Karaelmas Fen ve Müh. Derg. 12(2):146-154, 2022

Karaelmas Science and Engineering Journal
Journal home page: https://dergipark.org.tr/tr/pub/karaelmasfen
DOI: 10.7212/karaelmasfen.1030174

Research Article
Received / Geliş tarihi : 29.11.2021
Accepted / Kabul tarihi : 15.12.2021

Characteristics of Molecular Weight Distribution of Natural Organic Matter and Trihalomethane Formation Properties in Conventional Drinking Water Treatment Processes

Konvansiyonel İçme Suyu Arıtma Tesislerinde Doğal Organik Maddenin Moleküler Ağırlık Dağılımı ve Trihalometan Oluşumunun Özellikleri

Kadir Özdemir*

Zonguldak Bülent Ecevit Univversity, Faculty of Engineering, Department of Environmental Engineering, Zonguldak, Turkey

Abstract

In this study, ultrafiltration (UF) technique was used for natural organic matter (NOM) characterization in water samples taken from Ulutan drinking water treatment plant (UWTP) units (raw water, coagulation and disinfection process) in Zonguldak. The distribution of NOM fractioation was performed the carbon mass balance of the UF processes according to the Total organic carbon (TOC) measurements. The NOM fraction with molecular weight (MW) <1000 Da (1 kDa) is the dominant fraction among all the fractionated water samples. Its percentage ranged from 54.29% to 69.76% between raw and disinfection processes stages in UWKP. During treatment process, higher MW fractions were removed more efficiently than MW< 1kDa, especialy coagulation step. This result showed that low molecular weight organics are relatively hydrophilic and not effectively removed by coagulation. Disinfection stage had limited effect on removing organic fractions. On the other hand, as the raw water samples was chlorinated, the highest trihalomethane formation potential (THMFP) was observed the fraction of < 1kDa as 163.2 μg/L during the reaction times of 168 hours and followed by 1-3kDa (15.3 μg/L), 3-5kDa (12.6 μg/L) and >5kDa (8.4 μg/L), respectively., The highest specific trihalomethane formation potential (STHMFP) concentration was determined MW<1kDa as 35.8 μg THMFP/ mg TOC. As a result, the findings of this study demonstrated that the deterrmination of NOM fractions with the UF technique may be an applicable strategy for operation of conventional drinking water treatment plants.

Keywords: Ultrafiltration, Natural organic matter, Molecular weight, Trihalomethane

Öz

Bu çalışmada Zonguldak iline içme suyu sağlayan Ulutan içme suyu arıtma tesisi (USAT) ünitelerinden (Ham su, koagülasyon ve dezenfeksiyon) alın su numunelerinde bulunan doğal organik madde (DOM) karakteizasyonu ultrafiltrasyon (UF) tekniği kullanılarak gerçekleştirilmiştir. DOM fraksiyonlarının dağılımı UF prosesi ile toplam organik karbon (TOK) konsantrasyon değerleri esas alınarak karbon kütle dengesine göre yapılmıştır. USAT'de ham sudan dezenfeksiyon ünitelerinden alınan su numunelerinde UF prosesi ile karakterize edilmiş bütün organik fraksiyonlar arasında en fazla bulunan moleküler ağırlığı (MA) 1000 Da (1kDa)'dan daha küçük olan organik fraksiyonlar olduğu tespit edilmiştir. Ham sudan dezenfeksiyon ünitesine kadar 1kDa'dan küçük olan NOM fraksiyonlarının bulunma yüzdesi %54.26-%69.76 arasında yer almaktadır. Arıtma prosesi süresince, en yüksek giderim verimi koagülasyon adımında ve MA yüksek olan organik fraksiyonlarda meydana gelmiştir. Bu sonuç aynı zamanda koagülasyon prosesinde düşük MA sahip hidrofilik özellikteki fraksiyonların etkili bir şekilde giderilemediğini göstermektedir. Diğer yandan tüm organik fraksiyonlarda en düşük giderim verimi dezenfeksiyon prosesinde meydana gelmiştir. Klorlanmış ham su numunelerinde 168 saatlik reaksiyon süresinde en yüksek trihalometan oluşum potansiyeli (THMOP) miktarı (163.2 μg/L) MA 1kDa'dan küçük olan DOM fraksiyonlarda görülürken, sırası ile MA 1-3kDa olanlarda 15.3 μg/L, 3-5kDa olanlarda 12.6 μg/L ve MA 5kDa'dan büyük olan fraksiyonlarda ise 8.4 μg/L olarak ölçülmüştür. Bununla birlikte, DOM fraksiyonları arasında en yüksek spesifik trihalometan oluşum potansiyeli (STHMOP) konsantrasyonu (35.8 μg THMFP/ mg TOK) MA 1kDa'dan küçük olan fraksiyonlarda gözlenmiştir. Bu çalışmada elde edilen bulgular UF tekniği ile DOM fraksiyonlarının tespit edilmesinin konvansiyonel içme suyu arıtma tesislerinin işletmesinde uygulanabilir bir strateji olduğunu ortaya koymaktadır.

Anahtar Kelimeler: Ultrafiltrasyon, Doğal organik madde, Moleküler ağırlık, Trihalometan

---

*Corresponding author: kadirozdemir73@yahoo.com

Kadir Özdemir orcid.org/0000-0003-1464-7078

1. Introduction

Natural organic matter (NOM) in water consistitues of a wide variety of organic compounds and also plays a significiant role in water treatment. It forms from largely aliphatic to colored aromatics (Swietlik et al., 2004). Some of the organic substances are negatively charged compounds with different content and molecular size. The amount and characteristic features of natural organic substances in surface waters vary depending on the topography, climate and geology of that place (Fabris et al., 2008, Wei et al., 2008a).

On the other hand, NOM affects drinking water treatment on many aspects, like the dose of treatment chemicals (Yang et al., 2016). Further, ensuring a desired quality water production in drinking water treatment plants requires the removal of these organics with a high efficiency (Sillanpää et al., 2011). There are many studies on the removal technologies of natural organic substances in the related literature (Jiang et al., 2018, Mao et al., 2018).

Among these treatment technologies, the most common and economical method is coagulation and flocculation, followed by precipitation and filtration steps (Galjaard et al., 2018). The increase in the concentration of NOM causes negative effects in terms of water quality in drinking water resources. These problems include the level of taste and odor in the water, the increase in the amount of disinfectant with the dose of coagulant used, the occurrence of disinfection by-products with potentially harmful effects, the occurrence of microbial growth in the networks and the increase in complexed heavy metal concentrations. NOM reacts with disinfectants like chlorine, during water disinfection, halogenated disinfection byproducts (DBPs) form (Zha et al., 2014). Trihalomethanes (THMs) and haloacetic acids (HAAs) are the most common disinfection by-products (DBPs) from chlorinated drinking water reservoirs (Chu et al., 2017, Han and Zhang 2018). Some researches have reported that NOM is the main precursor of chlorinated by-products (Hua and Reckhow 2007). In the mean time, the chemical and physical structure of NOM has an important place in the formation of disinfection by-products Ozdemir (2014). On the other hand, if the organic matter consists of high MW substances such as aromatic compounds, higher amounts of THMs and HAAs are observed as a result of chlorination of hydrophobic organics. NOM is generally divided into hydrophobic, transphilic, and hydrophilic groups. Hydrophobic NOM consists of humic and fulvic acids. Hydrophilic NOM includes mostly aliphatic carbon and nitrogenous compounds (Chen et al., 2008). Additionally, NOM characterization focused on general parameters, including total organic carbon (TOC), UV absorbance at 254 nm wavelength (UV_{254}) and specific ultraviolet absorbance (SUVA) (Awad et al., 2016.) These are surrogate parameters for providing to information of DBP precursors (Uyak et al., 2007).

Fractionation techniques as physical and chemicsl can be useful for NOM characterization (Chow et al., 2005). Ultrafiltration, size separation chromatography, ultracentrifugation are the most well-known physical fractionation methods. On the other hand, one of the most widely used chemical separation methods is resin fractionation. UF technique has been used for separating of NOM fractions related to their moleculer sizes the range from 1000 to 30000 Daltons (Da) (Gang et al., 2003). Also, UF technique is no requirement for chemical reagents. The goal of study is to find the MW distribution of NOM fractions in conventional treament processes and analyze to the trihalomethane formation potential (THMFP) of different MW fractions of NOM. Also, this study is one of the first studies on the fractionation of natural organic materials found in drinking water sources in the Western Black Sea region by ultrafiltration method.

2. Materials and Methods

2.1. Water Sampling

In the study, water samples were taken from the Ulutan Drinking Water Treatment plant (UWTP) in Zonguldak. Ulutan Dam is the main water reservoir in Zonguldak and provides a maximum of 34,000m^3/day of water to UWTP. UWTP is a kind of conventional treatment plant including aeration, coagulation-flocculation, filtration and disinfection processes.

2.2. Ultrafiltration

UF process was used to fractionate the NOM components according to their molecular size. UF was conducted by using a stirred UF cell (Millipore 8200) with YM disc membrane made of regenerated cellulose (Amicon, USA). Prior to filtration, ultrapure water was passed through the membranes to remove any possible leached organics until TOC in the permeate was <0.1 mg/L. After that, the membrane was installed into the UF cell and rinsed two times using 0.01 mol L21 NaOH and HCl alternatively. The stirrer kept agitating more than 10 min for each rinse. High purity nitrogen (99.99%) was used to pressurize the

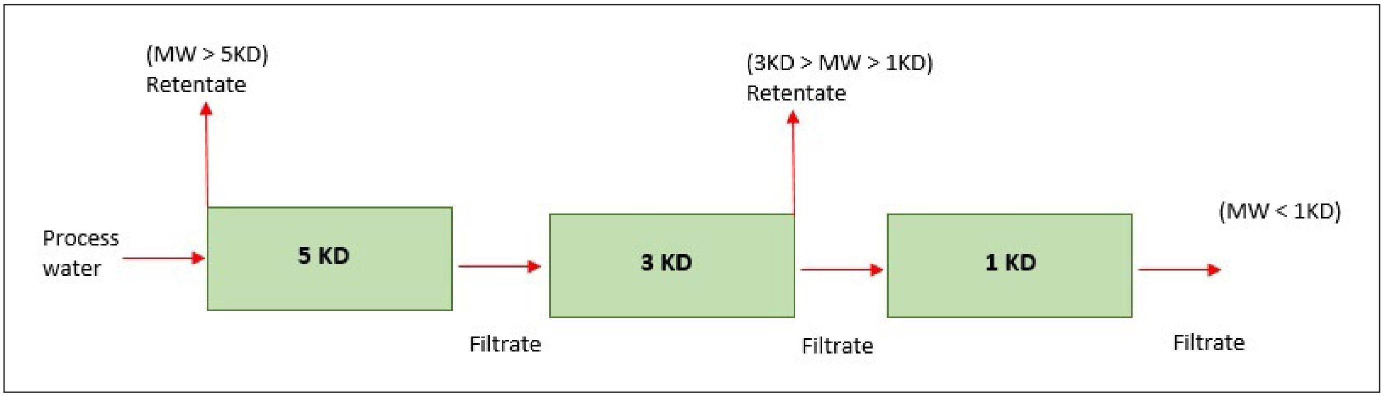

Figure 1: A schematic flow chart showing UF process.

filtration process, and the permeate was stored at +4 °C until analysis. The MW of the applied membranes was as follows: 1, 3 and 5 kDa. NOM was separeted by using ultrafiltration membranes, including a fraction with MW < 1 kDa, 1-3kDa, 3-5 kDa and > 5kDa. Water samples taken from raw water, coagulation and disinfection units were passed through the membranes of MW < 1 kDa, 1-3kDa, 3-5 kDa and > 5kDa. The cleaning process was performed by the procedure of Zhao et al. (2006). Transmembrane pressure value of 0.35 MPa was applied for UF tests with surface water samples. The shceme of the UF process is given in Figure 1.

2.3. Chlornation and THMFP Procedure

Chlornation of water samples was made in a 500 cm^3 amber-color glass bottle. Water samples were buffered to pH 7.5 with 5 mM phosphate buffer. Chlorine stock (1000 mg/L) solutions was prepared using commercial 4% NaOCl and standardized by iodometric titration. THMFP test was done according to in Standard Methods of 5710-B (APHA 2005). According to this method, the pH value of the water samples should be brought to 7 with phosphate buffer and chlorinated, and then kept at 25 °C for 7 days. The chlorinated samples were placed into 125-mL amber glass bottles with polypropylene screw caps and TFElined caps. Afterwards, residual chlorine amounts should be determined according to the DPD colorimetric method (APHA 2005).

2.4. Analytical Procedure

Ultrapure water (Sartorius Co., Germany) was used to prepare the standard solutions used in all experimental procedures and analyzes carried out in the laboratory. TOC analyses were performed with a Shimadzu TOC-5000 Analyzer, using high temperature combustion, according to APHA-3510B. UV–1608 Shimadzu spectrophotometer was used for measurements of UV_{254}. SUVA was found as the UV_{254} divided by the TOC values. Analyses involving THM compounds were conducted with the liquid-liquid extraction method in the EPA 551 method (USEPA 1998). HP 6890 Series II Gas Chromatograph equipped with a micro Electron Capture Detector (GC μECD) instrument with a DB-1 capillary column (30 m×0.32 mm I.D.×1.0 μm, J&W Science) was used for THM measurements.

3. Results and Discussion

3.1. Distribution of NOM

The UF technique is widely used for the determination of molecular weight distributions of NOM in water treatment. Prior to UF processes, a mass balance must be done for each NOM fraction with TOC analysis. In addition, any loss or contamination situations are also reviewed in the mass balance calculation for NOM fractions. The results of the mass balance for each NOM fraction are presented in Table 1. As can be seen Table 1, The TOC values of each NOM fraction analyzed in the purification steps are given in the left column. Then, the TOC mass of each NOM fraction was calculated by multiplying the volume of the sample with the measured TOC concentration in mg. The distribution of NOM fractions in each treatment step was found by dividing the TOC value of each fraction by the sum of TOC value. Also, in this section, the recovering percentage of each TOC in the raw water, coagulation and chlorination units of each fraction were found. TOC recovery including those in raw water, coagulation and chlorination process were recorded as (100 ± 10.21%), (100 ± 6.2%), (100 ± 3.53%), and (100±7.41%), respectively. Brockmeyer and Spitzy (2013) examined the TOC mass balance of fractionated NOM samples collected from Outer Alster Lake in Hamburg city,

Table 1: TOC Mass Balance for Each Water Treatment Unit

Water source	Molecular Dimension	TOC	Sample volume	TOC mass	TOC distribution
Raw water	Dalton (Da)	(mg/L)	(L)	mg	(%)
	Raw water	8.78	0.18	1.58	
	>5000 D (>5kDa)	0.34	0.54	0.18	12.14
	5000-3000 D (5kDa-3kDa)	0.46	0.54	0.25	13.93
	3000-1000 D (3kDa-1kDa)	0.48	0.54	0.26	15.36
	<1000 D (<1kDa)	4.56	0.18	0.82	54.29
	Total mass=	Sum of fractions	1.779	1.51	100
		Recovery (%)			101.4
Coagulated water	Coagulated water	6.45	0.18	1.16	
	>5000 D (>5kDa)	0.19	0.54	0.10	9.56
	5000-3000 D (5kDa-3kDa)	0.25	0.54	0.14	12.58
	3000-1000 D (3kDa-1kDa)	0.32	0.54	0.17	16.11
	<1000 D (<1kDa)	3.68	0.18	0.66	61.74
	Total mass=	Sum of fractions	1.779	1.07	100
		Recovery (%)			103.3
Chlorinated water	Chlorinated water	5.23	0.18	0.94	
	>5000 D (>5kDa)	0.16	0.54	0.09	9.68
	5000-3000 D (5kDa-3kDa)	0.21	0.54	0.11	12.70
	3000-1000 D (3kDa-1kDa)	0.29	0.54	0.16	17.54
	<1000 D (<1kDa)	3.46	0.18	0.62	69.76
	Total mass=	Sum of fractions	1.779	0.89	100
	Recovery (%)				105.6

Germany. The results of this study showed well recoveries. In other words, NOM fractions recoveries of 0.5kDa, 1kDa and 10kDa were found as (100 ±14), (100±7) and (100±5). Schwalger and Spitzy (2013) has reported that organic carbon recoveries were calculated as 99±13 for MW<1kDa, 100 ±20 for MW>5kDa and 100 ± 3 for MW >50kDa in fresh and estuarine waters in Germany. These experimental studies reveal that TOC mass balance values indicate no major loss or contamination of NOM fractions as a result of the UF process. On the other hand, when the results of this study were compared with previous studies, it was seen that the relevant literature was supported Wang et al. (2008). Similar recoveries have been presented in other literature studies (Wilding et al., 2005, Kottelat et al., 2008).

3.2. NOM Size Distribution in Water Sources

Figure 2 illustrates the distribution of fractions during the conventional treatment processes in ÜWTP. The results inluded that the predominant fraction of NOM in raw water stage was <1 kDa, accounting for 54.29 % of total TOC, followed by 1kDa-3kDa and 5kDa-3kDa with15.36% and 13.93 %, respectively. The least common fraction was >5kDa, as 12.14%. These results confirm to the data from previous studies (Han et al., 2015). Similar results were obtained in studies by Wei et al. (2008b). They have noted that the NOM fraction of < 1kDa composes at the major portion of TOC content in four water reservoir. Gu et. al (2006) collected water samples from Guangzhou section of the Pearl River in China to investigate soluble organic fractions with UF technique. They indicated that the majority of NOM was composed of fractions less than 500kDa as a result of the characterization of the water samples in the Pearl River. The results of this part of study show that organic carbon of NOM in raw water samples consists of hydrophilic fractions which are characterized by more aliphatic carbon and nitrogenous compound such as carbohydrates, sugars, and amino acids. Additionally, coagulation can remove organics. NOM fractions with MW >5 kDa, 5-3 kDa, 3-1 kDa, and < 1 kDa in coagulation step were determined as 9.56%, 12.58%; 16.11% and 61.74%, respectively, based on the TOC concentration calculations. In the meantime, while the removal rates of with MW >5 kDa and 5-3 kDa were observed as about 50%, the removal rates of 3-1 kDa, and < 1 kDa was recorded as 33% and 21%, respectively.

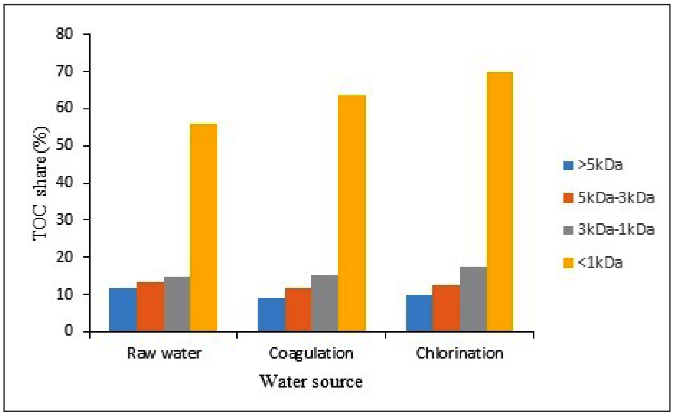

Figure 2. Fraction mass distribution of water treatment processes.

The findings presented that the removal ratio generally rose with the increase in MW. In addition, molecules with small size are not effectively removed by coagulation especially, < 1kDa. Chen et al. (2021) have performed that raw water (RW), settled water (SW), and filtered water (FW) samples collected from a drinking water treatment plant were fractionated into 24 NOM fractions with varying molecular weights. The results revealed that MW < 1kDa NOM fraction is the most abundant in raw water (RW) (71.22%), sediment water (SW) (46.26%) and filtrate water (FW) (41.12%). Also, the findings of this investigation illustrated that hydrophilic fractions can not be treated effectively in FW, which contributed to the low aliphatic precursors remaining in the FW. However, after the SW process, the hydrolysis and complexation induced by $AlO_4A_{112}(OH)^{+7}{}_{24}$ and $AlCl_3$ greatly contribute to the removal of the organics. On the other hand, some experimental studies in the literature have shown that most of the organic fractions with high molecular weight like 10 kDa can be removed by the coagulation process (Matlianen et al., 2002, Song et al., 2019). Disinfection with chlorine increased slightly the concentration of NOM fractions. The distributions of MW >5 kDa, 5-3 kDa and 3-1 kDa were calculated as 9.68%, 12.70% and 17.54 %, respectively. Altough the percentage of organic fraction with MW less than 1kDa (69.76%) was found to increase more with chlorination, the lowest removal rate as TOC concentration was detemined in the fraction of MW < 1kDa. Some researchers have found that organic fractions greater than 2.5kDa are decreased more than other NOM fractions during disinfection (Kristiana et al., 2013). This finding also revealed that chlorination leads to the partial oxidation of NOM and thus, hydrophilic fraction of NOM increased through chlorination. Similar observations have been reported by some researches (Zhao et al., 2013, Zheng et al., 2016).

Overall, the conventional applications removed the hydrophobic compounds more effectively than the hydrophilic ones. Further, low MW fractions of NOM were not effectively removed by conventional treatment process and also higher remaval in NOM fractions was coagulation unit in UWTP.

3.3. Identification of THM Precursors in Raw Water

Figure 3 shows the trihalomethane formation of NOM fractions in chlorinated raw warer samples at the reactio of 168 hours. According to Figure 2, while the fraction of < 1kDa had the highest THMFP level (163.2 μg/L), the fraction of > 5kDa had the lowest THM concentration (8.4 μg/L). The factions of 5-3 kDa and 3-1 kDa were accouted for 12.6 μg/L and 15.3 μg/L, respectively. These findings displayed that hydrophilic compounds play a greater role in the formation of THMs and studies on the subject in the previous literature support the results obtained in this study (Xu et al., 2012, Zhang et al., 2020). The removal efficiency of DBP precursors in conventional treatment systems largely depends on the hydrophobicity and MW of the NOM (Yan et al., 2017). Zhao et al. (2006) suggested that the low-molecular-weight 0.5–1K fraction was the major precursor of THM formation for effluent of each of the four treatment processes in a conventional drinking water plant in Guangzhou. Previous studies have shown that higher concentrations of THM are formed as a result of chlorination of NOM, which is composed of especially organic carbon aromatic compounds rather than aliphatic compounds (Li et al., 2016). In the results of study by Niu et al (2018) show that the main DBP precursors were the fraction with MW <1 kDa and fraction with MW 3–10 kDa, and the DBP's generation ability of lower molecular weight DOM (<10 kDa) was higher than that of higher molecular weight NOM. Therefore, we can generally report that the THMFP was closely related to the MW and the concentration of fractions.

On the other hand, Figure 4 gives specificTHMFP (STHMFP) levels. The STHMFP of MW > 5kDa, 5kDa-3kDa, 1kDa-3kDa and <1kDa increased in that order (24.7 μg/mg, 27.4 μg/mg, 31.8 μg/mg, 35.8 μg/mg), and

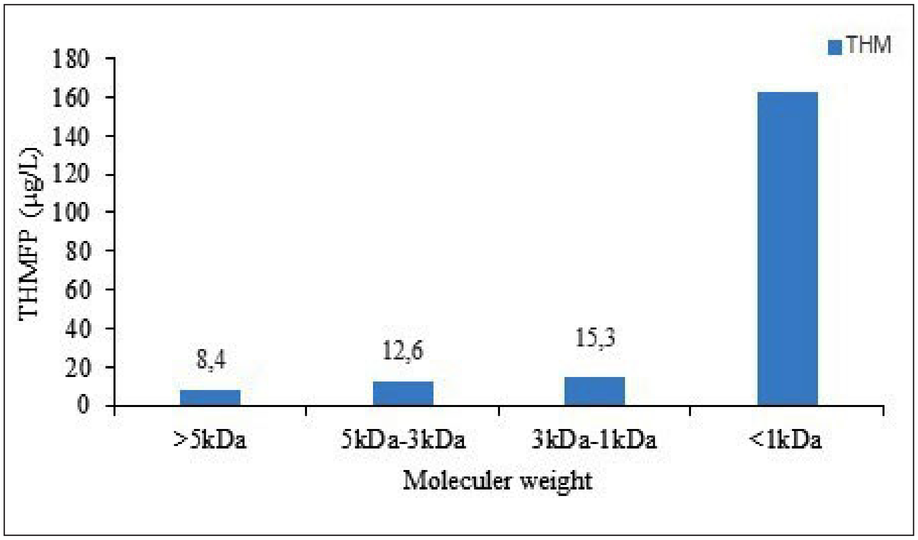

Figure 3: Trihalomethane formation potential of NOM fraction in Ulutan Dam water.

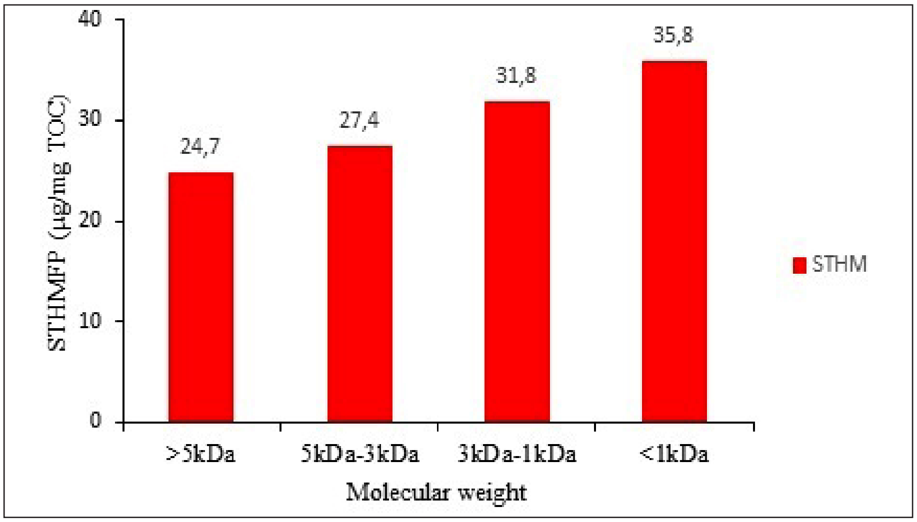

Figure 4: Specific trihalomethane formarion potential of NOM fractions in Ulutan Dam water.

MW <1 kDa had a stronger STHMFP than the higher MW ones (Figure 3). We can generally suggest that the highest STHMFP is observed with the decrease of MW and that lower NOM fractions produce more THMs. In the study of Nkambule et al. (2019) on THM formations for the optimization of drinking water treatment plant, higher amount of THM formation was observed during the chlorination of NOM fractions with hydrophobic organic carbon. The results displayed that there is a strong correlation between STHMFP and the aromatic fraction of NOM in the treatment plant. Similar results have also been cnfirmed by other researches, which have shown that lower MW fractions as the important precursors in the THM formation (Roe et al., 2008). In the study of Karapinar et al. (2014) on seasonal NOM characterization, they took water samples from Terkos Lake, which provides drinking water to the province of Istanbul, and carried out the fractionation process with the UF technique. Then, as a result of chlorination of each fraction, it was determined that the highest STHMFP occurred in NOM fractions of MW<1kDa. In other words, this result might be revealed that the STHMFP level depends on the origin of NOM.

4. Conclusion

In this study, NOM characterization in water samples taken from Ulutan drinking water treatment plant (UWTP) units was used by using UF technique has been carried out. As a result of the experimental studies, it was observed that NOM fractions with a molecular weight less than 1 kDa were dominant in each treatment unit. This result also shows that NOM fractions with a hydrophilic molecular weight less than 1 kDa cannot be effectively removed. It has been determined that the hydrophilic fraction of NOM plays an important role in THM formations that occur as a result of chlorinated water samples during the treatment period. In other words; the fraction of < 1kDa had the highest THMFP level (163.2 µg/L). Further, the highest STHMFP concentration as 35.8 µg THMFP/ mg TOC was recorded in MW < 1kDa. The results of this study show that the realization of the NOM fractionation process with the UF technique can make an important contribution to the efficient operation of conventional drinking water treatment plants.

5. References

APHA, 2005. Standard Methods for the Examination of Water and Wastewater, 22th ed. American Public Health Association, Washington DC. http://www.apha.org/

Awad, J., Van Leeuwen, J., Chow, C., Drikas, M., Smernick J., Bestland, E. 2016. Characterization of dissolved organic matter for prediction of trihalomethane formation potential in surface and sub-surface waters. *J. Hazard Mater*. 308:430-439. DOI: https://doi.org/10.1016/j.jhazmat.2016.01.030

Brockmeyer, B., Spitzy, A. 2013. Evaluation of a Disc Tube Methodology for Nano- and Ultrafiltration of Natural Dissolved Organic Matter (DOM). *Int. J. Organic. Chem*. 3: 17-25. DOI: http://dx.doi.org/10.4236/ijoc.2013.31A002

Chen, Z., Zhao, S., Shen, J., Huo, X., Li, J., Zhou,Y., Kang, J., Zhang, X., Wang, B. 2021. Variations of disinfection byproduct precursors through conventional drinking water treatment processes and a real-time monitoring method. *Chemosphere.* 272: 1-11. DOI: https://doi.org/10.1016/j.chemosphere.2021.129930.

Chen, C., Zhang, X., Zhu, L., Liu, J., He, W., Han, H. 2008. Disinfection by-products and their precursors in a water treatment plant in North China: seasonal changes and fraction analysis. *Sci. Total Environ.* 397: 140–147. DOI: 10.1016/j.scitotenv.2008.02.032

Chow, A.T., Gao, S., Dahlgren, R.A. 2005. Physical and chemical fractionation of dissolved organic matter and trihalomethane precursors: a review, *J. Water Supply*, 54(8): 475–507 DOI: https://doi.org/10.2166/aqua.2005.0044

Chu, W., Yao, D., Deng, Y., Sui, M., Gao, N. 2017. Production of trihalomethanes, haloacetaldehydes and haloacetonitriles during chlorination of microcystin-LR and impacts of pre-oxidation on their formation. *J. Hazard Mater*. 327: 153-160. DOI: https://doi.org/10.1016/j.jhazmat.2016.12.058

Fabris, R., Chow, C.W.K., Drikas, M., Eikebrokk, B. 2008. Comparison of NOM character in selected Australian and Norwegian drinking waters. *Water Res.* 42:4188–4196. DOI: 10.1016/j.watres.2008.06.023

Galjaard, G., E. Koreman, E., Metcalfe, D., G. Moore, G., Ericsson, P. 2018. NOM-removal by the SIX-process. *Water Pract. Technol*. 13(3): 254-541. DOI: 10.2166/wpt.2018.072.

Gang, D., Clevenger, T. E., Banerji, S.K. 2003. Relationship of chlorine decay and THMs formation to NOM size. *J. Hazard Mater.* 96(1): 1–12. DOI: 10.106/s0304-3894(2)00164-4.

Gu, J.D., Fan, X.J., Li, H.B., Zhao, Z.Y. 2006. Molecular size distribution of dissolved organic matter in water of the Pearl River and trihalomethane formation characteristics with chlorine and chlorine dioxide treatments. *J. Hazard Mater.* 134: 60-66. DOI: 10.1016/j.jhazmat.2005.10.032.

Han, Q., Yan, H., Zhang, F., Xue, N., Wang, Y., Chu, Y., Gao, B. 2015. Trihalomethanes (THMs) precursor fractions removal by coagulation and adsorption for biotreated municipal wastewater: molecular weight, hydrophobicity/hydrophily and fluorescence. *J. Hazard Mater.* 297: 119-126. DOI: https://doi.org/10.1016/j.jhazmat.2015.04.070.

Han, J., Zhang, X. 2018. Evaluating the comparative toxicity of DBP mixtures from different disinfection scenarios: a new approach by combining freeze-drying or rotoevaporation with a marine polychaete bioassay. *Environ. Sci. Technol.* 52: 10552-10561. DOI: https://doi.org/10.1021/acs.est.8b02054.

Hua, G., Reckhow, D.A. 2007. Characterization of disinfection byproduct precursors based on hydrophobicity and molecular size. *Environ. Sci. Technol*. 41: 3309–3315. DOI: 10.1021/es062178c.

Jiang, J., Li, W., Zhang, X., Liu, J., Zhu, X. 2018. A new approach to controlling halogenated DBPs by GAC adsorption of aromatic intermediates from chlorine disinfection: effects of bromide and contact time. *Separ. Purif. Technol*. 203: 260-267. DOI: https://doi.org/10.1016/j.seppur.2018.04.050.

Karapinar, N., **Uyak, V., Soylu, S., Topal, T. 2014**. Seasonal Variations of NOM Composition and their Reactivity in a Low Humic Water. *Environ. Prog. Sustain. Energy.* 33(3): 962-971. DOI: 10.1002/ep.11878.

Kottelat, R., Vignati, D. A. L., Chanudet, V. & Dominik, J. 2008. Comparison of small- and large-scale ultrafiltration systems for organic carbon and metals in freshwater at low concentration factor. *Water Air Soil Pollut*. 187(1): 343–351. DOI: 10.1007/s11270-007-9504-z.

Kristiana, I., Tan, J., Joll, C.A., Heitz, A., von Gunten, U., Charrois, J.W.A. 2013. Formation of N-nitrosamines from chlorination and chloramination of molecular weight fractions of natural organic matter. *Water Res*. 47 (2), 535–546. DOI: 10.1016/j.watres.2012.10.014.

Li, J., Moe, B., Vemula, S., Wang, W., Li, X.F. 2016. Emerging Disinfection Byproducts, Halobenzoquinones: Effects of Isomeric Structure and Halogen Substitution on Cytotoxicity, Formation of Reactive Oxygen Species, and Genotoxicity *Environ. Sci. Technol.* 50: 67446752. DOI: 10.1021/acs.est.5b05585

Matilainen, A., Lindqvist, N., Korhonen, S., Tuhkanen, T. 2002. Removal of NOM in the different stages of the water treatment process, *Environ. Int*. 28: 457–465. DOI: 10.1016/s0160-4120(02)00071-5.

Mao, Y., Guo, D., Yao, W., Wang, X., Yang, H., Xie, Y.F., Komarneni, S., Yu, G., Wang, Y. 2018. Effects of conventional ozonation and electro-peroxone pretreatment of surface water on disinfection by-product formation during subsequent chlorination. *Water Res*. 130: 322-332. DOI: https://doi.org/10.1016/j.watres.2017.12.019.

Niu, Z., Zhao, P., Zhang, N., Zhang, Y. 2018. Characteristics of molecular weight distribution of dissolved organic matter in bromide-containing water and disinfection by-product formation properties during treatment processes. *J. Environ. Sci.* 65: 179-189. DOI: http://dx.doi.org/10.1016/j.jes.2017.03.013.

Nkambule, T.T.I., Mamba, B., Msagati, T.A.M., Ncube, E.C., Marais, S.S. 2019. Assessment of trihalomethane (THM) precursors using specific ultraviolet absorbance (SUVA) and molecular size distribution (MSD). *J. Water. Process. Eng*. 27: 143-151. DOI: https://doi.org/10.1016/j.jwpe.2018.11.0

Özdemir, K. 2016. The use of carbon nanomaterials for removing natural organic matter in drinking water sources by a combined coagulation process. *Nanomater Nanotechnol*.,6: 1-12. DOI: 10.1177/1847980416663680.

Roe, J., Baker, A., Bridgeman, J. 2008. Relating organic matter character to trihalomethanes formation potential: a data mining approach, *Water Sci. Technol*. 8(6): 717–723. DOI:10.2166/ws.2008.150

Sillanpää, M., Bhatnagar, A., Hed, L., Lahtinen, T., Gjessing, ET., Matilainen, A. 2011. An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment. Chemosphere. 83: 1431-1442. DOI: 10.1016/j.chemosphere.2011.01.018.

Song, J., Jin, P., Jin, X., Wang, X.C. 2019. Synergistic effects of various in situ hydrolyzed aluminum species for the removal of humic acid. *Water Res.* 148,106-114. DOI: https://doi.org/10.1016/j.watres.2018.10.039.

Schwalger, B., Spitzy, A. 2009. Separation of natural organic colloids with a PALL tangential flow filtration system**.** *Water Sci. Technol.* 9(5): 583-590. DOI: 10.2166/ws.2009.574

Swietlik,, J., Dabrowska, A., Raczyk-Stanislawiak, U., Nawrocki, J. 2004. Reactivity of natural organic matter fractions with chlorine dioxide and ozone. *Water Res*. 38: 547–558. DOI: 10.1016/j.watres.2003.10.034.

USEPA (US Environmental Protection Agency), 1998. National primary drinking water regulations: disinfectants and disinfection byproducts notice of data availability. Fed. Regist. 63 (61): 15673-15692. http://www.epa.gov/.

Uyak, V., Özdemir, K., Toröz, İ. 2007. Seasonal variations of disinfection by-productprecursors profile and their removal through surface water treatment plants. *Sci. Total. Environ*.390: 417-424. DOI: 10.1016/j.scitotenv.2007.09.046.

Wang, DS., Feng, CH., Wei, QS., Shi, B., Zhang, L., Tang, HX. 2008a. Seasonal variations of chemical and physical characteristics of dissolved organic matter and trihalomethane precursors in a reservoir: a case study *J. Hazard Mater.* 150: 257-264. DOI: 10.1016/j.jhazmat.2007.04.096

Wei, Q., Feng, C., Wang, D., Shi, B., Zhang, L., Wei, Q., Tang, H. 2008a. Seasonal variations of chemical and physical characteristics of dissolved organic matter and trihalomethane precursors in a reservoir: a case study. *J. Hazard. Mater*. 150: 257–264. DOI: 10.1016/j.jhazmat.2007.04.096.

Wei, Q., Wang, D., Qiao, C., Shi, B., Tang, H. 2008b. Size and resin fractionations of dissolved organic matter and trihalomethane precursors from four typical source waters in China. *Environ. Monit. Asses.* 141: 347-357. DOI: 10.1007/s10661-007-9901-1.

Wilding, A., Liu, R., Zhou, J. L. 2005. Dynamic behaviour of river colloidal and dissolved organic matter through cross-flow ultrafiltration system. *J. Colloid Interface Sci*. 287(1): 152–158. DOI:10.1016/j.jcis.2005.01.114.

Xu, B., Zhu, H.Z., Lin, Y.L., Shen, K.Y., Chu, W.H., Hu, C.Y., Tian, K.N., Mwakagenda, S.A., Bi, X.Y. 2012. Formation of volatile halogenated byproducts during the chlorination of oxytetracycline. *Water Air Soil Pollut*. 223: 4429- 4436. DOI: https://doi.org/10.1007/s11270-012-1206-5.

Yan, M., Roccaro, P., Fabbricino, M., Korshin, G.V. 2018. Comparison of the effects of chloramine and chlorine on the. aromaticity of dissolved organic matter and yields of disinfection by-products. *Chemosphere.* 191: 477-484. DOI: https://doi.org/10.1016/j.chemosphere.2017.10.063.

Yang, P., Huan, L., Xiangru, Z., Aimin, L. 2016. Characterization of natural organic matter in drinking water: Sample preparation and analytical approaches. *Trends Environ. Anal. Chem.* 12: 23-30. DOI: http://dx.doi.org/doi:10.1016/j.teac.2016.11.002.

Zha, X.S., Liu, Y., Liu, X., Zhang, Q., Dai, R.H., Ying, L.W. 2014. Effects of bromide and iodide ions on the formation of disinfection by-products during ozonation and subsequent chlorination of water containing biological source matters. *Environ. Sci. Pollut. Res.* 21 (4): 2714–2723. DOI: 10.1007/s11356-013-2176-x

Zhang, X., Chen, Z., Shen, J., Zhao, S., Kang, J., Chu, W., Zhou, Y., Wang, B. 2020. Formation and interdependence of disinfection byproducts during chlorination of natural organic matter in a conventional drinking water treatment plant. *Chemosphere*. 242: 125227. DOI: https://doi.org/10.1016/j.chemosphere.2019.125227.

Zhao, Z.-Y., Gu, J.-D., Fan, X.-J., Li, H.-B. 2006. Molecular size distribution of dissolved organic matter in water of the Pearl River and trihalomethane formation characteristics with chlorine and chlorine dioxide treatments. *J. Hazard Mater*. 134(1–3): 60–66, DOI: 10.1016/j.jhazmat.2005.10.032.

Zhao, Y., Xiao, F., Wang, D., Yan, M., Bi, Z. 2013. Disinfection byproduct precursor removal by enhanced coagulation and their distribution in chemical fractions. *J. Environ. Sci.* 25 (11): 2207–2213. DOI: 10.1016/s1001-0742(12)60286-1

Zheng, Q., Yang, X., Deng, W., Le, X.C., Li, X.F. 2016. Characterization of natural organic matter in water for optimizing water treatment and minimizing disinfection by-product formation. *J. Environ. Sci*. 42 (4): 1–5. DOI:10.1016/j.jes.2016.03.005