Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1145602

57 (2016) 25057–25069
November

Taylor & Francis
Taylor & Francis Group

Effect of phosphorus addition on biofiltration pre-treatment to reduce ultrafiltration membrane fouling

Ishita Rahman[a], Michele I. Van Dyke[a,*], William B. Anderson[a], Xiaohui Jin[b], Souleymane Ndiongue[b], Peter M. Huck[a]

[a]*NSERC Chair in Water Treatment, Department of Civil & Environmental Engineering, University of Waterloo, 200 University Avenue West, Waterloo, ON N2L 3G1, Canada, email: i.rahman.040@gmail.com (I. Rahman), Tel. +519 888 4567, ext. 36193; emails: mvandyke@uwaterloo.ca (M.I. Van Dyke), wbanderson@uwaterloo.ca (W.B. Anderson), pm2huck@uwaterloo.ca (P.M. Huck)*
[b]*Walkerton Clean Water Centre, 20 Ontario Rd., P.O. Box 160, Walkerton, ON N0G 2V0, Canada, emails: xjin@wcwc.ca (X. Jin), sndiongue@wcwc.ca (S. Ndiongue)*

Received 19 August 2015; Accepted 18 January 2016

ABSTRACT

A pilot-scale study investigated the effect of phosphorus addition on a drinking water biofilter used to reduce fouling of an ultrafiltration membrane. Biofiltration without pre-treatment (BF_{WP}) has been shown to be an effective pre-treatment for the removal of natural organic matter (NOM) components that cause membrane fouling. However, the river source used in this study was found to have low phosphorus concentrations that could potentially affect biofilter biomass levels and NOM biodegradation. The river water source (Saugeen River located at Walkerton, Ontario, Canada) had a high total organic carbon (4.34–6.61 mg/L) of primarily humic content, variable turbidity, and seasonal changes in water temperature (9.7–19.9°C) as measured over the study period. Phosphorus was added to the biofilter influent at 0.01 mg P/L, and later at 0.05 mg P/L, over a four-month period. Biofilter activity, NOM removal, and membrane performance were compared to a control system operating under identical conditions but without nutrient addition. Filter biomass measured by ATP and fluorescein diacetate hydrolysis (overall enzyme activity) was stable over time, with no difference between control and phosphorus-amended biofilters. As well, phosphorus addition did not improve the removal of NOM fractions, especially biopolymers that are important for membrane fouling. There was a small initial increase in the removal of dissolved organic carbon and humic substances after phosphorus addition, but this effect diminished over time. The effluent from each biofilter was used to operate an ultrafiltration membrane system using conditions similar to full scale. Membrane fouling for each experiment was measured over 1.5 d, and operating cycles included 30-min permeation followed by backwashing/air sparging. Results showed that there was no difference in hydraulically reversible or irreversible fouling of membranes fed with the effluent from control or phosphorus-amended biofilters. It was found that biofilter nutrient feed requirements are likely site specific, and affected by factors including biomass and NOM characteristics.

Keywords: Biofiltration; Fouling; Natural organic matter; Phosphorus; Ultrafiltration

*Corresponding author.

1. Introduction

Biofiltration in drinking water treatment typically involves slow or rapid filtration using sand, anthracite, or activated carbon in the absence of chlorine. Biofiltration without pre-treatment (i.e. without prior coagulation/flocculation or ozonation), defined as BF_{WP} by Huck et al. [1], has shown potential as a pre-treatment for ultrafiltration (UF) membranes. BF_{WP} can reduce the concentrations of specific fractions of natural organic matter (NOM) considered responsible for membrane fouling (e.g. [2]). Fouling continues to be a major operational challenge associated with membranes, as it increases operating costs and reduces membrane life. Recent studies to assess factors affecting biomass development and organic fraction removal provide more insight into biofilter performance. For example, biopolymers, which include polysaccharides and protein-like substances, have recently been shown to contribute most to fouling of low pressure polymeric membranes [2–7].

Less is known about biofilter conditions that are optimal for microbial degradation of membrane foulants. The removal of NOM is typically accomplished by heterotrophic micro-organisms, which use organic carbon for biosynthesis and energy, but also require nitrogen and phosphorus, as well as other elements in lesser amounts (i.e. S, K, Mg, Ca, Na, Fe, and micronutrients). C:N:P ratios of 100:10:1 are typically considered optimal for microbial growth, likely derived from the elemental composition of marine phytoplankton (106:16:1) first determined by Redfield [8]. Based on a larger number of observations, Sterner et al. [9] presented an overall stoichiometric ratio for marine and freshwater environments of 100:12:0.6, but also showed that this value varied for smaller or regional data-sets. Others have also shown that C:N:P composition and requirements for growth will vary between species and environments (as reviewed by Sardans et al. [10]). As well, biofilm processes can be affected by nutrient cycling within the biofilm [11].

In drinking water systems, carbon has typically been found to be the nutrient that limits microbial growth. Nitrogen is rarely limiting in water; however, it has been shown that phosphorus can be the limiting nutrient in certain natural or treated waters [12–14]. Granger et al. [15], Lauderdale et al. [16], Li et al. [17], Sang et al. [18], and Yu et al. [19] all found positive changes in biofilter performance (increased organic carbon or nitrogen removal, and/or higher biomass quantity and activity) with the addition of phosphorus at doses between 0.014 and 0.025 mg P/L. On the other hand, Vahala et al. [20] found that the addition of 0.027 mg/L phosphorus to a biofilter influent did not enhance biofilter performance or biomass growth, even though the raw water appeared to be phosphorus-limited. As phosphorus addition to biofilters has been shown to improve the removal of organics, the removal of potential membrane foulants may be enhanced as well and would result in better performance of biofiltration as a membrane pre-treatment.

In a previous phase of this study [7], direct biofiltration pre-treatment of a river water (Saugeen River in southern Ontario, Canada) resulted in 14–68% and 8–55% improvement in the hydraulically irreversible and reversible fouling rates, respectively, of a UF membrane, compared to water without pre-treatment. However, the phosphorus concentration in the source water used for these experiments was known to be low [21,22]. Hence, the study was expanded to investigate the effect of phosphorus addition on biofilter activity and the removal of potential membrane foulants and fouling rates of a UF membrane.

2. Materials and methods

2.1. Water source

Biofilters were fed with untreated water from the Saugeen River, which is located near Walkerton in southern Ontario, Canada, within the 908 km^2 Lower Saugeen watershed. The watershed consists primarily of agricultural land (76%), with 19% forest cover, and 1.2% urban area [23]. Water was collected weekly from the Saugeen River and transported by tanker truck to an outdoor 40,000 L tank at the Walkerton Clean Water Centre. The outdoor storage tank was maintained at atmospheric temperature with circulation to ensure consistent water quality, but the tank had a heating system which was automatically activated when the atmospheric temperature dropped below 7˚C to prevent freezing. The water was pumped directly to the biofilters without any pre-treatment (i.e. no coagulation or ozonation). The maximum retention time of water in the storage tank was 7 d.

2.2. Experimental setup

A pilot treatment train (Fig. 1) was constructed and operated at the technology demonstration facility at the Walkerton Clean Water Centre. The two parallel dual media biofilters consisted of 5.1 cm diameter × 2.1 m high glass columns (BF1 and BF2). The media layer consisted of 55 cm of anthracite (effective size of 1 mm, uniformity coefficient of 1.6) over 25 cm sand (effective size of 0.5 mm, uniformity coefficient of 1.5) supported by 15 cm of gravel. The biofilters were operated at an empty bed contact time (EBCT) of

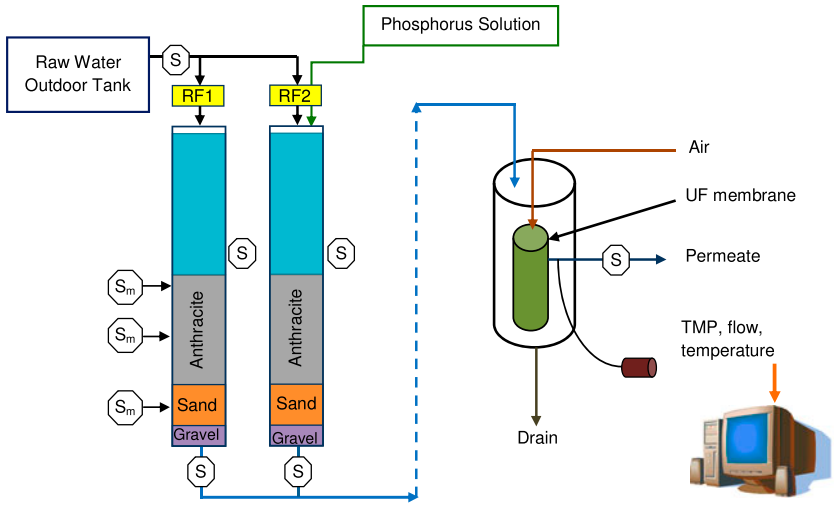

Fig. 1. Experimental setup schematic.
Notes: RF: roughing filter; S: water sample; S_m: media sample; TMP: transmembrane pressure.

10 min, corresponding to a hydraulic loading rate of 5 m/h. They were gravity fed and operated in downflow mode. The biofilters were each preceded by a roughing filter (RF1 and RF2) to minimize the impact of varying turbidity and particle loads on the biofilters. The roughing filters were constructed of clear PVC cylinders (10 cm diameter, 23 cm high) containing two 5 cm layers of gravel (9.5 mm over 5 mm diameter). Both biofilters were backwashed once per week using biofilter effluent. The backwash process included air scour for 1 min to break up media plugs, followed by 4 min of air-water collapse pulsing. The water flow was then gradually increased to achieve a 25% bed expansion (1 min) followed by 50% bed expansion for 4 min after the air scour was stopped.

BF1 and BF2 were operated similarly using Saugeen River water for the first 10 months of the study (March 2012–February 2013). Phosphorus addition to BF2 was then initiated on 4 February 2013, while BF1 was maintained as a control. The period during which phosphorus was added is the focus of this paper. K_2HPO_4 (BDH Chemicals; ASC grade) was dosed continuously at 0.01 mg P/L into the BF2 influent for 75 d using a dosing pump (LMI Milton Roy model P021-35251). The dose was then increased to 0.05 mg P/L on 19 April 2013 and continued at this level for an additional 42 d. K_2HPO_4 stock solutions were prepared in 1 L ultrapure water and autoclaved for 30 min.

For the membrane fouling experiments, a bench-scale GE Water & Process Technologies (Oakville, Ontario, Canada) ZeeWeed®-1 polymeric (PVDF) UF hollow fiber membrane was used. The membrane had an outside-in configuration with a nominal surface area of 0.047 m^2, nominal pore size of 0.04 μm, and was operated at a constant flux of 57 L/m^2 h (LMH) (temperature corrected to 20°C). The clean membrane surface was non-ionic and hydrophilic [24]. The membrane module was mounted in a vertical position in a clear PVC cylindrical tank and was designed to cycle automatically using a programmable logic controller (Allen-Bradley 1760-L18AWA-EX Pico Controller, Rockwell Automation) as described by El-Hadidy et al. [4,25]. Each cycle included 30 min of permeation using a peristaltic pump (Masterflex L/S Easy-Load II pump head, model 77202-50) followed by a 20 s backwash with air sparging. At the end of each cycle, the tank was completely drained and then refilled with fresh feedwater (40 s). The setup also included a temperature sensor (Onset HOBO 12-Bit Temperature Smart Sensor), pressure transducer (Cole-Parmer model 68075-02), and flow monitor connected to a data logger (Onset HOBO Energy Logger model H22–001) for continuous measurements during the fouling experiments. The membrane was chemically cleaned between each fouling experiment by placing it in 200 mg/L NaOCl for 5 h, followed by 5 g/L citric acid at room temperature for 5 h, and rinsed thoroughly with deionized water between steps. Before each experiment, the module was tested for integrity using a pressure calibrator (Meriam Meri-cal DP2001I) so that the pressure drop through the membrane was not more than 2 kPa (0.3 psi) over 2 min, as recommended by the manufacturer. Each experiment was also preceded by a clean water permeability test with deionized water at four different fluxes (32, 45, 57, 70 LMH) to test for cleaning efficiency. A detailed description of the methods can be found in El-Hadidy et al. [4,25].

2.3. Membrane fouling experiments

Membrane fouling experiments were conducted in batch mode using biofiltered Saugeen River water. To assess water from each biofilter column separately, but using the same batch of river water, the run length was set at 1.5 d or until the target maximum TMP was reached 55.2 kPa (8 psi). The transmembrane pressure during the experiments was recorded every 10 s using a data logger. This was later normalized to 20˚C, and fouling rates were calculated using the normalized transmembrane pressure data. Reversible and irreversible fouling were calculated as described by El-Hadidy et al. [4]. Briefly, fouling within a backwash cycle was considered to be due to reversible fouling. The reversible fouling rate was calculated as the increase in TMP within each cycle over the permeation time. Irreversible fouling was considered as the difference in TMP between the start of two consecutive 30-min cycles (after backwash), and the rate was calculated using the increase in this value over the permeation time.

2.4. Sampling procedure

Water samples were collected approximately every two weeks from selected points in the treatment train including the roughing filter inlet (raw), biofilter influent approximately 15 cm above the media surface (BF1 and BF2 influent), and biofilter outlets (BF1 and BF2 effluent). From March 2012 to May 2013 (14 months), the samples were collected for turbidity, pH, temperature, alkalinity/hardness, UV_{254}, TOC, DOC, and LC-OCD fraction analysis. Samples for nitrogen compounds and orthophosphorus were collected from November 2012 to May 2013 (seven months), and for total phosphorus from April to May 2013 (two months). After water samples were collected, the filters were drained and media samples were acquired. Media samples were collected from three sampling ports from: (i) the top anthracite layer (8 cm below media surface), (ii) the mid-anthracite layer (28 cm below media surface), and (iii) the mid-sand layer (67 cm below the media surface). Samples from the mid-sand and mid-anthracite layer were collected approximately every 2 weeks from March 2012 to May 2013 (14 months), and samples from the top port were only collected during phosphorus dosing (February–May 2013). The biofilters were replenished with sand and anthracite to replace what was removed, and the columns were backwashed before restarting the inflow. During the membrane fouling experiments, water samples were collected after the UF membranes approximately 1.5 h after membrane permeation was started and analyzed for turbidity, TOC, DOC, and NOM fractions. All samples were stored at 4˚C until analysis.

2.5. Water quality analysis

Phosphorus and nitrogen in raw and biofiltered water were analyzed by ALS Global Environmental Laboratory, Waterloo, Ontario, Canada. Total phosphorus and orthophosphorus were measured based on method 4500-P B E [26] and both had method detection limits (MDLs) of 0.003 mg/L. Nitrate and nitrite were measured based on US Environmental Protection Agency (EPA) method 300.0 IC, ammonia based on EPA method 350.1 and total Kjeldahl nitrogen (TKN) based on method 4500-N [26]. Total nitrogen concentrations were calculated by adding the concentrations of nitrate, nitrite, and TKN.

Samples that required filtering were passed through pre-rinsed 0.45 μm Supor membrane disk filters (Pall Life Sciences, Mississauga, Ontario, Canada), and both filtered and unfiltered samples were stored at 4˚C until analysis. Total and dissolved organic carbon (TOC and DOC) were measured by wet oxidation using an OI-Analytical model 1010 TOC analyzer. Liquid chromatography-organic carbon detection (LC-OCD; DOC-Labor, Karlsruhe, Germany) analysis was employed to measure the concentrations of the various NOM fractions in water, and the chromatograms were analyzed using DOC-Labor ChromCALC software as described by Huber et al. [27]. LC-OCD separates organic carbon using size exclusion chromatography into biopolymers (molecular weight greater than 10 kDa), humic substances, building blocks (lower molecular weight humics), low-molecular weight (LMW) acids, and LMW neutrals. Turbidity was measured using a Hach 2100P Portable Turbidimeter, and UV_{254} absorbance was measured with a Hewlett-Packard UV–vis model 8453 spectrophotometer.

2.6. Biomass analysis

Total ATP was measured using the LuminUltra™ DSA adenosine triphosphate (ATP) test kit (LuminUltra, Fredericton, New Brunswick, Canada). Fluorescein diacetate (FDA) hydrolysis was measured based on the method of Green et al. [28]. Briefly, 1 g of media was added to 50 mL of 60 mM sterile sodium phosphate buffer (pH 7.6) containing 0.5 mL of 4.9 mM FDA, and incubated for 3 h at 37˚C. Fluorescein production was measured at 490 nm using a spectrophotometer and compared with a fluorescein

standard curve. All biofilter biomass and water quality data are presented graphically, but individual data points are available from Rahman [29].

3. Results and discussion

3.1. Biofilter feedwater quality

DOC concentrations ranged from 2.73 to 7.03 mg/L (Table 1). NOM fractions measured using LC-OCD showed that humic material made up the largest component of NOM in the raw river water (54–79% of the DOC). Other components, including biopolymers and low-molecular weight acids and neutrals, were present at lower concentrations (Table 1). Biopolymers, which are important in membrane fouling, accounted for 2–11% of the total DOC. These values are similar to those of Croft [30] who also analyzed NOM fractions in the Saugeen River. Nitrate in the river water was higher than the other forms of nitrogen and made up 70–90% (average 82%) of the total nitrogen. Nitrate concentrations were higher at cold temperatures, which is in agreement with historical data for the Saugeen River [22]. Nitrite-N remained below the detection limit (MDL 0.10 mg/L) throughout the test period, and ammonia-N (MDL 0.05 mg/L) was only detected once (May 23). TKN, which measures organic nitrogen and ammonia, was reasonably consistent and ranged between 0.3 and 0.6 mg/L. Orthophosphorus was low and typically close to the MDL (0.003 mg/L), with a peak value of 0.01 mg/L on March 18, and made up 25–70% of the total phosphorus (average 38%; std. dev. 17%).

The nutrients available in the biofilter feedwater were initially assessed using data collected on November 26, 2012 using DOC, TKN, and orthoP concentrations. The elemental molar C:N:P ratio was found to be 100:10:0.01, and suggested that phosphorus concentrations were limiting but nitrogen levels were not limiting (based on a theoretical C:N:P requirement of 100:10:1). The average C:N:P ratio of the raw water during the experimental period (February to May 2013; n = 10) was 100:8:0.02, showing a similar low phosphorus concentration. Although the ammonia concentration in the river was low, it is reasonable to assume that micro-organisms can to some extent also utilize organic nitrogen for growth in addition to ammonia [31]. In addition, the river also had high levels of nitrate, which can also be assimilated by bacteria for growth (e.g. [32]). The biodegradable portion of DOC was not measured in this study, however, biodegradable dissolved organic matter (BDOC) has been reported to be typically in the range of 10–30% of the total DOC in surface waters [33–36]. We can test the most limiting scenario based on these values by assuming a theoretical BDOC to DOC ratio

Table 1
Raw water quality in the Saugeen River

Parameter	Average	SD[a]	Range	n[b]	Sample period
Turbidity (NTU)	5.66	4.40	0.71–17.9	26	March 2012–May 2013 (14 months)
pH	8.06	0.13	7.76–8.39	31	
Temperature (°C)	17.5	4.08	9.7–23.6	30	
Alkalinity (mg/L as $CaCO_3$)	227	21.5	156–256	30	
Hardness (mg/L as $CaCO_3$)	327	45.0	200–380	24	
UV_{254}	0.13	0.04	0.07–0.24	31	
TOC (mg/L)	4.48	1.10	2.85–7.29	31	
DOC (mg/L)	4.36	1.09	2.73–7.03	31	
Biopolymers (mg/L)	0.13	0.05	0.06–0.26	25	
Humic substances (mg/L)	3.03	0.91	1.36–5.06	25	
Building blocks (mg/L)	0.47	0.14	0.04–0.77	25	
LMW acids (mg/L)	0.01	0.03	ND[c]–0.11	25	
LMW neutrals (mg/L)	0.31	0.08	0.22–0.49	25	
Total nitrogen (mg/L)	2.71	0.56	1.92–3.48	11	November 2012–May 2013 (7 months)
Nitrate (mg N/L)	2.24	0.55	1.35–2.94	11	
TKN (mg N/L)	0.47	0.09	0.32–0.60	11	
Ammonia (mg N/L)	0.03	0.03	<0.02–0.13	11	
Orthophosphorus (mg P/L)	0.004	0.003	<0.003–0.010	11	
Total phosphorus (mg/L)	0.011	0.004	0.004–0.016	6	April 2013–May 2013

[a]SD—standard deviation.
[b]n—sample number.
[c]ND—not detected.

of 10%, and under these conditions the phosphorus level in the Saugeen River during the experimental period would still be limiting with a C:P ratio of 100:0.2. Bacteria use inorganic soluble phosphorus for growth, but can also utilize certain dissolved organic phosphorus compounds for their requirements (e.g. [37,38]). Total-P concentrations in the Saugeen River were higher than orthoP values, but the proportion of total-P that is microbially available is unknown. The contribution of both organic P and N to meet the nutrient requirements for optimal biofilter performance is an area requiring further research.

3.2. Effect of phosphorus addition on filter biomass

During initial biofilter acclimation, biomass quantity measured using ATP showed a rapid increase in both the anthracite layer (measured at mid-layer, 28 cm from the media surface) and the lower sand layer (measure at 67 cm from the media surface) and reached a steady maximum value after about 2 months (Fig. 2). There was no significant difference (paired t-test, $\alpha = 0.05$) in ATP levels between the parallel biofilters (BF1 and BF2) during start-up and steady-state operation. There was a drop in the ATP values in December 2012, which was more prominent in BF2 media samples, but the reason for this is unknown. However, ATP levels recovered quickly and overall results show that there was little change in ATP concentrations in the biofilters over time or at different temperatures. After phosphorus addition (0.01 mg P/L), there was a small decrease in ATP levels in BF2 compared to the control filter (BF1). However, ATP values recovered to those of the control filter after a month, and there was no significant difference between BF1 and BF2 when the phosphorus dose was increased to 0.05 mg P/L.

Microbial activity in the media was also measured using FDA hydrolysis. The FDA assay has been used to measure total microbial activity in soil, but is not often used to measure biofilter activity. This method provides a measure of overall microbial enzymatic activity, as FDA can be hydrolyzed by a wide range of non-specific esterases, proteases, and lipases which are widespread among micro-organisms [39]. Similar to ATP, there was a rapid initial increase in FDA hydrolysis activity in the upper anthracite layer, but a lag in the lower sand media (Fig. 3). FDA hydrolysis plateaued within two months and then remained essentially constant over time and with temperature, and there was no significant difference between parallel biofilters (BF1 and BF2) as measured by a paired t-test ($\alpha = 0.05$). There was no change in FDA hydrolysis in BF2 following phosphorus addition (Fig. 3). Others have shown that FDA hydrolysis was correlated with ATP and cell density [40]; however, in this study ATP and FDA hydrolysis were poorly correlated (r = 0–0.5 for different depths and media).

The absence of an effect on biomass quantity and activity during the four months of phosphorus enhancement could be attributable to a number of factors. It is possible that the raw water feeding the biofilters was not phosphorus limited, and that the biomass was adapted to grow and function in a low

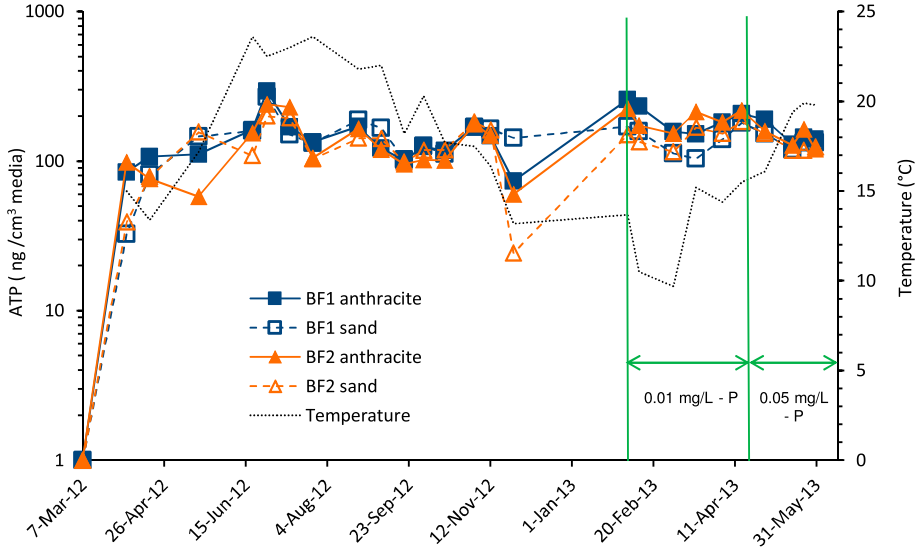

Fig. 2. Comparison of biomass quantity (as ATP) in biofilter media.

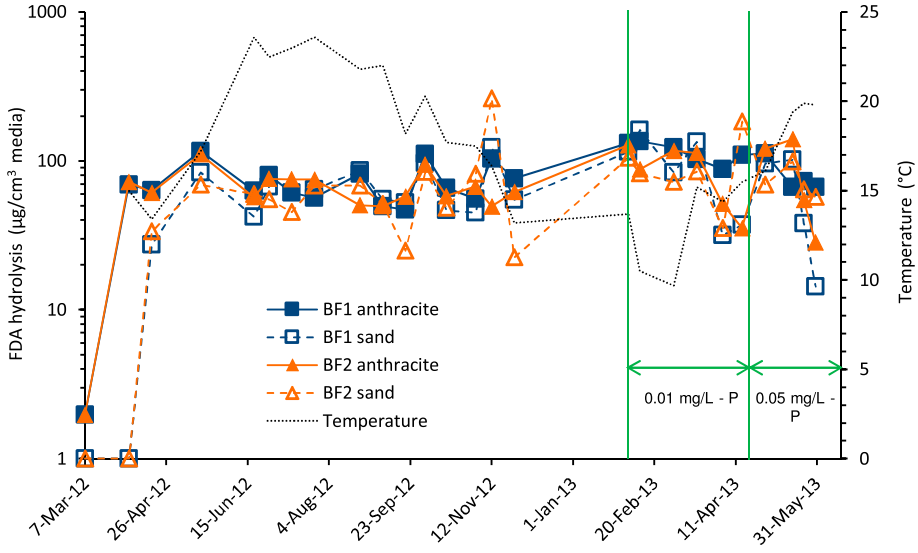

Fig. 3. Comparison of biomass activity (as FDA hydrolysis) on biofilter media.

phosphorus environment, as the river has historically had low levels of phosphorus. As noted earlier, standard nutrient ratios may not apply for biofilm systems, because of recycling of the P within the biofilm. As well, phosphorus addition may have resulted in either no change or altered the microbial community in a way that did not affect ATP or FDA hydrolysis measurements.

3.3. Effect of phosphorus on NOM removal

In the steady-state operation period before phosphorus addition was started in February 2013, DOC removal by the biofilters ranged from 0 to 12% (Fig. 4), and removal in BF1 and BF2 was similar on each sample date (paired *t*-test; $\alpha = 0.05$). The removal of biopolymers ranged from 0 to 58% (average 21%), and removals by BF1 and BF2 were also identical (paired *t*-test; $\alpha = 0.05$) (Fig. 5). Substantial removal of humic substances by the biofilters was not observed during the pre-phosphorus-dosing operation (Fig. 6). The concentrations of LMW compounds in the raw water were very low and therefore removals were difficult to assess, however, overall there was also no significant difference (paired *t*-test; $\alpha = 0.05$) in removal of these fractions between parallel biofilters (data not shown).

After the addition of 0.01 mg/L-P to BF2, there was an initial increase in DOC removal (7.2% for BF2, 1.2% for BF1 control) in four samples collected over the first month (February–March; Fig. 4). This is especially important as the DOC removal had previously been similar (average 4.1% for BF2, 3.7% for BF1 control) for both biofilters since acclimation (eight months).

However, after one month DOC removal in BF2 dropped back to the level of the control filter (BF1). Humic substance removal by BF2 was also slightly higher on the first sample date after phosphorus addition (Fig. 6), as were UV-absorbing constituents, as measured by UV absorbance at $\lambda = 254$ nm (data not shown). There was no significant difference in biopolymer concentration in the effluents of BF1 and BF2 during the phosphorus dosing period (including the low and high dose period, $n = 10$, $\alpha = 0.05$) (Fig. 5). Therefore, the increased removal in DOC immediately after P dosing began was probably associated with the humic substances and/or another DOC fraction and not the biopolymers.

When no changes in biofilter performance were observed after two months of dosing at 0.01 mg P/L, the phosphorus concentration was increased to 0.05 mg P/L. DOC, biopolymer and humic substances removals after dosing at 0.05 mg P/L were similar in BF1 and BF2 (Figs. 4–6), however a meaningful statistical significance test during this period could not be done due to the limited number of data points. These findings are consistent with those reported by Vahala et al. [20], who also found no effect of phosphorus addition on biofilter TOC removal or activity. However, other studies have shown improved biofilter performance following phosphorus addition. Lauderdale et al. [16] observed a 75% increase in DOC removal by GAC biofilters following a P-dose of 0.02 mg/L (P-dosing duration of 6 weeks), and this corresponded with a 30% increase in ATP. Granger et al. [15] also showed an 11% increase in DOC removal and higher ATP levels in GAC/sand and

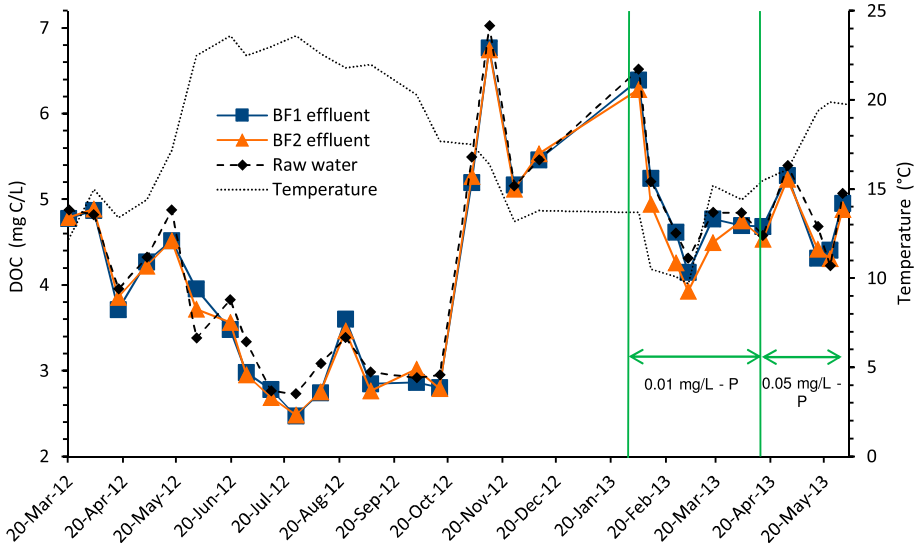

Fig. 4. DOC concentration in the raw water and BF1 and BF2 effluents.

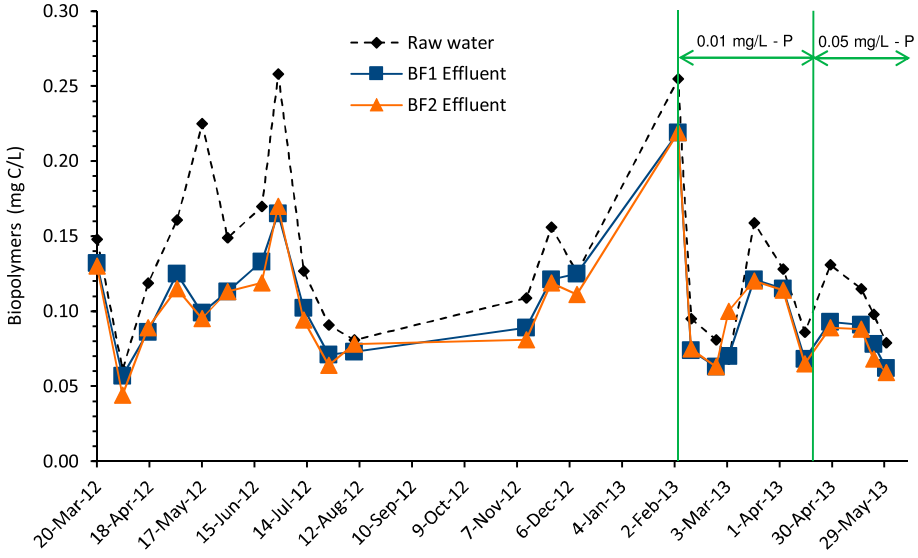

Fig. 5. Biopolymers in the raw water and biofilter effluents.

anthracite/sand biofilters following phosphorus addition. Sang et al. [18] found that phosphorus addition to biofilters containing a ceramic media resulted in higher removal of TOC (5.7%) and BDOC (26–30%) and increased biomass quantity (phospholipids) and activity (oxygen uptake rate).

By comparing the literature available to date, there does not appear to be a relationship between influent organics concentration and its increased removal with P-dosing. Lauderdale et al. [16], Granger et al. [15], Li et al. [17] and Sang et al. [18] all found increased organics removal with phosphorus addition using influent waters with TOC levels in the range of <2 to 8.5 mg/L, while the same effects were not observed by Azzeh et al. [41], Vahala et al. [20] and the present study using influent waters with generally similar TOC values. As well, temperature does not seem to be responsible for the difference in results, since both Granger et al. [15] and Sang et al. [18] showed increases in biomass and TOC/DOC removal with phosphorus addition at temperatures similar to those of the present study (10–20°C). It would appear that the effect of phosphorus addition may be site specific, depending on feedwater characteristics that, in turn,

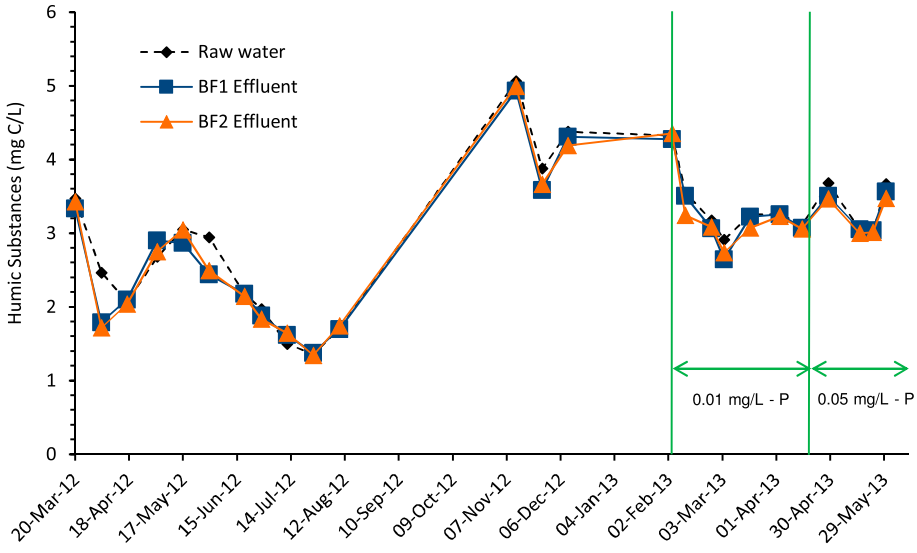

Fig. 6. Humic substances in the raw water and biofilter effluents.

influence the biofilm microbial community. In addition, it is possible that there are other factors or nutrient limitations that may affect biofilter biomass or performance. Thus considerable further work remains to be done to better understand these ecosystems so that drinking water biofiltration can be effectively used in a given situation.

3.4. Effect of phosphorus addition on membrane fouling

For the membrane fouling experiments, the effluent from biofilter 1 or biofilter 2 was used to feed a UF membrane. Because only one bench-scale UF unit was available, the fouling experiments with control (BF1) and P-dosed (BF2) effluent were conducted on separate days during the same week, using the same tank load of raw water to keep the water quality as comparable as possible. Table 2 summarizes the removal of biopolymers and humic substances by the UF membrane, calculated by subtracting the concentration in the membrane permeate from that in the feed. Results show on average very low removal of humics, similar to that found by Rahman et al. [7] using the same membrane and source water. Other studies have also shown that humic substances were not retained by UF membranes [2,4,6]. Biopolymer removal was much higher, ranging from 56 to 85% (Table 2).

The effect of phosphorus addition on irreversible and reversible fouling rates of UF membranes was also measured. A typical TMP profile (Fig. 7) for the experiment done on 23 May shows the increase in TMP within each 30 min cycle, which is defined as the reversible fouling rate. Irreversible fouling in this

Table 2
Biopolymer removal by a UF membrane fed with either BF1 or BF2 effluent

Experiment start date (2013)[a]	Biofilter	Biopolymers		Humic substances	
		UF feed (mg/L)	Removed by UF (%)	UF feed (mg/L)	Removed by UF (%)
4 March	BF1 (control)	0.070	67	2.641	−1
7 March	BF2 (0.01 P)	0.068	85	2.442	0
18 March	BF1 (control)	0.121	73	3.219	1
21 March	BF2 (0.01 P)	0.085	76	3.066	0
22 May	BF1 (control)	0.080	71	3.029	−8
23 May	BF2 (0.05 P)	0.068	74	3.013	0
28 May	BF1 (control)	0.068	56	3.631	0
30 May	BF2 (0.05 P)	0.059	63	3.469	−4

[a]Experiments conducted in the same week used the same batch of raw water.

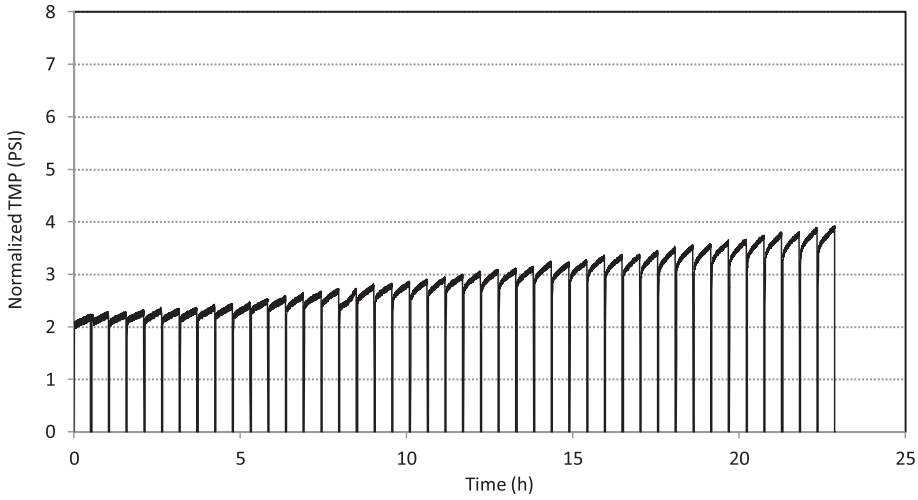

Fig. 7. Membrane fouling experiment showing the normalized TMP profile over time. Experiment was done using BF2 effluent on 23 May.

context is defined as the rate of increase in the non-backwashable TMP during the full length of the experiment. Because BF1 and BF2 membrane experiments were conducted on different days, there were slight variations in feedwater turbidity and biopolymer concentration in the membrane feedwater. Thus, although the experiments in a given week were conducted using the same batch of water, the use of a paired *t*-test to analyze the result is precluded. From Table 3 it is clear that phosphorus addition did not make an appreciable change with respect to membrane fouling rates, and a standard *t*-test showed no significant difference for either reversible or irreversible fouling. Although there were slight variations in feedwater turbidity, it is unlikely that this affected fouling rates (an examination of results in Table 3 shows that there is not a direct relationship between either the reversible or the irreversible fouling rate and turbidity). It has been shown previously that turbidity is not directly related to membrane fouling, although particles may become associated with organic compounds and play a role in forming the combined fouling layer [2,6,42]. An additional set of experiments was done during the week of 15 May [29], but were affected by a large change in feedwater turbidity caused by a temporary problem with tank mixing, and therefore these results were not included. Results of this study were similar to Azzeh et al. [41], who showed that nitrogen

Table 3
Fouling of a UF membrane fed with either BF1 (control) or BF2 (P-dosed) effluent

	Biofilter effluent (membrane feed)			UF membrane		
Starting date (2013)[a]	Biofilter	Biopolymers (mg/L)	Turbidity (NTU)	Reversible fouling rate[b] (kPa/h)	Irreversible fouling rate[c] (kPa/h)	Length of experiment (h)
4 March	BF1 (control)	0.070	2.35	4.33	0.35	29.8
7 March	BF2 (0.01 P)	0.068	1.09	3.86	0.33	
18 March	BF1 (control)	0.121	3.23	6.68	0.88	28.2
21 March	BF2 (0.01 P)	0.085	2.94	5.14	0.66	
22 May	BF1 (control)	0.080	0.80	4.49	0.37	22.9
23 May	BF2 (0.05 P)	0.068	0.98	4.13	0.45	
28 May	BF1 (control)	0.068	0.81	3.65	0.30	24.5
30 May	BF2 (0.05 P)	0.059	0.89	3.09	0.36	

[a]Experiments that were conducted in the same week used the same batch of raw water.
[b]Measured as the average reversible fouling rate for the total length of each experimental run.
[c]Measured as the average irreversible fouling rate per 30 min cycle.

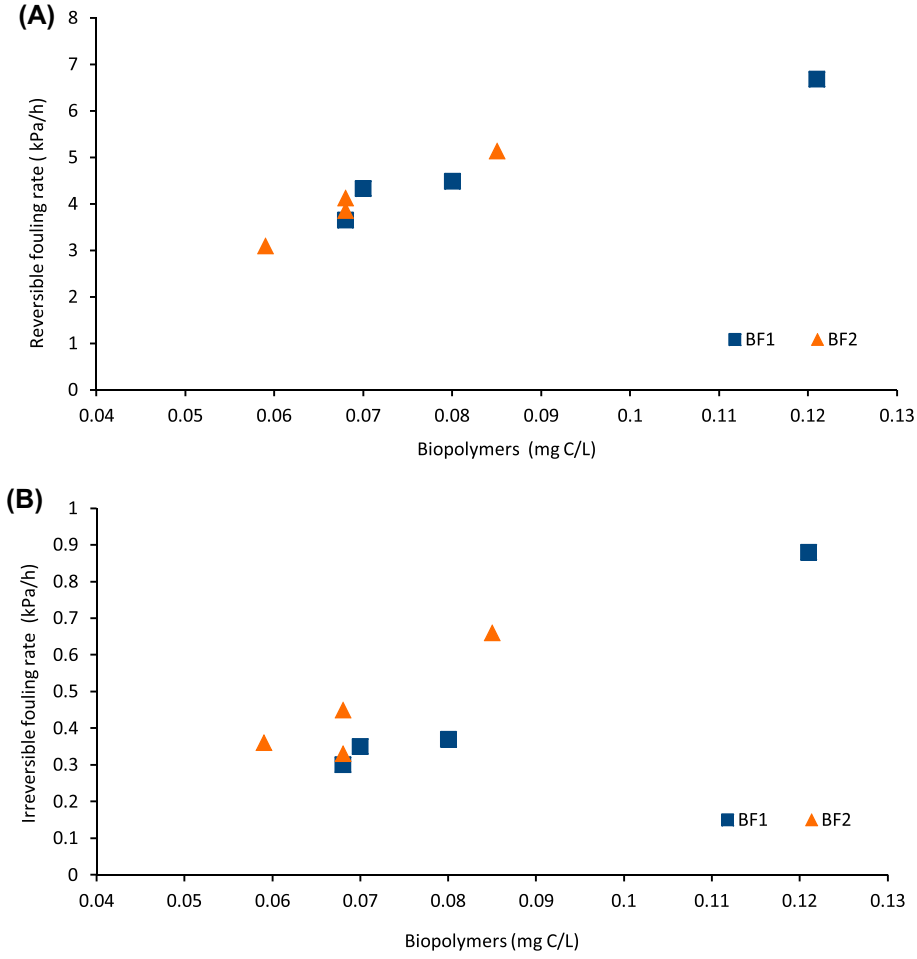

Fig. 8. Relationship between biopolymer concentration and reversible (A) and irreversible (B) membrane fouling rates.

and phosphorus addition did not improve biopolymer removal by biofiltration or fouling of a subsequent UF membrane process.

The data in Table 3 show that, overall, the reversible fouling rate was slightly lower for BF2 effluent compared with BF1. This may be due to the slightly lower concentration of biopolymers in the feedwater in the second experiment in a given week. It is likely that this was related to the increased hold time of the raw water in the storage container and not due to phosphorus addition, since Fig. 5 showed that phosphorus addition did not measurably affect effluent biopolymer concentration. Irreversible fouling rates, however, were very close and in fact were slightly higher for BF2 in two of the four weeks. The rates of reversible and irreversible fouling were essentially linearly related to the biopolymer concentration (Fig. 8) for both the control (BF1) and phosphorus-enhanced (BF2) biofilter effluents. These results are similar to those found previously using the same source water without phosphorus addition [7]. Other studies have shown that biopolymer concentration was related to reversible fouling only [2,4,6] or only to irreversible fouling [5]. Although beyond the scope of the current investigation, further investigation would be warranted to elucidate possible reasons for the observed difference between these studies and the current research.

4. Conclusions

Results of this study using pilot-scale anthracite–sand biofilters showed that phosphorus addition did not affect long-term biofilter performance or membrane fouling. The following conclusions can be made:

(1) After the addition of 0.01 mg/L phosphorus to an acclimated biofilter, DOC removal increased by approximately 6% (average) compared to the control filter during the first 40 d. DOC removal then returned to that of the control filter, and did not change over the remaining

experimental period (2.5 months), even when the phosphorus dose was increased to 0.05 mg/L. There was no significant difference in biopolymer removal between control and P-dosed biofilters over the entire study period.

(2) The addition of phosphorus did not change the biomass quantity (as measured by ATP) or activity (as measured by FDA hydrolysis) in the biofilters, even though the raw water appeared to be phosphorus-limiting.

(3) For this particular water, biofilter phosphorus addition at doses of 0.01 and 0.05 mg/L did not improve the hydraulically reversible or irreversible fouling rate of a downstream UF membrane. This was expected as the removal of biopolymers, previously demonstrated to be important UF foulants, did not change following phosphorus addition.

(4) Since the results are in agreement with some previous investigations on the effect of P-dosing on biofilter performance, but differ from others, the study underlines the complexity inherent in biological systems applied to drinking water. This highlights the need for a more fundamental understanding of such systems if they are to be optimally applied in drinking water treatment.

Acknowledgements

This project was funded by an Ontario Research Fund Research Excellence grant, and by the Natural Sciences and Engineering Research Council of Canada in the form of an Industrial Research Chair in Water Treatment at the University of Waterloo (UW) together with the Chair partners including Associated Engineering Group Ltd, the cities of Barrie, Brantford, Guelph, Hamilton and Ottawa, Conestoga-Rovers & Associates Limited, EPCOR Water Services, GE Water & Process Technologies Canada, Lake Huron and Elgin Area Water Supply Systems, the Ontario Clean Water Agency (OCWA), the Regions of Durham, Halton, Niagara and Waterloo, RAL Engineering Ltd, Toronto Water, and the Walkerton Clean Water Centre. We thank the Walkerton Clean Water Centre for access to their facility and sampling related expenses, and GE Water & Process Technologies (Dr Daniella B. Mosqueda-Jimenez) for providing the UF membrane units. Additional thanks to Drs Monica Tudorancea and Sigrid Peldszus (UW) for LC-OCD analysis, and also Terry Ridgway (UW), and Laura Zettler (WCWC) for their valuable contributions to this study.

References

[1] P.M. Huck, S. Peldszus, W.B. Anderson, F. Chen, A.M. El-Hadidy, R.L. Legge, B. Siembida-Lösch, M.I. Van Dyke, T. Walton, B. Wilson, Biofiltration with and without pre-treatment—Are there differences? IWA Specialized Conference: Biofilms in Drinking Water Systems, Arosa, Switzerland, August 24, 2015 (Biological Treatment: Biofiltration session), IWA Publishing, London.

[2] C. Hallé, P.M. Huck, S. Peldszus, J. Haberkamp, M. Jekel, Assessing the performance of biological filtration as pretreatment to low pressure membranes for drinking water, Environ. Sci. Technol. 43(10) (2009) 3878–3884.

[3] G. Amy, Fundamental understanding of organic matter fouling of membranes, Desalination 231(1–3) (2008) 44–51.

[4] A.M. El-Hadidy, S. Peldszus, M.I. Van Dyke, Effect of hydraulically reversible and hydraulically irreversible fouling on the removal of MS2 and φX174 bacteriophage by an ultrafiltration membrane, Water Res. 61 (2014) 297–307.

[5] K. Kimura, K. Tanaka, Y. Watanabe, Microfiltration of different surface waters with/without coagulation: Clear correlations between membrane fouling and hydrophilic biopolymers, Water Res. 49 (2014) 434–443.

[6] J. Tian, M. Ernst, F. Cui, M. Jekel, Correlations of relevant membrane foulants with UF membrane fouling in different waters, Water Res. 47(3) (2013) 1218–1228.

[7] I. Rahman, S. Ndiongue, X. Jin, M.I. Van Dyke, W.B. Anderson, P.M. Huck, Fouling of low pressure membranes during drinking water treatment: Effect of NOM components and biofiltration pretreatment, Water Sci. Technol. Water Supply 14(3) (2013) 453–460.

[8] A.C. Redfield, The biological control of chemical factors in the environment, Am. Sci. 46(3) (1958) 205–221.

[9] R.W. Sterner, T. Andersen, J.J. Elser, D.O. Hessen, J.M. Hood, E. McCauley, J. Urabe, Scale-dependent carbon: nitrogen: phosphorus seston stoichiometry in marine and freshwaters, Limnol. Oceanogr. 53(3) (2008) 1169–1180.

[10] J. Sardans, A. Rivas-Ubach, J. Peñuelas, The elemental stoichiometry of aquatic and terrestrial ecosystems and its relationships with organismic lifestyle and ecosystem structure and function: A review and perspectives, Biogeochemistry 111 (2012) 1–39.

[11] H.-C. Flemming, J. Wingender, The biofilm matrix, Nat. Rev. Microbiol. 8 (2010) 623–633.

[12] M. Polanska, K. Huysman, C. Van Keer, Investigation of microbially available phosphorus (MAP) in Flemish drinking water, Water Res. 39(11) (2005) 2267–2272.

[13] M.J. Lehtola, I.T. Miettinen, T. Vartiainen, P.J. Martikainen, Changes in content of microbially available phosphorus, assimilable organic carbon and microbial growth potential during drinking water treatment processes, Water Res. 36(15) (2002) 3681–3690.

[14] I.T. Miettinen, T. Vartiainen, P.J. Martikainen, Phosphorus and bacterial growth in drinking water, Appl. Environ. Microbiol. 63(8) (1997) 3242–3245.

[15] H.C. Granger, A.K. Stoddart, G.A. Gagnon, Direct biofiltration for manganese removal from surface water, J. Environ. Eng. 140(4) (2014) 04014006.

[16] C. Lauderdale, P. Chadik, M.J. Kirisits, J. Brown, Engineered biofiltration: Enhanced biofilter performance through nutrient and peroxide addition, J. Am. Water Works Assoc. 104(5) (2012) E298–E309.
[17] X. Li, G. Upadhyaya, W. Yuen, J. Brown, E. Morgenroth, L. Raskin, Changes in the structure and function of microbial communities in drinking water treatment bioreactors upon addition of phosphorus, Appl. Environ. Microbiol. 76(22) (2010) 7473–7481.
[18] J. Sang, X. Zhang, L. Li, Z. Wang, Improvement of organics removal by bio-ceramic filtration of raw water with addition of phosphorus, Water Res. 37(19) (2003) 4711–4718.
[19] X. Yu, X. Zhang, X. Zhao, Z. Wang, Phosphorus limitation in biofiltration for drinking water treatment, J. Environ. Sci. 15(4) (2003) 494–499.
[20] R. Vahala, V. Moramarco, R.M. Niemi, J. Rintala, R. Laukkanen, The effects of nutrients on natural organic matter (NOM) removal in biological activated carbon (BAC) filtration, Acta Hydroch. Hydrob. 26(3) (1998) 196–199.
[21] Saugeen Valley Conservation Authority, Saugeen Conservation Water Quality Status Report 2010, Ontario, 2011. Available from: <http://www.saugeenconservation.com/downloads/SaugeenConservation_WaterQualityStatusReport2010.pdf> (accessed 9 September, 2014).
[22] Ontario Ministry of the Environment, Water Quality in Ontario, 2012 Report, PIBS# 9493e. Available from: <http://www.ontario.ca/environment-and-energy/ministry-environment-ministers-annual-report-drinking-water-2013> (accessed 9 September 2014).
[23] Saugeen Valley Conservation Authority, Lower Main Saugeen River Watershed Report Card 2008, Hanover, Ontario, 2008. Available from: <http://www.saugeenconservation.com/downloads/Lower_Main_2.pdf?phpMyAdmin=82c3bRHhDPE3QA%2CLIdaJ3S823H4> (accessed 6 October 2013).
[24] GE, ZeeWeed 500D Module Fact Sheet, Doc# FSpw500D-MOD_EN, 2013. Available from: <https://knowledgecentral.gewater.com/kcpguest/documents/Fact%20Sheets_Cust/Americas/English/FSpw500D-MOD_EN.pdf> (accessed 9 September 2014).
[25] A.M. El-Hadidy, S. Peldszus, M.I. Van Dyke, An evaluation of virus removal mechanisms by ultrafiltration membranes using MS2 and φX174 bacteriophage, Sep. Purif. Technol. 120 (2013) 215–223.
[26] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater (twenty-second ed.), American Public Health Association, American Water Works Association, Water Environment Federation, Washington, DC, 2012.
[27] S. Huber, A. Balz, M. Abert, W. Pronk, Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography–organic carbon detection–organic nitrogen detection (LC-OCD-OND), Water Res. 45(2) (2011) 879–885.
[28] V.S. Green, D.E. Stott, M. Diack, Assay for fluorescein diacetate hydrolytic activity: Optimization for soil samples, Soil Biol. Biochem. 38(4) (2006) 693–701.
[29] I. Rahman, Direct Biofiltration and Nutrient (Phosphorus) Enhancement for Polymeric Ultrafiltration Membrane Fouling Control, Master's thesis, Department of Civil Engineering, University of Waterloo, Waterloo, Ontario, Canada, 2013. Available from: <https://uwspace.uwaterloo.ca/handle/10012/8073> (accessed 14 August 2013).
[30] J. Croft, Natural Organic Matter Characterization of Different Source and Treated Waters; Implications for Membrane Fouling Control, Master's thesis, Department of Civil Engineering, University of Waterloo, Waterloo, Ontario, Canada, 2012. Available from: <http://uwspace.uwaterloo.ca/handle/10012/7107>.
[31] T. Berman, D.A. Bronk, Dissolved organic nitrogen: A dynamic participant in aquatic ecosystems, Aquat. Microb. Ecol. 31 (2003) 279–305.
[32] J.J. Middelburg, J. Nieuwenhuize, Nitrogen uptake by heterotrophic bacteria and phytoplankton in the nitrate-rich Thames estuary, Mar. Ecol. Prog. Ser. 203 (2000) 13–21.
[33] A.K. Camper, P. Butterfield, B. Ellis, W.L. Jones, W.B. Anderson, P.M. Huck, R.M. Slawson, C. Volk, N. Welch, M. LeChevallier, Investigation of the biological stability of water in treatment plants and distribution systems, AWWA Research Foundation Report No. 90794, Denver, CO, 2000, ISBN 1-58321-072-5.
[34] H.G. Knapik, C.V.S. Fernandes, J.C.R. de Azevedo, M.M. dos Santos, P. Dall'Agnol, D.G. Fontane, Biodegradability of anthropogenic organic matter in polluted rivers using fluorescence, UV, and BDOC measurements, Environ. Monit. Assess. 187(3) (2015) 104.
[35] M. Søndergaard, J. Worm, Measurement of biodegradable dissolved organic carbon (BDOC) in lake water with a bioreactor, Water Res. 35(10) (2001) 2505–2513.
[36] P. Servais, A. Anzil, C. Ventresque, Simple method for determination of biodegradable dissolved organic carbon in water, Appl. Environ. Microbiol. 55(10) (1989) 2732–2734.
[37] W. Siuda, R.J. Chróst, Utilization of selected dissolved organic phosphorus compounds by bacteria in lake water under non-limiting orthophosphate conditions, Pol. J. Environ. Stud. 10(6) (2001) 475–483.
[38] M. Nausch, G. Nausch, Bioavailable dissolved organic phosphorus and phosphorus use by heterotrophic bacteria, Aquat. Biol. 1(2) (2007) 151–160.
[39] G. Adam, H. Duncan, Development of a sensitive and rapid method for the measurement of total microbial activity using fluorescein diacetate (FDA) in a range of soils, Soil Biol. Biochem. 33(7–8) (2001) 943–951.
[40] L.C.F. Stubberfield, P.J.A. Shaw, A comparison of tetrazolium reduction and FDA hydrolysis with other measures of microbial activity, J. Microbiol. Methods 12(3–4) (1990) 151–162.
[41] J. Azzeh, L. Taylor-Edmonds, R.C. Andrews, Engineered biofiltration for ultrafiltration fouling mitigation and disinfection by-product precursor control, Water Sci. Technol. Water Supply 15(1) (2015) 124–133.
[42] S. Peldszus, C. Hallé, R.H. Peiris, M.A. Hamouda, X. Jin, R.L. Legge, H. Budman, C. Moresoli, P.M. Huck, Reversible and irreversible low-pressure membrane foulants in drinking water treatment: Identification by principal component analysis of fluorescence EEM and mitigation by biofiltration pretreatment, Water Res. 45(16) (2011) 5161–5170.