

# DBP PRECURSORS REMOVAL BY MEMBRANE BIOREACTORS

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## ABSTRACT

Natural Organic Matter (NOM) can react with disinfectants and form disinfection byproducts (DBPs). Because of the potential adverse health influence of DBPs, the removal of DBP precursors is required by U.S. Environmental Protection Agency. The membrane bioreactor (MBR) process is an emerging technology that can achieve exceptional effluent quality. The objective of this research is to investigate the removal of DBP precursors by MBR in drinking water treatment. A laboratory-scale MBR was set up to investigate DBP precursors removal from a reservoir water, which had relatively high concentration of organic matter and was difficult to treat using conventional drinking water treatment processes. The MBR has an effective volume of 1.8L and consists of a hollow fiber membrane module, which has pore size of 0.4 $\mu$ m. DBP precursors in both MBR influent and effluent were evaluated based on the DBP formation potential test. The results showed that the haloacetic acid (HAA) precursors from the reservoir water could be removed by the MBR process while the trihalomethane (THM) precursors were not removed. The operational conditions (hydraulic retention time (HRT) and concentration of mixed liquor suspended solids (MLSS)) of the MBR could affect the removal efficiency for DBP precursors. The results of this study also indicated that a shorter HRT and higher MLSS concentration could enhance the removal of HAA precursors. A challenge in this study is to maintain the concentration of MLSS in the MBR system. The addition of new sludge temporarily raised the DBP precursors' level and increased the effluent TOC. Future studies will be focused on optimizing the operational conditions of the MBR system.

## 1. INTRODUCTION

The use of chlorine and other disinfectants for disinfection in drinking water treatment, although reducing the risk of waterborne diseases, produces undesirable compounds

known as disinfection byproducts (DBPs). It has been determined that the trihalomethanes (THMs) and haloacetic acids (HAAs), formed during the disinfection process, are the DBPs occurring most consistently and at overall highest concentrations in finished water [1]. Because of their potential health risks [2], the removal of DBP precursors is required by U.S. Environmental Protection Agency. It has been demonstrated that natural organic matter (NOM) is a DBP precursor in surface water [3]. For some surface waters that have high concentrations of NOM, they are difficult to treat using conventional drinking water treatment processes and meet the U.S. EPA's Stage 1 D/DBP rule [4].

Membrane bioreactor (MBR) process is an emerging bio-treatment technology that has demonstrated many benefits, such as exceptional effluent quality and small footprint [5]. MBR could also be used to reduce the DBP precursors in drinking water treatment. According to Li, et al [6], the MBR produced superior effluent quality in contaminated surface water treatment and was highly effective for eliminating water impurities. The objective of the present study is to investigate the removal of DBP precursors from surface water by MBR. The impact of hydraulic retention times (HRTs) and sludge addition was also studied.

## 2. MATERIALS AND METHODS

### 2.1. Experimental setup

An MBR (Figure 1) was constructed with acrylic plastic and a hollow fiber membrane module, which has a 0.4 $\mu$ m nominal, 0.5 $\mu$ m absolute pore size and a total surface area of 0.03m<sup>2</sup>. The MBR had a dimension of 27.7 $\times$ 7.0 $\times$ 29.0cm<sup>3</sup> (L $\times$ W $\times$ H), and an effective working volume of 1.8L. The MBR was placed into a water bath container and the temperature was controlled at 25°C. A level controller was used to regulate the water level in the bioreactor. The influent and effluent flows were facilitated by two peristaltic pumps operated with an 8 minutes on and 2 minutes off cycle. A manometer was mounted between the membrane module and the effluent suction pump to monitor the trans-membrane pressure (TMP). Continuous aeration was provided through an air diffuser

at the bottom of the reactor to generate strong turbulence for membrane cleaning. Seed-activated sludge was transferred from the Middletown Wastewater Treatment Plant, Middletown, Pennsylvania, USA. The membrane module was chemically backwashed with NaOCl (1.5% free Cl<sub>2</sub>) solution before the experiments started.

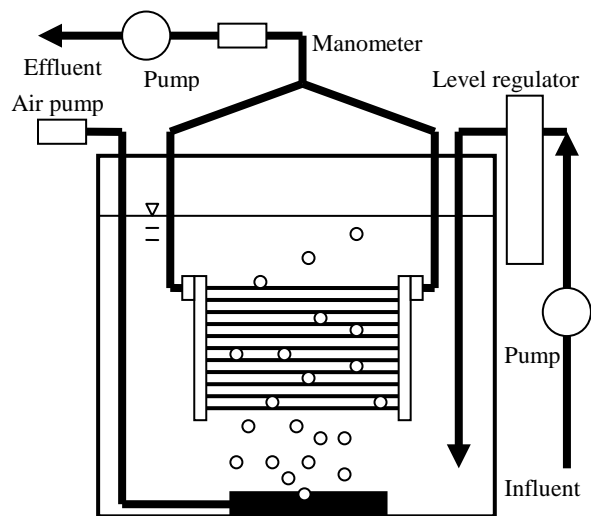


Figure 1: Schematic diagram of the MBR

Water from a reservoir in Middletown, Pennsylvania, USA was collected and used as the MBR influent. The reservoir water had relatively high organic content compared to other nearby water sources and was difficult to treat using conventional drinking water treatment processes. The parameters of the reservoir water were summarized in Table 1.

Table 1: Parameters of the reservoir water

Parameters	Reservoir water
pH	7.94
Temperature (°C)	18.7
Turbidity (NTU)	19.4
Fe (mg/L)	0.52
Mn (mg/L)	0.154
TOC (mg/L)	4.78

## 2.2. Analytical methods

### 2.2.1. TOC

The MBR influent and effluent samples were acidified with concentrated phosphoric acid and immediately stored at 4°C before they were tested for TOC using an OI Analytical 1010 TOC analyzer. The samples were tested within 14 days.

### 2.2.2. MLSS

MLSS were measured using Standard Method 2540D (Total Suspended Solids dried at 103-105°C). A 0.45µm glass fiber filter was prepared ahead of time by rinsing with organic free water and drying in a 105°C oven. A 10mL mixed liquor sample was collected from the MBR and filtered through the pre-rinsed filter. The sample was dried for at least 24 hours in the 105°C oven and then cooled in a desiccator. The MLSS concentration was then determined based on the difference in weight.

### 2.2.3. DBP formation potential test

DBP formation potential test is the measurement of the extent to which the organic material in a water sample reacts with chlorine under a set of controlled conditions and in the presence of excess free chlorine to form a suite of disinfection byproducts [7].

In this study, a chlorine dosage of 20mg/L, an incubation time of 3 days, and a temperature of 20°C were applied to the MBR influent and effluent samples that were stored in 250mL amber bottles [8, 9]. According to Li, et al. [6], the 3-day THM formation potential (THMFP) accounts for approximated 75% of the 7-day THMFP. After incubation, the residual chlorine was measured with a portable spectrophotometer (DR/2010, HACH).

Samples were then taken into pre-weighed 40mL glass vials preserved with ammonia chloride to quench the excess free chlorine. The vials were then capped with Teflon lined septa.

3mL of pentane with internal standard was added to the vials followed by addition of approximately 12g of sodium sulfate for THM extraction. Samples were shaken for 2 minutes and separated for 5 minutes. 1mL of the top layer was transferred to a vial for analysis by a GC (HP6890) following EPA method 551.1 [10]. The THM precursors presented in this study were the sum of four individual THM compounds: CHCl<sub>3</sub>, CHBrCl<sub>2</sub>, CHBr<sub>2</sub>Cl and CHBr<sub>3</sub>.

HAA samples were first acidified by adding 1.5mL concentrated sulfuric acid. Then 3mL of MTBE with internal standard was added followed by addition of approximately 12g of sodium sulfate. Samples were shaken for 2 minutes and separated for 5 minutes. Then 1mL of the top layer was transferred to a HACH test tube. Each tube was added with 1mL of 10% sulfuric acid in methanol and placed in 50°C water bath for 2 hours. After 2 hour methylation, 1mL of MTBE was added to each tube, along with 3mL of 10% sodium sulfate solution. Samples were shaken for 30 seconds, and then the bottom layer was removed. Another 1mL of 10% sodium sulfate was added. After the tube was shaken and the layers were separated, the top layer was transferred to a vial for analysis by a GC (HP6890) following EPA method 552.3 [11]. The HAA precursors were presented in terms of the

sum of six individual HAA compounds: MCAA, MBAA, DCAA, TCAA, BCAA and DBAA.

### 3. RESULTS AND DISCUSSION

#### 3.1. MBR operation

Compared to wastewater, the organic content of the reservoir water was much lower. To provide a sufficient substrate loading for biomass growth and improve the water production of the MBR, shorter HRTs were used. In this study, an HRT of 3 hours and an HRT of 1.5 hours were applied separately for 7 successive days. At the HRT of 3 hours, no regular backwash was required during the study because of the low trans-membrane pressure (TMP) while at the HRT of 1.5 hours, the membrane module was backwashed every 12 hours with the MBR permeate because the TMP increased quickly to the limit of the membrane.

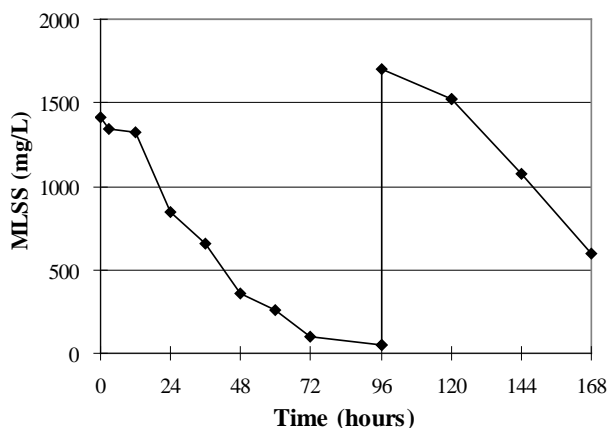


Figure 2: MLSS of the MBR at the HRT of 1.5 hours.

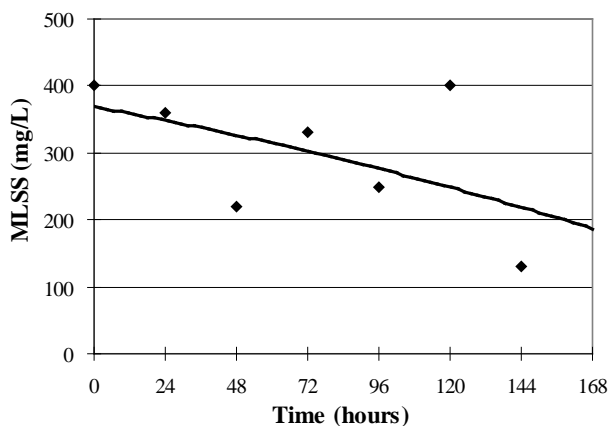


Figure 3: MLSS of the MBR at the HRT of 3 hours.

The concentration of MLSS in the MBR decreased continuously in the experiment (Figure 2), which indicated

that the decay rate of biomass was faster than its growth rate. This could be the reason why there was no biomass accumulation in the MBR. At the 96th hour, there was a sharp increase of the MLSS concentration because additional seed-activated sludge was added into the system to maintain the operation of the MBR system. The concentration of MLSS kept decreasing in the following experimental hours. In addition to the decay of biomass, membrane backwash could also bring some biomass out of the system. At the HRT of 1.5 hours, the membrane was backwashed every 12 hours, and there was an estimated sludge waste rate of 50mg in suspended solids (SS) each time in average.

A lower initial concentration of MLSS was applied for the operation of MBR at the HRT of 3 hours (Figure 3) because the substrate loading rate was lower due to the longer HRT. It was found that the concentration of MLSS was also decreasing although no membrane backwash was performed during the experiment, which indicated that the substrate loading rate at the HRT of 3 hours was difficult to feed the biomass in the MBR.

#### 3.2. Removal of HAA precursors

In the first 24 hours, MBR effluent samples were taken at the 3rd, 12th and 24th hours to examine the removal of DBP precursors in the start-up period of the MBR at the HRT of 1.5 hours. From the 24th to 72nd hours, samples were taken every 12 hours followed by membrane backwash.

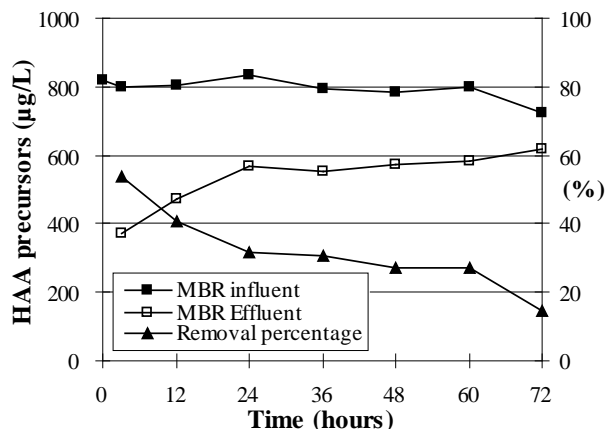


Figure 4: Removal of HAA precursors in the first 72 hours (HRT = 1.5 hours).

As shown in Figure 4, higher removal efficiencies of HAA precursors were observed in the start-up period of the MBR. A maximum removal of 54% HAA precursors was observed at the 3rd hour. Then the removal efficiencies decreased continuously in the following experimental hours. It could be deduced that the removal of HAA precursors was related with the concentration of

MLSS in the MBR. The optimal removal efficiency was achieved when the concentration of MLSS was the highest because there was sufficient active biomass in the MBR to digest HAA precursors in the start-up period since the seed-activated sludge was recently transferred into the system. The removal efficiencies leveled off between the 24th and 60th hours although the concentration of MLSS was decreasing. This was a period that some HAA precursors digesting biomass was still alive in the system while some other functional biomass was decaying. After the 60th hour, biomass was barely observed in the MBR and the removal efficiency of HAA precursors at this time was only 15%.

Samples were taken every 24 hours after the 72nd hour. After sampling at the 96th hour, additional seed-activated sludge was added into the system. As shown in Figure 5, the addition of sludge in the experiment temporally improved the removal efficiency of HAA precursors because more HAA precursors digesting biomass were introduced into the system. After that, the removal efficiency decreased again to as low as 16% at the 168th hour as the biomass decayed.

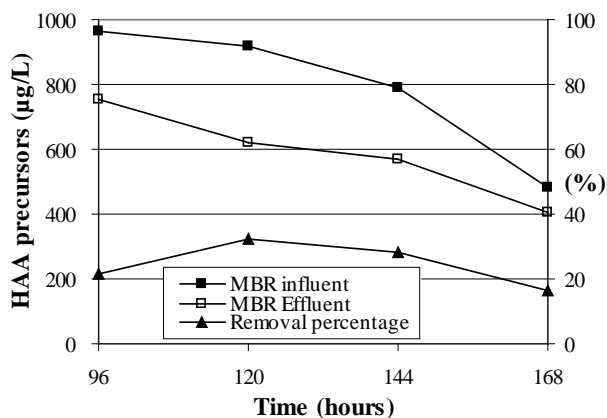


Figure 5: Removal of HAA precursors after 72 hours (HRT = 1.5 hours).

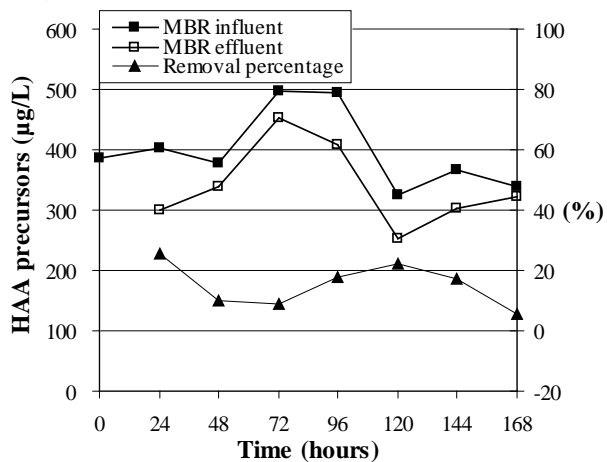


Figure 6: Removal of HAA precursors (HRT = 3 hours).

For the MBR experiment at the HRT of 3 hours, no additional sludge was added after initial inoculation. Samples were taken every 24 hours. It is demonstrated in Figure 6 that the maximum removal of 25% HAA precursors was observed at the 24th hour. As the concentration of MLSS increased at the 124th hour, another peak of removal efficiency occurred at the same time. The lowest removal efficiency was observed at the 168th hour when there was only 130mg/L of MLSS.

According to the results (Figures 4, 5, 6), it could be summarized that a shorter HRT was recommended for the MBR process aimed at HAA precursors removal from the surface water because it could increase the substrate loading rate and sustain the growth of biomass. The results indicated that the decrease of HRT from 3 to 1.5 hours could accordingly increase the average removal efficiency of HAA precursors from 15% to 32%. The result of the addition of seed-activated sludge further proved that the concentration of MLSS had a relationship with the performance of MBR on the removal of HAA precursors.

### 3.3. Removal of THM precursors

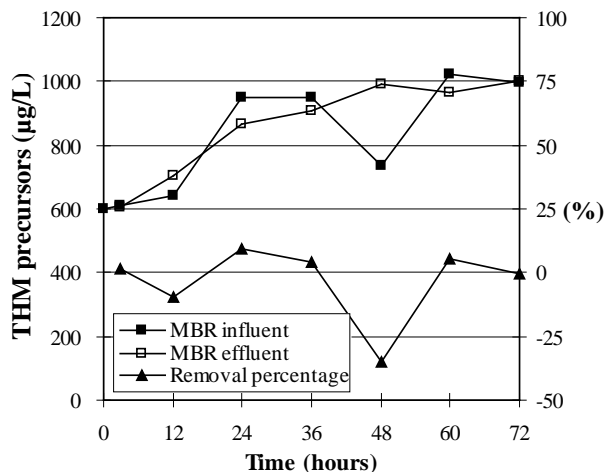


Figure 7: Removal of THM precursors in the first 72 hours (HRT = 1.5 hours).

It is shown in Figure 7 that the THM precursors were not well removed in the experiment. It was found that the concentration of THM precursors in the MBR effluent was even increased after MBR treatment and the biggest negative peak of removal efficiency was observed at the 48th hour when the biomass in the MBR decreased sharply. At the 72nd hour when biomass was barely observed, the removal efficiency of THM precursors was 0%. The results indicated that the decay of biomass could possibly produce more THM precursors. THM precursors were not removed from the reservoir water at the 72nd hour because there was little biomass activity as well as biomass decay.

Before the additional seed-activated sludge was added into the system at the 96th hour, the MBR yielded a removal efficiency of 0% for THM precursors due to the low concentration of MLSS. At the 120th hour (24 hours after sludge addition), a big negative peak of removal efficiency was observed, which was due to the sharp decay of biomass that possibly produced more THM precursors. Different from the removal of HAA precursors, the maximum removal efficiency of THM precursors was observed at the 168th hour when 18% of THM precursors were removed, which indicated that the THM precursors could be removed if the operational conditions of the MBR were optimized.

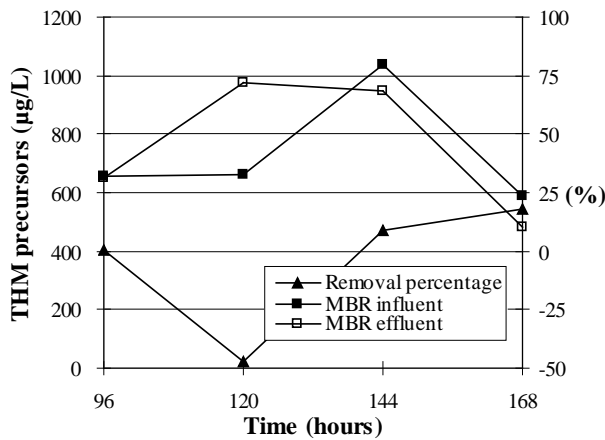


Figure 8: Removal of THM precursors after 72 hours (HRT = 1.5 hours).

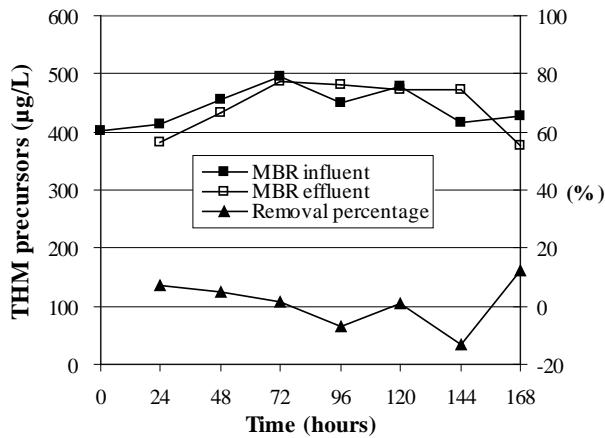


Figure 9: Removal of THM precursors (HRT = 3 hours).

It is shown in Figure 9 that the removal efficiency of THM precursors decreased continuously in the first 96 hours at the HRT of 3 hours. In consistent with the results at the HRT of 1.5 hours, the maximum removal efficiency was also observed at the 168 hours when 12% of THM precursors were removed.

According to the results of the experiment (Figures 7, 8, 9), it could be summarized that the THM precursors

were not well removed from the reservoir water by the MBR. The decrease of the HRT from 3 to 1.5 hours did not improve the removal efficiency. However, it is demonstrated in Figures 8 and 9 that the positive peak of the removal efficiency occurred at the 168th hour when the biomass was little while the negative peak was observed when the biomass decreased sharply, which possibly indicated that the decay of biomass produced more THM precursors. To avoid the biomass decay and improve the MBR performance, higher substrate loading rate was suggested in the future study.

### 3.4. Removal of TOC

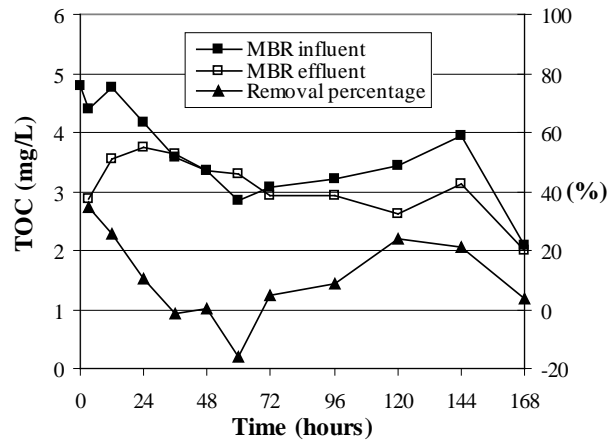


Figure 10: Removal of TOC (HRT = 1.5 hours).

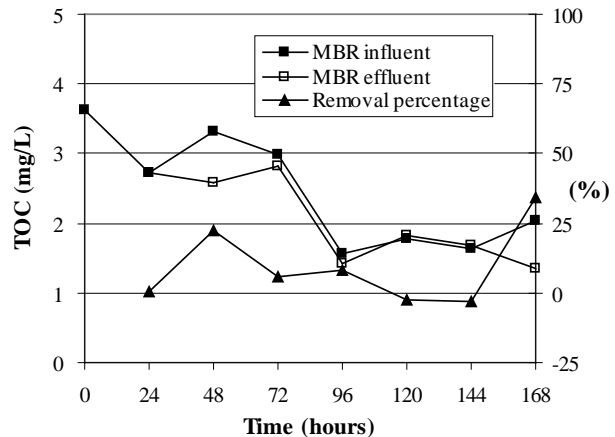


Figure 11: Removal of TOC (HRT = 3 hours).

As shown in Figure 10, at the HRT of 1.5 hours, the MBR yielded an average TOC removal efficiency of 11%. The deterioration of MBR performance was observed when the biomass concentration was decreasing. It may be deduced that better removal efficiency could be maintained if the MBR was kept at a higher MLSS concentration. The increase of HRT from 1.5 to 3 hours (Figure 11) slightly

deteriorated the MBR effluent as the average TOC removal efficiency was 9% at the HRT of 3 hours.

Super pure water was used as the MBR feed to examine the impact of sludge addition on the MBR effluent. Sludge was added at the 0th hour and 3rd hour, respectively. As shown in Table 2, the TOC and DBPFP in the MBR effluent showed a sudden increase after inoculation and then decreased, which indicated that the addition of seed-activated sludge could temporarily raise the DBPFP levels and increased the effluent TOC. It was also noted that the THMFPP of the MBR effluent was higher than the HAAFP several hours after sludge inoculation, which was possibly due to the decay of biomass.

Table 2: Parameters of the MBR effluent after sludge inoculation (HRT = 1.5 hours).

Time hours	TOC mg/L	THMFPP µg/L	HAAFP µg/L
0	2.71	303	549
1.5	1.28	153	234
3.0	0.74	103	121
3.0	2.02	261	189
4.5	1.34	174	76
6	0.84	118	0

#### 4. CONCLUSIONS

The study indicated that the HAA precursors and TOC could be removed from the reservoir water by the MBR process and a maximum removal of 54% HAA precursors was observed at the HRT of 1.5 hours. However, the THM precursors were not well removed from the reservoir water. It was possibly because the biomass, although could reduce some HAA precursors, produced more THM precursors in the MBR effluent when there was much decay. The addition of sludge could temporarily increase the effluent TOC and DBPFP, and it could enhance the removal efficiency of HAA precursors as more biomass was introduced into the MBR system.

It was found that the operational conditions had large impact on the performance of the MBR. A higher concentration of MLSS and a shorter HRT were recommended for the removal of DBP precursors by MBR from surface water. However, it is a big challenge to maintain a higher concentration of MLSS in the MBR due to the low substrate content of surface water. Further studies will be focused on the optimization of MBR operation.

#### 5. ACKNOWLEDGEMENTS

This study was supported by U.S. Environmental Protection Agency (EPA) Small Public Water Systems Technology Assistance Center (SPWSTAC) at Penn State Harrisburg.

#### 6. REFERENCES

- [1] P.D. Cohn, M. Cox, and P.S. Berger, "Health and aesthetic aspects of water quality," Chapter 2 in R. D. Letterman (e.d.), *Water Quality and Treatment: A Handbook of Community Water Supplies*, McGraw-Hill, New York, 1999.
- [2] A.M. Comerton, R.C. Andrews, and D.M. Bagley, "Evaluation of an MBR-RO system to produce high quality reuse water: Microbial control, DBP formation and nitrate," *Water Research*, 39, pp. 3982-3990, 2005.
- [3] M.D. Williams, "Membrane bioreactor process for removing biodegradable organic matter and disinfection by-product precursors from water: modeling and process efficiency," Doctoral dissertation, University of Southern California, U.S.A., 2002.
- [4] United States Environmental Protection Agency (USEPA), *National Primary Drinking Regulations: Disinfectants and Disinfection Byproducts; Final Rule*. 40 CFR Parts 9, 141, and 142, Federal Register 63 (241), 69390-69486, 1998.
- [5] Water Environment Federation, "Membrane bioreactors", Chapter 3 in *Membrane Systems for Wastewater Treatment*, WEF Press, U.S.A., 2006.
- [6] X.Y. Li, and H.P. Chu, "Membrane bioreactor for the drinking water treatment of polluted surface water supplies," *Water Research*, 37, pp. 4781-4791, 2003.
- [7] T.Sirivedhin, and K.A. Gray, "Comparison of the disinfection by-product formation potentials between a wastewater effluent and surface waters," *Water Research*, 39, pp. 1025-1036, 2005.
- [8] J.F. Stile, "Membrane bioreactors for disinfection byproduct control," M.S. thesis, The Pennsylvania State University, U.S.A., 2006.
- [9] Y.F. Xie, *Drinking water: Formation, Analysis, and Control*, CRC Press, U.S.A., 2003.
- [10] USEPA Method 551.1 Revision 1.0, "Determination of Chlorination Disinfection Byproducts, Chlorinated Solvents, and Halogenated Pesticides/Herbicides in Drinking Water by Liquid-Liquid Extraction and Gas Chromatography with Electron Capture Detection," National Exposure Research Laboratory, Office of Research and Development, Cincinnati, OH, 1995.
- [11] USEPA Method 552.3 Revision 1.0, "Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid-Liquid Microextraction, Derivatization, and Gas

Chromatography with Electron Capture Detection,” Technical Support Center, Office of Groundwater and Drinking Water, EPA 815-B-03-002, July 2002.