precipitation the river shows a more intensive brownish color than in dry seasons (Hongve et al. 2004). The NOM in Maji ya Chai originates from a tropical swamp which affects the nature of NOM and specifically molecular weight (MW), size, structure and functional groups. Aquatic NOM contains autochthonous organic substances originating from primary producers and macrophytes in the surface water itself, as well as allochthonous substances derived from surrounding terrestrial ecosystems, transported by water flowing over or through the soil and often transformed in waterways (Findlay and Sinsabaugh 2002, Johnson et al. 2011b).

Many environmental factors affect NOM quality and quantity, precipitation being one of them (Bouillon et al. 2012, Cawley et al. 2012, Wantzen et al. 2008). Rainfall is affected by climate change (Yamashita et al. 2010, Zhang et al. 2009) and global climate modelling (GCM) projections for Tanzania indeed predict increasing precipitation during the rainy season (McSweeney et al. 2010a, McSweeney et al. 2010b).

Naturally, tropical waters, including blackwaters, are expected to contain different organic matter to non-tropical waters (Gomez et al. 1991, Wantzen et al. 2008). Seasonal changes in precipitation will affect surface water quality, NOM characteristics, and low molecular weight (LMW) content and in consequence may challenge treatability (Vasyukova et al. 2012). One such challenge is biological regrowth potential of treated water, which increases with temperature (Baribeau et al. 2005). If the LMW compounds that are naturally abundant in tropical blackwaters are more biologically available is unknown. Given the naturally elevated temperatures in tropical regions producing water low in organic matter is paramount, yet to date no studies exist that treat and characterize tropical waters.

Humic substances (HS) are the major fraction of NOM, about 50% in river waters, extractable by sorption to XAD8 resin at acidic pH (Thurman 1985). Total organic carbon (TOC) or dissolved organic carbon (DOC) and ultraviolet absorbance at 254 nm (UV_{254nm}) are used to quantify the concentration of organic matter. Specific UV absorbance (SUVA) is used to estimate the aromatic

content and defined as the quotient of UV_{254nm} and DOC (Weishaar et al. 2003). The correlation between HS aromaticity, measured as molar absorptivity at 280 nm, and MW, was initially measured by high-performance size exclusion chromatography (HPSEC) (Chin et al. (1994)). A higher SUVA is correlated with a higher nominal MW and, thus, can give information about the size distribution of NOM. This correlation can be presented in form of a humification diagram (Huber and Frimmel (1996), Huber et al. (2011)) Using liquid chromatography coupled with on-line organic carbon detection (LC-OCD), biopolymers, HS, building blocks, LMW acids and neutrals can be quantified (Huber et al. 2011). LC-OCD can be utilized to compare organic matrices of different surface waters (Kimura et al. 2014) or to analyze seasonal changes of single fractions (Zietzschmann et al. 2013). With regards to membrane filtration it has been used to investigate the influence of feed water characteristics on membrane fouling (Filloux et al. 2012, Zheng et al. 2009), partial retention of LMW fractions (Schäfer et al. 2004), or regrowth potential of a treated water (Meylan et al. 2007). In this study LC-OCD is used to characterize the seasonal variation of a tropical surface water as well as the impact of UF on the NOM characteristics.

About 50% of the population in Tanzania do not have access to safe water supply (Dzimiri 2010). Contamination by waterborne or water-related pathogens and missing or insufficient disinfection can lead to severe diseases like cholera or typhoid (Szewzyk et al. 2000). Tumwine et al. (2002) showed that one third of households in East Africa using surface water as drinking water are frequently affected by diarrhea, which is linked to high child mortality. Tanzania has one of the highest numbers of diarrheal deaths of children under 5 years worldwide (Boschi-Pinto et al. 2008). Clearly, there is a need for treatment and in particular effective disinfection of surface water.

A side effect to this important disinfection is the risk of carcinogenic disinfection by-products (DBP) like trihalomethanes (THM) when water contains NOM. This risk is enhanced by the elevated temperatures (Zhang et al. 2009). In rural parts of Tanzania water supply and treatment is often organized privately in an uncontrolled manner which includes household based disinfection (Davis et al. 2011). Hereby, one method of choice is the use of chlorine products in water storage tanks. NOM hence poses a secondary health risk that is of course secondary to the immediate loss of life that is prevented, yet this can be limited by organic matter removal.

Ultrafiltration (UF) is an effective barrier for pathogens and therefore is a physical disinfection process (Arnal et al. 2004, Madaeni 1999). UF was indeed indicated to be an interesting alternative in tropical climates where water quality alters rapidly with rainfall (Vasyukova et al. 2012). In principle UF is a suitable option for drinking water treatment in rural areas in countries such as Tanzania (Davey and Schäfer 2009, Peter-Varbanets et al. 2012, Peter-Varbanets et al. 2009).

However, UF is available with pore sizes in the range of 2 to 50 nm. Larger pore size UF can be operated at lower TMP while tighter UF requires significantly higher TMP can hence be operated a small hydrostatic pressure, while tight UF required significant pressure to operate. While all UF membranes will physically disinfect water and hence alleviate child mortality, NOM removal requires tight membranes which are further from likely implementation in developing countries.

NOM in raw waters is not a direct health risk, but leads to aesthetical problems like taste, color and odor as well as to the risk of microbial recontamination in distribution or storage systems (Owen et al. 1995). If distribution and storage, or preventative measures for membrane integrity failure, require chemical disinfection, the formation of byproducts, and hence the secondary long term risk of cancer, is significantly reduced through effective NOM removal.

For substantial NOM removal by UF, a pore size of 6 nm (MWCO 5-10 kDa) is required, while this shifts to a larger MWCO once fouled by NOM during operation (Schäfer et al. 2001). This is confirmed by other authors, and variability is usually explainable with MWCO as well as organic matter characteristics (Gorenflo (2003), Kennedy et al. (2005), Lowe and Hossain (2008)). Overall reported results indicate that size exclusion is the dominant retention mechanism. Other retention mechanisms are charge repulsion and membrane-solute interactions. The usually negatively charged NOM is rejected by the negatively charged membrane surface when the MW is near the MWCO. Increase of ionic strength can lead to decreased innermolecular electrostatic repulsion and a more compact size of NOM compounds, while cations are suggested to decrease electrostatic repulsion between solute and membrane by charge shielding. Both effects can result in a lower retention of NOM by UF with increasing ionic strength (Küchler and Miekeley 1994, Schäfer et al. 2002).

Metals, especially cations, naturally associate with NOM (Oliva et al. 1999, Shi et al. 2011). The origin of such interactions has been explained with the role of NOM in chemical weathering of minerals (Oliva et al. 1999) and an association with colloidal NOM (Viers et al. 1997). For UF membranes with higher MWCOs it has been reported that multivalent cations like calcium lead to higher retention of HS due to complexation and aggregate formation aiding size exclusion (Aoustin et al. 2001). At alkaline pH, due to deprotonation of carboxylic and phenolic groups of HS, the NOM has a negative charge and shows anionic character. Therefore, metal ions, especially multivalent cations, can form complexes with HS and cause electrostatic charge shielding (Clark and Lucas 1998). Thus, making the chain hydrophobic in aqueous solution leads to enhanced aggregation by forming a small, coiled conformation via intramolecular complexation (Shi et al. 2011). Using atomic force microscopy (AFM) it was shown that calcium complexation enhances

NOM-NOM and membrane-NOM interactions leading to membrane fouling (Li and Elimelech 2004).

The objective of this study was a detailed investigation of 1) the seasonal water quality of Maji ya Chai as an example for a tropical river, 2) the correlation of water quality with local precipitation over one year and 2) the effect of this water quality variation on UF retention behaviour. Further, the association of multivalent cations calcium, magnesium, iron, and aluminium with TOC and their retention by UF was investigated. Removal of fluoride which is an issue in Maji ya Chair river will be reported in a subsequent paper.

3. Materials and Methods

3.1. Water sampling

During the sampling period of one year (21/12/2012 to 7/12/2013) 15 samples were taken from Maji ya Chai River at a bridge inside Arusha National Park (geo coordinates S03°18.179, E36°52.955, elevation 1,417 m, Figure 1). The samples were taken in 5 liter containers without pre-filtration and stored air tight at ambient temperature until filtration experiments during the entire test period. To avoid external contamination no biocide was added to the permeate samples. Permeate samples for LC-OCD and ICP-MS analyses were freshly filtered and stored in 25 mL transparent polypropylene tubes (Sarstedt, Germany) at ambient temperature and airlifted to KAUST in October 2013.

Figure 1: Map of northern Tanzania and Maji ya Chai river catchment area and water sampling point at geo coordinates of S03°18.179, E36°52.955, and elevation 1,417 m (adapted from T4A).

3.2. Analytical methods

The 'pure water' used for all experimental and analytical procedures was "Mount Meru" bottled water. This water is local surface water treated by reverse osmosis, ozonation, and UV irradiation. It was selected due to its superior chemical quality compared to all other available waters (pH 7.2, EC $\leq 18 \mu\text{S cm}^{-1}$, TOC $< 0.01 \text{ mg L}^{-1}$, fluoride $< 0.01 \text{ mg L}^{-1}$). All measurements were performed in Tanzania unless otherwise specified.

TOC and DOC of samples were analyzed with a Sievers 900 TOC analyzer (GE Analytical Instruments, Colorado, USA). Samples with expected TOC/DOC $> 10 \text{ mg L}^{-1}$ were diluted with pure water. UV_{254nm} was analyzed using UV-2800 Spectrophotometer (UNICO, New Jersey, USA)

using quartz cuvettes with a path length of 1 cm and pure water reference. Specific UV absorbance, SUVA, was determined by the quotient of UV_{254nm} and DOC. For UV and DOC analyses the feed water samples were pre-filtered using Minisart syringe filter (cellulose acetate, Sartorius, Germany) with a pore size of 0.45 μm . UF permeate samples were analyzed without pre-filtration.

For pH and electric conductivity analyses a Multimeter (Multi 340i, WTW, Germany) was used with a pH electrode SentTix 41, and a TetraCon 325 conductivity electrode, respectively. Turbidity of the feed waters was measured using a Turbidimeter (TN-100, Eutech Instruments, USA).

Size exclusion chromatography analyses were performed using a high-performance liquid chromatography (LC-OCD) equipped with TOC and UV-Vis detectors placed in series (DOC-LABOR, Germany). The method is described elsewhere (Huber and Frimmel 1992). Cations were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) using the EPA 200.8 method and a Perkin Elmer Elan DRC-II instrument. Both analyses were conducted at KAUST. Streaming potential measurements were performed with a SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria) at the University of Rennes, France.

3.3. *Precipitation data*

Precipitation data were calculated and provided by Meteoblue AG (Switzerland) using nonhydrostatic meso-scale models (NMM) with a spatial resolution of 18 km, at geo coordinates of $S03^{\circ}20.733$, $E36^{\circ}53.950$. The Meteoblue AG obtained the data of precipitation in the Arusha region from satellite pictures of cloud pattern to generate local precipitation data which are not available. In general such data correlate very well with precipitation data. Precipitation data were used to start each model run. No actual precipitation data were available from Arusha National Park where significant local variation of rainfall is common. Typically, there are two rainy seasons in northern Tanzania with an amount of rainfall from 50-200 mm per month. The “short” season occurs from October to December, the “long” season from March to May (McSweeney et al. 2010a).

3.4. *Ultrafiltration setup and protocol*

All experiments were conducted in dead-end mode under a constant trans-membrane pressure of 3 bar and carried out in stainless steel batch cells illustrated in Figure 2. The pressure was chosen to achieve a reasonable permeability for both membranes used. The cells were pressurized using medical air (BOC Kenya Limited) and permanently stirred at 300 rpm using a magnetic stirrer table (setting 2.5, Stuart UC151, Bibby Scientific Limited, UK). Permeate mass, $m_{permeate}$, was measured with an electronic balance (Adventurer Pro AV 2102, Ohaus, New Jersey, USA) and digitally

recorded (with time intervals Δt 20 s for the 10 kDa membrane and 60 s for the 5 kDa membrane, see Table 1 for membrane details) using a COM port interface and Hyperterminal software. Recorded data were then inserted in Excel and used for further calculations. Cell pressure and feed water temperature were measured and digitally recorded every second.

Figure 2: Schematic design of stirred cell ultrafiltration set-up (described in detail by Neale (2009))

Prior to sample filtration the cell and membrane were flushed by filtering pure water for 1 h and water flux was determined by filtration of pure water for 10 minutes. Initial volume was 1,000 mL, 950 mL were filled into the cell whereas the remaining 50 mL were collected as feed sample. During filtration nine permeate samples (100 mL each) were collected. After filtration of 900 mL (corresponding to a recovery of 95 %) the respective experiment was stopped, the cell was opened and the remaining 50 mL solution in the cell was collected as the retentate sample. After each experiment the filtration cell and membrane surface were flushed gently with 20 mL pure water to remove loosely associated material before pure water flux after filtration was determined for 30 minutes. Ambient temperature during experiments could not be controlled and varied between 24.5 °C and 30.3 °C. In consequence, an increase in the stirred cell temperature was observed due to heating from the magnetic stirrer table and/or changing in ambient temperature during the course of the experiment. Maximum temperature difference in experiments was 4.8 °C after an experiment time of 5.5 hours. As the water viscosity changes due to changing in temperature, an increase in flux of about 5% for the 5 kDa, and about 2% for 10 kDa membrane is expected per 1 °C temperature increase (see Figure S 1). In order to correct the effect of temperature in the data analysis the flux was normalized to a standard temperature, i.e. 25 °C, using Eqn (1) according to ASTM method D5090-07 (ASTM 2007):

$$J_s = J_m(1.03)^{T_s - T_m} \quad (1)$$

Where J_s is the normalized flux at standard temperature, J_m is the actual flux, T_s is the standard temperature and T_m is the measured temperature.

3.5. Calculation of filtration parameters

Permeate flux, J , was calculated using Eqn (2)

$$J = \frac{1}{A_M \rho_w} \frac{\Delta m_{\text{Permeate}}}{\Delta t} \quad (2)$$

Where A_M is the membrane surface area. Water density, ρ_w , was determined with average feed water temperature during filtration. Pure water flux determined before sample filtration is named J_0 . Normalized flux was determined as the J/J_0 ratio.

TOC retention, R , was calculated using Eqn (3)

$$R = 1 - \frac{TOC_{Permeate}}{TOC_{Retentate}} \quad (3)$$

TOC_{Permeate} of respective permeate samples was measured after experiments, while TOC_{Retentate} was calculated stepwise on the basis of the measured TOC in the respective feed sample. Based on mass balance calculation this proved to be a more reliable method than measuring retentate which provided erratic and hence unreliable to determine membrane deposit. This was partially due to the nature of the samples. As such no assessment of TOC deposition on the membrane can be made while the calculated retention data are correct. For calculation of recovery, R_w , Eqn (4) was used.

$$R_w = \frac{\sum V_{Permeate}}{V_{Feed}} \quad (4)$$

Where V is the volume of the respective sample. It should be noted that the results of membrane performance as a function of recovery reflect the concentration changes within a module and hence likely information on retention alongside a module.

3.6. Membrane type and characteristics

Two different UF regenerated cellulose membranes manufactured by Merck Millipore and supplied as flat sheet were used for filtration experiments; PLHCC and PHLGC with a MWCO of 5 kDa and 10 kDa, respectively. Filtration experiments were conducted with circular flat sheet membranes with an effective membrane area of 38.48 cm² (membrane diameter of 70 mm). For each experiment a new membrane was used. Prior to use the membranes were stored in pure water for at least 24 h. Table 1 shows characteristics of the selected membranes. As can be seen from the data the two membranes used have different permeabilities due to a different MWCO.

Table 1: Characteristics of selected Merck Millipore regenerated cellulose UF membranes (pure water flux was measured at 3 bar)

Membrane Type	Material	MWCO* [kDa]	Equivalent pore radii** [nm]	Zeta Potential at pH 7 [mV]	Pure water flux*** (+ max, - min) [L m ⁻² h ⁻¹]	Permeability**** [L m ⁻² h ⁻¹ bar ⁻¹]
PLHCC	Regenerated cellulose on	5	1.9	-46.1	42.0 (+3.4, -4.7)	14.0

PLHGC	PP/PE support	10	3.9	-44.6	237.8 (+55.4, -36.4)	79.3
<p>* Personal communications with one of the R&D directors of MilliporeSigma (March 2016)</p> <p>** Determined using the Stokes Einstein equation $r = 2.37 \cdot 10^{-11} \cdot MW^{0.53}$ (Worch 1993)</p> <p>*** Average of the experimental values after temperature normalization to a standard temperature of 25 °C (see Eqn. 1).</p> <p>**** Values calculated on the basis of average pure water fluxes at 3 bar (after temperature normalization).</p>						

Streaming potential measurements were performed with a SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria) and zeta potential was calculated as described by Mouhoumed et al. (2014). As can be seen in Table 1 both membranes have a highly negative and almost identical surface charge at neutral pH.

4. Results and Discussion

4.1. Raw water characteristics and seasonal variation of precipitation

The seasonal variation of raw water quality was determined and is summarized in Table 2 and Figure 3. The two samples in early November 2013 were taken immediately before and after a heavy rainfall event that resulted in significant swelling of the river. This was the first heavy rainfall event of the rainy season after a long dry season. These high precipitations are not resolved in the average precipitation data. An important observation is that during the high rainfall events the turbidity of the water does not increase significantly as opposed to many common scenarios in Africa. This is due to the fact that the catchment of the Maji ya Chai River of this sampling site is located in a national park with high tree coverage and hence minimal erosion.

Table 2: Raw water parameters of Maji ya Chai River water samples from Arusha National Park over the sampling period

Date of sampling [dd/mm/yyyy]	pH [-]	Turbidity [NTU]	EC [$\mu\text{S cm}^{-1}$]	IC [mg L^{-1}]	TOC [mg L^{-1}]	DOC [mg L^{-1}]	UV _{254nm} [cm^{-1}]	SUVA [$\text{L mg}^{-1} \text{m}^{-1}$]
21/12/2012	8.76	3.7	922	83.2	2.3	2.1	0.068	3.2
03/01/2013	8.77	1.08	930	82.2	3.2	3.0	0.069	2.3
01/02/2013	8.23	0.69	868	76.7	4.2	3.4	0.129	3.7
07/03/2013	8.77	0.27	718	82.3	2.4	2.0	0.070	3.4
03/04/2013	7.97	16.82	775	59.5	35.8	34.4	1.859	5.4
05/05/2013	7.85	0.42	308	30.1	16.4	12.7	0.686	5.4
05/06/2013	8.58	0.37	793	74.0	14.6	14.0	0.756	5.4
07/07/2013	8.52	0.82	807	74.3	10.8	9.6	0.490	5.1
23/07/2013	8.77	2.89	800	76.8	9.2	8.9	0.412	4.6
04/08/2013	8.35	0.57	787	93.6	14.5	13.8	0.725	5.2
10/09/2013	8.42	0.54	924	82.8	5.9	5.3	0.225	4.2
07/10/2013	8.88	1.21	994	82.6	5.2	3.4	0.165	4.8
01/11/2013	8.78	0.37	878	84.1	3.4	2.9	0.100	3.4
05/11/2013	8.07	0.84	722	68.3	35.0	33.9	1.728	5.1

301

302 Figure 3 illustrates the strong correlation between DOC, UV_{254nm} and precipitation. With
 303 beginning rainy season and rising precipitation both parameters show a strong increase. This
 304 indicates a strong influence of allochthonous organic matter that is flushed into the river by rain on
 305 the NOM concentration of Maji ya Chai. SUVA equally shows a seasonal trend. After each of the
 306 first heavy rainfall events of the rainy seasons, in March and November 2013, the SUVA increases
 307 rapidly to a high level, i.e. above $5 \text{ L mg}^{-1} \text{ m}^{-1}$. This indicates a strong inflow of highly aromatic
 308 organic matter of pedogenic origin and subsequent change in NOM quality. In contrast to DOC and
 309 UV_{254nm} values, SUVA stays high with decreasing rainfall. This is caused by the swampy catchment
 310 area of Maji ya Chai continuing to flow into Maji ya Chai River due to exceptionally high
 311 precipitation in April and May 2013. The swamp is first saturated by inflowing rain water and with
 312 further rain continuously releases high aromatic organic matter, which contributes to the variation in
 313 DOC and SUVA. As swamp water levels gradually fall, Maji ya Chai SUVA values eventually
 314 decrease. Studies characterizing NOM in other East African surface waters are rare; Kalibbala et al.
 315 (2011) reported a SUVA value of $4 \text{ L mg}^{-1} \text{ m}^{-1}$ from a surface water in Masaka, Uganda. Although
 316 not dealing with seasonal changes, it indicates a high appearance of highly aromatic surface waters
 317 in East Africa. A similar range of SUVA values was reported in a seasonal study of a tropical black
 318 water from a lake in Brazil (Barreto et al. (2004)). This indicates that the NOM quality of Maji ya
 319 Chai is similar to black water sources in other tropical countries.

320 UF studies of high NOM surface waters are rare and feed waters do often not exceed 5 L mg^{-1}
 321 m^{-1} (Fan et al. 2001, Kennedy et al. 2005, Lee et al. 2004, Zularisam et al. 2007). Isolated fulvic
 322 acid from Suwannee River, often used as model NOM, shows a SUVA below $5 \text{ L mg}^{-1} \text{ m}^{-1}$ (Amy et
 323 al. 2001). The DOC concentration of Maji ya Chai River during 1 year sampling varied between 2.0
 324 and 34.4 mg L^{-1} (see Table 2). This significant fluctuation in organic matter inherently affects the
 325 treatability of the water. In contrast, black water of Jiulong River in southeastern China showed a
 326 DOC concentration variation from 0.4 to 13.1 mg L^{-1} (Hong et al. 2012), while a tropical catchment
 327 in the Amazon basin in Brazil showed a variation from 1 to 15 mg L^{-1} in DOC concentration
 328 (Johnson et al. 2011a). No UF study of such tropical waters has been found.

329 In terms of drinking water treatment, SUVA is used as a surrogate to the presence of DBP
 330 precursors. For example, in Irish EPA SUVA is correlated with DBP formation potential and
 331 disinfection with chlorine. According to this EPA treated waters should have a TOC less than 2
 332 mg/L and a SUVA less than $2 \text{ L mg}^{-1} \text{ m}^{-1}$ (EPA 2012). Thus, disinfection of Maji ya Chai raw water

with chlorine would lead to a very high risk of DBP formation during most periods of the year. It should be noted that the risk of cancer formation is a long term risk and a significantly lower immediate health risk than diarrhoea infections due to failure to maintain a disinfection residual in the water following the physical disinfection by ultrafiltration.

Figure 3: Monthly precipitation from December 2012 to December 2013 compared with DOC, UV_{254nm} absorbance and SUVA over sampling period

4.2. Seasonal variation in NOM composition of raw water

LC-OCD was used to investigate how the NOM quality in terms of molecular weight and fractions (biopolymers, HSs, LMW neutrals and acids) vary with seasons (Figure 4). Selected feed water samples were analyzed with LC-OCD, namely April (highest DOC), October (low DOC), May and August (medium DOC).

Figure 4A shows the ‘recorded’ LC-OCD chromatograms which confirm the results observed in Table 2. In April, the month with highest precipitation and high SUVA of the selected samples, the HS peak (peak centered between 42 and 45 min) in raw water is considerably higher compared to the other samples, which emphasizes the major allochthonous organic carbon contribution. The chromatograms of the May and August samples, which are very similar in all measured organic parameters, show very similar elution profiles and thus, NOM composition.

In Figure 4B the OCD chromatograms are normalized in intensity. In this case the Y-axis shows the relative OC signal which is the detected OC signal divided by the maximum OC signal of the chromatogram. With this illustration different waters can be compared in their DOC composition. It can be seen that in April with high precipitation the relative abundance of low molecular substances (peak centered at 57 min) is lower compared to other samples and the ratio of HS to total NOM is increased due to the inflow of allochthonous substances. In October (lowest rainfall) the strongest relative abundance of biopolymers (peak centered near 30 min) is observed. This indicates a higher ratio of autochthonous organic substances during the dry season due to higher metabolic activity of primary producers.

Figure 4: LC-OCD results of selected raw waters sampled at different times of precipitation, OCD chromatograms (A) and normalized OCD chromatograms (B)

The normalized chromatograms further provide information about the organic size composition of samples, where a lower elution time indicates higher MW of HS. This leads to the following order of MW of HS in the selected samples: April > May $\geq$ August > October (Figure 4B). With higher precipitation not only the concentration of HS increases but also their size/MW.

4.3. Ultrafiltration permeate flux

All Maji ya Chai samples collected throughout the year were used for UF experiments with both membranes, while only the results of filtration of samples from April, with high TOC, and October, with low TOC, are presented (Figure 5). Figure 5A shows the normalized flux of the selected samples over recovery. Independent of feed water, the 5 kDa membrane does not show any flux decline but a stable flux around 1. All samples show similar filtration behavior. Raw water characteristics like DOC or SUVA do not affect flux (Figure 5 and Figure S 2).

In contrast, the 10 kDa membrane shows flux decline for all samples with increasing recovery. This is strongest for the April sample (highest DOC) with a decline of ~50% whereas all other samples show very similar decline of 10 to 15% (Figure 5 and Figure S 2). This general flux decline can be explained by the higher permeability of the 10 kDa membrane, with the pure water flux being 5 to 6 times higher than for the 5 kDa membrane (Table 1 and Figure S 2). This higher flux (and the higher concentration of the April sample) results in increased concentration polarization which in turn leads to flux decline, while the lower retention of the 10 kDa membrane allows for more pore penetration and potential pore restriction and irreversible flux decline (Figure S 2) (Aoustin et al. 2001).

4.4. Ultrafiltration organics removal and permeate organics characterization

Retention of organic matter by the two different membranes as a function of recovery is shown in Figure 5B and Figure S 3. The 5 kDa membrane retains organic substances better due to its smaller pore size. The April sample contains HS with higher MW (see Figure 4) which results in a higher retention by both membranes compared to the October sample. TOC retention generally increases with recovery. This effect is stronger for the 10 kDa membrane with the higher MWCO. A similar observance was made by Aoustin et al. (2001) who explained this with the raising concentration of rejected substances in the cell and/or with pore penetration or blockage in course of filtration. Change in membrane surface charge (Childress and Elimelech 1996) and/or aggregation of organic matter with higher concentration (Costa et al. 2006) are other possible mechanisms.

Figure 5: Normalized permeate flux (A), TOC retention (B), calculated retentate TOC concentration (C), and permeate SUVA (D) of selected samples (April (high TOC) and October (low TOC)) as a function of recovery (filtration at 3 bar, 26.5 °C to 31.8 °C; 90 min for April, 10 kDa; 56 min for October, 10 kDa; 326 min for April, 5 kDa; and 290 min for October 5 kDa)

The 5 kDa membrane has a lower permeate SUVA (Figure 5D). As SUVA increases with the MW of organic compounds (Huber et al. 2011) permeate SUVA would be expected to be reduced seeing only low MW, low aromatic C content NOM can go through the 5 kDa membrane (Schäfer et al. 2002). However, permeate SUVA of the 5 kDa membrane shows a stronger increase compared to 10 kDa membrane with recovery. This can be attributed to the gradual depletion of LMW fractions in the stirred cell and accumulation of the remaining larger MW humic fraction. This increase of concentration with increasing recovery may result in more diffusion and hence increased permeate SUVA. To verify this trend, permeate samples at low recovery (P1: $0\% < R_w < 10.5\%$), medium recovery (P5: $42\% < R_w < 53\%$) and high recovery (P9: $84\% < R_w < 95\%$) from the April water sample (highest TOC) were analyzed with LC-OCD (Figure 6).

Indeed, the permeate concentration of HS of the 10 kDa membrane increases during filtration (P1 to P9). The NOM composition and relative abundance of HS in the permeate show only small changes with rising recovery which is in agreement with the relatively constant permeate SUVA values for the April sample (see Figure 5D). During the filtration the minor difference in size distribution of permeates of 10 kDa membrane indicates that the size exclusion mechanism is not affected by the increase of concentration in the cell. Thus, no pore narrowing caused by permeating organics is obvious, even though the retention by the 10 kDa membrane increases.

Figure 6: LC-OCD results of feed and permeates at different recovery of April sample (high TOC) for 10 kDa and 5 kDa membrane; left: OCD chromatograms; right: Normalized OCD chromatograms

LC-OCD results of the 5 kDa permeate indicate that the chromatographic bands are shifted to lower retention time and hence a higher MW and hence higher MW structures are going through the membrane with increasing recovery and hence cell concentration (Figure 5C). Increasing SUVA values (Figure 5D) during filtration further confirm a strong increase of relative abundance of HS as well as a shift in size of HS in the permeate. A stronger size exclusion compared to the 10 kDa membrane, which leads to an overall lower TOC and lower SUVA in the permeate, is obvious.

However, some small HS are able to pass through the membrane. In comparison, the humic peak of 5 kDa membrane permeates starts at around 38 minutes whereas HS in 10 kDa permeates eluate around 3 minutes earlier. This observation confirms results of Schäfer et al. (2001) in that a cut-off of about 5 kDa is required for substantial NOM removal. The same trend was observed in LC-OCD chromatograms of the October sample with low TOC for both membranes (Figure S 5).

As expected, both membranes do not effectively reject small HS and LMW organic compounds. LMW compounds in particular are of high relevance in terms of microbial regrowth after treatment. Meylan et al. (2007) showed that even after a removal of more than 95% organics of an initial concentration of 3.2 mg C L^{-1} by NF permeate still has regrowth potential. Thus, it is expected that permeate produced by UF is not stable in terms of microbial regrowth and requires adequate post-treatment.

The permeate quality of all the samples is shown in Figure 7. Increasing feed DOC and $\text{UV}_{254\text{nm}}$ (in particular April and November, see Figure 3) lead to increasing values in the permeate of the 10 kDa membrane, which confirms that organics discharged into Maji ya Chai during rainy season can only partly be retained by the 10 kDa membrane despite their more aromatic nature. Permeate of 5 kDa membrane shows lower and more constant DOC concentrations providing a more stable permeate quality with seasonal variation. SUVA values are lower throughout the year which is in accordance with lower abundance of HS in LC-OCD-chromatograms compared to the 10 kDa membrane (see Figure 5D).

Figure 7: Permeate DOC, $\text{UV}_{254\text{nm}}$ and SUVA at medium recovery ($42\% < R_w < 53\%$) for 5 kDa (top) and 10 kDa (bottom) membranes over the entire sampling period

An important consequence of the results is that all permeate SUVA values are above the US EPA guideline of $2 \text{ L mg}^{-1} \text{ m}^{-1}$ and hence not suitable for further chlorination due to potential by-product formation (EPA 2012, US-EPA 1998, USEPA 2010), independent of raw water or membrane. Hua et al. (2015) showed that SUVA correlated strongly with trihaloacetic acids (THAAs) and unknown total organic halogen (UTOX) formation during chlorination. Their findings confirm that the aromatic content of NOM is the predominant source of precursors to these two groups of DBPs. Thus, high permeate SUVA that can be expected for the ultrafiltration of such tropical waters, combined with the regrowth potential of the organics is clearly an issue for further water distribution and storage. For high organic matter waters UF is certainly a good pretreatment process, especially suitable for decentralized point-of-use treatment without further storage and

hence disinfection, whereas for centralized treatment and distribution systems a more advanced technology such as NF is required prior to disinfection. It is worth noting that more conventional technologies such as coagulation suffer from some limitations. For example, coagulant doses are high if significant quantities of organic matter are to be removed (Jacangelo et al. 1995) and the adjustment of such coagulant doses is a fine art that should be performed carefully.

4.5. Ultrafiltration Metal/Ion removal

NOM plays an important role in environmental transport processes of metal ion via the formation of NOM-metal complexes. Depending on the NOM composition, concentration, and chemistry in natural waters the mobility and ultimate fate of the metals can differ (ElBishlawi and Jaffe 2015). In other words, for metal complexation the NOM quality is as important as NOM quantity (Baken et al. 2011). In Figure 8 the variation in metal content and quotient of metal and TOC concentration ($c(\text{Me})/\text{TOC}$) of selected feed samples are presented. For all the analyzed ions, the April sample shows the highest concentrations, while the same trend is observed for ion concentration and TOC; April > May $\geq$ August > October. This observation confirms the existence of metal ions complexation and/or aggregation with NOM and the transport of metal ions from soils into the Maji ya Chai River through rainfall run-off and weathering processes.

The order of ratio of metal to TOC concentration for four selected feed samples shown in Figure 8 is Ca > Mg > Fe > Al. Rey-Castro et al. (2009) modeled the effective distribution of affinities for binding a metal ion to HS under natural water conditions and in the presence of a general mixture of competing cations. Three groups of cations were distinguished, (i) Ca, Mg, and Fe(II) showed an effective affinity for carboxylic sites, (ii) Al preferred to bond with the phenolic sites of the Fulvic acids ligand, and (iii) Fe(III) had phenolic and carboxylic distributions overlap (Rey-Castro et al. 2009). Therefore, the competition of ions to interact with NOM and the strength of complexation strongly depends on the structure of NOM. Measuring Ca/DOC ratios as a function of season (Figure 8) indicates some variation in NOM composition in Maji ya Chai River during the year. For example, the October sample with a lower $\text{UV}_{254\text{nm}}$ absorbance and lower DOC (see Figure 3) has a higher Ca/DOC ratio (Figure 8 and Figure 11), and the same correlation exists for the April sample. According to the findings by Rey-Castro et al. (2009) Ca, Mg, and Fe have a relatively high concentration and their effective affinity is for carboxylic sites. It can hence be concluded that carboxylic sites play a dominant role in the composition of Maji ya Chai River organic matter.

Figure 8: Ion analysis (top) and quotient of metal and TOC concentration (bottom) of selected feed samples

The distribution of cations in the feed and permeate samples of both membranes is shown in Figure 9. During the filtration of the April sample Al and Fe are mainly retained by both membranes, while Mg and Ca can pass through both membranes up to a certain extent. This indicates that Al and Fe most likely occur in colloidal forms or form larger aggregates with NOM. Mg and Ca either exist as free metals or are bound to LMW fractions that can pass through the UF membrane (Dupré et al. 1999). Similar results were obtained by (Viers et al. 1997) where Al and Fe occurred entirely in the colloidal phase of a colored water, while Mg and Ca was found in both colloidal as well as a truly dissolved phase.

Figure 9: Comparison of ion concentration in feed and permeates (P1, P5, P9) of April sample

Figure 10: Concentration of selected ions in feed and retentate of 20 kD and 5 kDa membrane, (left: April (high TOC), right: October (low TOC))

The ratio of selected cations $c(\text{Me})/\text{TOC}$ of feed, permeates and retentates for the April and October samples are compared in Figure 11. Regardless of the type of sample, the $c(\text{Me})/\text{TOC}$ of Mg, Fe, and Al of April and October samples are very similar. In contrast, the $c(\text{Ca})/\text{TOC}$ is significantly different in the April and the October samples. In other words, there is a higher ratio of $c(\text{Ca})/\text{TOC}$ in feed and permeate of October samples, indicating that with decreasing TOC in Maji ya Chai River the concentration of Mg, Fe, and Al is linearly decreased, while the decrease in Ca concentration is much less. This can be explained by the existence of truly dissolved Ca that is not associated with NOM and/or a different composition of NOM that complexes Ca more readily. Seeing that the retentate $c(\text{Ca})/\text{TOC}$ in April and October samples are very similar, 0.11 and 0.12 mg mg^{-1} , respectively, the existence of truly dissolved Ca appears more likely (Dupré et al. 1999, Viers et al. 1997).

Figure 11: Quotient of metal and TOC concentration for feed, permeates and retentates of April and October sample and 10 kDa membrane

5. Conclusion

Results from this study show that; (1) the composition of NOM and metals in Maji ya Chai River are strongly dependent on precipitation. High TOC, HS and metal concentrations are observed in periods of high precipitation, while lower TOC and lower SUVA occurred during the dry season; (2) Seasonal variation affects differences in UF performance and retention. Raw waters with high TOC leads to higher permeate TOC. Dependent on the used membrane this water can cause high flux decline. Although affecting permeate concentration, changes in raw water do not affect permeate composition as the relative abundance of different fractions in permeate is very similar; (3) Permeate of 5 and 10 kDa membranes have high SUVA values and high Ca and Mg concentration. Depending on the precipitation, raw water can contain high concentrations of HS fractions that are able to pass through both membranes. In consequence, permeate still contains high DBP formation and regrowth potential. Thus, a combination of UF and chlorination for drinking water treatment is not recommendable for water containing tropical NOM.

In summary, seasonal variation in TOC very clearly affects permeate quality. As such this is no health issue, but the water is unfit for chlorination as well as distribution or storage because of potential regrowth. This speaks for decentralized systems where no disinfection residual is required, the potential of coupling UF with sorption to remove other dissolved species (such as fluoride) and LMW organics together or using nanofiltration for a more complete removal of NOM. Such advanced technologies are far from implementation in particular in developing countries.

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8. Supporting Information

Figure S 1: Variation of pure water flux of 5 kDa and 10 kDa membranes by temperature at 3bar.

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749 *Figure S 2: Normalized permeate flux of May and August samples as a function of recovery*
750 *(filtration at 3 bar, 27 °C to 31 °C; and 61 min for May, 10 kDa; 71 min for August, 10 kDa; 322*
751 *min for May, 5 kDa; and 290 min for August, 5 kDa)*

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754 *Figure S 3: Permeate TOC concentration of selected samples of April, May, August, and October*
755 *of 10 kDa membrane as a function of recovery (filtration at 3 bar, 26.5 °C to 31.8 °C, 90 min for*
756 *April, 61 min for May, 71 min for August, and 56 min for October)*

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759 *Figure S 4: Pure water flux (normalized to 25 °C (see Eqn. 1)) of 5 kDa (top) and 10 kDa*
760 *(bottom) membranes before and after filtration of different raw waters (3 bar, 24.5 °C to 30.3 °C)*

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764 *Figure S 5: LC-OCD results of feed and permeates at different recovery of October sample (low*
765 *TOC) for 10 kDa and 5 kDa membrane; left: OCD chromatograms; right: Normalized OCD*
766 *chromatograms;*

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769 *Figure S 6: Normalized LC-OCD chromatograms of permeates from different raw waters at*
770 *medium recovery ($42\% < R_w < 53\%$)*

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773 **Figure S 7: LC-OCD chromatograms (left) and normalized OCD chromatograms (right) of**
774 **retentate samples after filtration with 5 and 10 kDa membranes**

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777 ***Figure S 8: Comparison of OCD and normalized OCD chromatograms of feed and retentates for***
778 ***April (high TOC) and October (low TOC) samples***

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Figure 1: Map of northern Tanzania and Maji ya Chai river catchment area and water sampling point at geo coordinates of $S03^{\circ}18.179$, $E36^{\circ}52.955$, and elevation 1,417 m (adapted from T4A).

Figure 2: Schematic design of stirred cell ultrafiltration set-up (described in detail by Neale (2009))

Figure 3: Monthly precipitation from December 2012 to December 2013 compared with DOC, UV_{254nm} absorbance and SUVA over sampling period

Figure 4: LC-OCD results of selected raw waters sampled at different times of precipitation, OCD chromatograms (A) and normalized OCD chromatograms (B)

Figure 5: Normalized permeate flux (A), TOC retention (B), calculated retentate TOC concentration (C), and permeate SUVA (D) of selected samples (April (high TOC) and October (low TOC)) as a function of recovery (filtration at 3 bar, 26.5 °C to 31.8 °C; 90 min for April, 10 kDa; 56 min for October, 10 kDa; 326 min for April, 5 kDa; and 290 min for October 5 kDa)

Figure 6: LC-OCD results of feed and permeates at different recovery of April sample (high TOC) for 10 kDa and 5 kDa membrane; left: OCD chromatograms; right: Normalized OCD chromatograms

Figure 7: Permeate DOC, UV_{254nm} and SUVA at medium recovery ($42\% < R_w < 53\%$) for 5 kDa (top) and 10 kDa (bottom) membranes over the entire sampling period

Figure 8: Ion analysis (top) and quotient of metal and TOC concentration (bottom) of selected feed samples

Figure 9: Comparison of ion concentration in feed and permeates (P1, P5, P9) of April sample

Figure 10: Concentration of selected ions in feed and retentate of 10 kD and 5 kDa membrane, (left: April (high TOC), right: October (low TOC))

Figure 11: Quotient of metal and TOC concentration for feed, permeates and retentates of April and October sample and 10 kDa membrane

Highlights:

- Organic matter quality and quantity in a tropical stream is affected by precipitation.
- Increased raw water TOC results in increased permeate TOC and SUVA of 2-4 L mg⁻¹ m⁻¹.
- Regrowth potential and disinfection by-product formation is a challenge for tropical waters.