Water Research 104 (2016) 397–407

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Field-analysis of potable water quality and ozone efficiency in ozone-assisted biological filtration systems for surface water treatment

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ARTICLE INFO

Article history:
Received 16 May 2016
Received in revised form
19 August 2016
Accepted 21 August 2016
Available online 22 August 2016

Keywords:
Ozonation
Biofiltration
Potable water
Surface water treatment
Water quality
Small-scale

ABSTRACT

Potable water treatment in small communities is challenging due to a complexity of factors starting with generally poor raw water sources, a smaller tax and consumption base that limit capital and operating funds, and culminating in what is typically a less sophisticated and robust water treatment plant for production and delivery of safe, high quality potable water. The design and optimization of modular ozone-assisted biological filtration systems can address some of these challenges. In surface water treatment, the removal of organic matter (e.g., dissolved organic carbon – DOC), inorganic nutrients and other exposure-related contaminants (e.g., turbidity and dissolved solids) from the raw water source is essential. Thus, a combination of chemical and biological oxidation processes can produce an effective and efficient water treatment plant design that is also affordable and robust. To that end, the ozone-assisted biological filtration water treatment plants in two communities were evaluated to determine the efficacy of oxidation and contaminant removal processes. The results of testing for in-field system performance indicate that plant performance is particularly negatively impacted by high alkalinity, high organics loading, and turbidity. Both bicarbonate and carbonate alkalinity were observed to impede ozone contact and interaction with DOC, resulting in lower than anticipated DOC oxidation efficiency and bioavailability. The ozone dosage at both water treatment plants must be calculated on a more routine basis to better reflect both the raw water DOC concentration and presence of alkalinities to ensure maximized organics oxidation and minimization of trihalomethanes production.

1. Introduction

In 2011, Canadian drinking water plants produced 5.1 billion cubic meters of potable water. The raw water sources for potable water production is primarily surface water (89%), with approximately 10% derived from ground water and the remaining 1% from ground water under the direct influence of surface water (Statistics Canada, 2011). In Saskatchewan, rivers and lakes are accessed by major cities to supply the urban population with potable water whereas a large number of small rural communities depend on local reservoirs and dugouts. Such water sources are primarily recharged by seasonal precipitation and surface runoff from the surrounding terrain. Over time, water quality tends to deteriorate due to increases in organic matter quantified as dissolved organic carbon (DOC) accompanied by high total dissolved solids (TDS) (CBCL Limited, 2011; Watson and Lawrence, 2003). This is particularly challenging for small, rural, and remote communities relying on heavily agrarian economic development where agricultural residues (cropping materials) and inputs (fertilizers and pesticides) and exposed soils are commonplace and in close proximity to raw surface water sources used for potable water production. These challenges are exacerbated due to the lack of economies of scale and ability of small communities to employ dedicated, expert staff to build, operate, and maintain sophisticated potable water treatment facilities capable of handling such deterioration of raw water quality (Gottinger et al., 2011, 2013). Nitrogen and phosphorous input stimulates growth of algae in the reservoir, which not only influences the colour, taste and odor of treated water, but will also increase DOC (Zaitlin et al., 2003). In addition, DOC input and potential for trihalomethanes (THM) and haloacetic acids formation

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http://dx.doi.org/10.1016/j.watres.2016.08.043

will depend on the specific algal communities present, particularly given that chlorophyll *A* can contribute to the formation of these disinfection byproducts (Abd El-Aty et al., 2009; Knappe et al., 2004). Reduction of DOC, especially under alkaline conditions is currently a major challenge for conventionally engineered water treatment plants.

Ozone-assisted biofiltration offers great potential for removal of impurities from raw water including DOC, metals, and even pesticides (Reungoat et al., 2010). Ozone is a strong oxidizing and disinfecting agent that has been used in water treatment for more than 100 years (Rakness, 2011). Disinfection by ozone, which is solute-dependent, occurs either by direct oxidation of a substrate, decomposition via hydroxyl radicals, or a combination of both (Hoigné and Bader, 1976). Water conditions, however, can impact oxidation efficiency. Alkalinity due to the presence of carbonate and bicarbonate can reduce oxidation efficiency due to scavenging of hydroxyl radicals (Gottschalk et al., 2010), while increasing water temperature results in higher ozone depletion rates and ozone instability (Elovitz et al., 2000; Okafor, 2011). The pH, natural organic matter (NOM) and dissolved solids can interact to alter oxidation efficiency (Okafor, 2011). The pH can influence the rate of ozone decomposition in that NOM reacts with ozone directly and/or indirectly through scavenging hydroxyl radicals. Ultimately, the reaction between hydroxyl radicals and NOM produces a degree of superoxide radicals that react quickly with ozone to reconstitute hydroxyl radicals. However, that chain reaction ends in the presence of inhibitors or compounds that do not release superoxide after reaction with hydroxyl radicals, such as carbonate (CO_3^{2-}) and bicarbonate (HCO^{3-}) ions (von Gunten, 2003). It has been demonstrated that hydroxyl scavenging can be as much as 2.5 times higher in drinking water at pH 7 than in wastewater at pH 9, suggesting that low pH and/or low bicarbonate and carbonate levels can impact removal efficiencies (Tang, 2003). Also, Glaze and Kang (1988) showed that direct oxidation of trichloroethylene and tetrachloroethylene in ground water with high alkalinity is a slow process. They also concluded that processes employing hydroxyl radicals in contaminants-removal from high alkalinity water are less efficient because of the presence of carbonate and bicarbonate ions that are known radical scavengers. Camel and Bermond (1998) also reported inhibition of DOC oxidation in water containing carbonates due to the scavenging effect of carbonate ions. In addition, ozone performance is impacted by iron, manganese, sulfur, nitrogen and phosphorous levels, depending on temperature and pH (Langlais et al., 1991). Thus, disinfection of source water with elevated turbidity and DOC remains a significant challenge.

In Saskatchewan, more than 50% of the population relies on surface water as a primary source of drinking water. Surface water DOC concentration can range between 4 and 35 mg/L or even higher (SaskH2O, 2015). Because of inadequate DOC removal efficiency, disinfection by-products (DBPs) such as THMs often exceed the 100 μg/L limit recommended in the *Guidelines for Canadian Drinking Water Quality* (Health Canada, 2014). Whereas urban centres may have access to higher quality raw water and more sophisticated water treatment plants (WTPs), rural communities more routinely access water collected from rain and snowmelt runoff, often from agricultural fields, and almost always collected into small reservoirs and shallow wells (Peterson, 2000). Regardless of geographical location, rural communities the world over tend to make use of poorer quality raw water for production of potable water, as reflected by higher DOC concentrations and significant turbidity that affects physical, chemical and biological water quality (McLeod et al., 2015; Peterson, 2000).

The objective of this research is to identify and understand the conditions that lead to poor filter performance in potable water treatment plants employing ozone-assisted biofiltration, focusing on surface water quality and filter-related performance factors that contribute to enhanced DOC removal efficiency. Additionally, the intent is to provide communities, regardless of geographical location, with useful and applicable recommendations for optimizing plant efficiency through performance enhancements and source water protection measures that improve source water quality.

2. Methods

2.1. Study sites

Two municipal WTPs in southern Saskatchewan, one in the Village of Osage and one in the Hamlet of Benson, were chosen for this study since both operate under ozone-assisted biofiltration and were noted to be underperforming in terms of meeting all permit requirements and regulatory water quality standards in recent years. Further, each community can be seen as representative of the rural context in which access to high quality source water is challenging, few source water protection measures have been investigated or implemented, and overland flows dramatically and drastically influence inflow water quality requiring significant WTP responsiveness. The operating conditions for each WTP are provided in Table 1 and further described below.

The Village of Osage draws its source water from a small surface water reservoir that is roughly 70 × 24 m and approximately 4 m deep. To the north, a berm prevents direct runoff from agricultural fields into the reservoir. Osage installed the first ozone-assisted biological filtration facility regulated by the province of Saskatchewan in 2004. At that time, the ozone-assisted biofiltration treatment train was launched as a pilot project with an average flow rate of 4.4 m^3/day and peak consumption of 6.3 m^3/day. The full-scale water treatment plant (WTP) was constructed and brought online in 2007 with a design flow rate of 11 m^3/day. It is composed of one 0.66 m diameter roughing filter, one 1.75 m diameter biological sand filter and one 1 m diameter biologically activated carbon (BAC) filter (Fig. 1). From the raw water intake, the water stream is subjected to ozone injection, off-gassing of the ozone, filtration through one roughing filter for turbidity reduction, one sand filter and one BAC filter. A small volume of non-chlorinated treated water is recirculated through the BAC filter while the remainder of the final product is disinfected using chlorine and stored in storage tank.

The filtration rate for the biological sand filter is 0.24 m/h and contact time for the BAC filter is 30–56 min. An air diffuser is installed in the sand filter to aid with backwash and maintenance activities; a re-circulation system recycles non-chlorinated water at 0.6 m^3/h through the BAC filter to increase aeration. Treated water is then chlorinated and stored in a storage tanks prior to distribution (Mainstream Water Solutions Inc., 2004). Two ozone generators (VMUS-04) are installed, each with capacity of up to 7 mg/L of ozone at 6 L/min of oxygen. The report on WTP design and operation states that the ozone dosage is 4 g/h at 5 L/min airflow and 7 mg/L at average flow rate. Thus, the applied ozone dose is approximately 17 mg/L. Average ozone contact time is 60 min (Mainstream Water Solutions Inc., 2004). An air dryer was installed in April 2012 to improve the efficiency of the ozone generator. The design report also provides instructions for backwash timing and protocols with the established practice being a schedule of backwashing the roughing filter every 10–14 days, the sand filter once per month and the BAC filter every 4–5 months.

The Hamlet of Benson draws its raw source water from two surface impoundments located in an agricultural field north of the community. Neither reservoir includes berms or buffer zones to separate the raw water sources from agricultural operations or overland runoff. The larger of the two, built in 1974, is 119 × 61 m

Table 1
Design and operating parameters of two WTP – Osage and Benson.

Operating parameters	Osage	Benson
Raw water source	Dugout 70 × 24 × 4 m	Dugout (1) 119 × 61 × 7.3 m Dugout (2) 91 × 58 × 6–7 m
Flow rate	11 m^3/day	45 m^3/day
Roughing filter diameter	0.66 m	1.5 m
Sand filter diameter	1.75 m	2.1 m
BAC filter diameter	1 m	2.1 m
Ozone	17 mg/L	17 mg/L

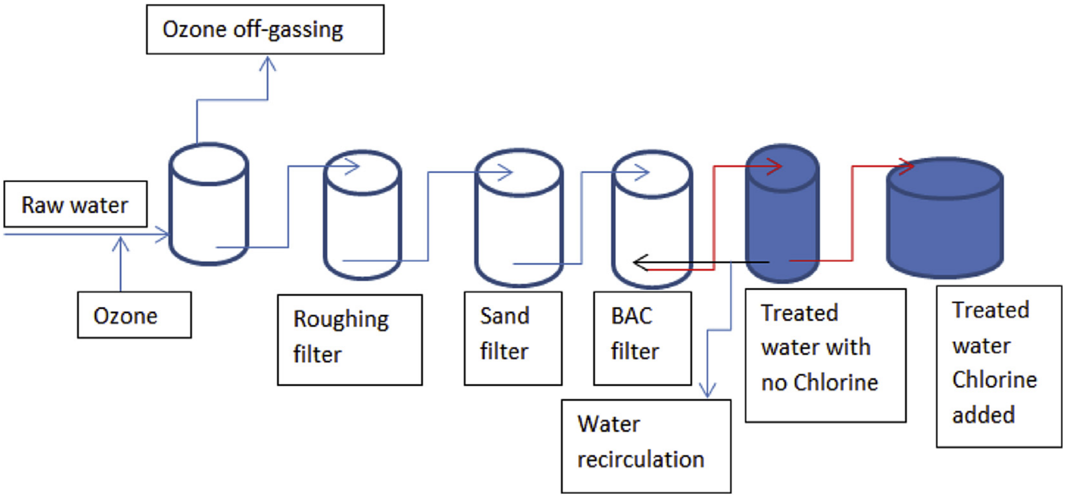

Fig. 1. Schematic of the Osage WTP treatment train.

and an average of 7.3 m deep. The smaller impoundment, built in 2001 to supplement raw water availability, is 91 × 58 m and between 6 and 7 m deep. The smaller reservoir is used to recharge the larger impoundment on an as-needed basis, particularly in dry years and peak water consumption periods. In spring, both reservoirs are recharged by a creek that flows through 50 km of agricultural fields from the west prior to reaching the surface impoundments. The biologically-activated filtration WTP system was installed in Benson in 2008 and designed to provide potable water at a rate of 45 m^3/day. The system is composed of a 1.5 m diameter roughing filter, two 2.1 m diameter biological sand filters and two 2.1 m diameter BAC filters (Mainstream Water Solutions Inc., 2007) (Fig. 2). Generally, the schematic of the Benson WTP (Fig. 2) shows the raw water intake followed by ozone injection, off-gassing of the ozone, filtration through one roughing filter for turbidity reduction, two sand filters and two biologically activated carbon filters (BAC). By design, a small volume of treated non-chlorinated water is recirculated through the BAC filters while the majority of the treated water is disinfected and stored in a clearwell prior to distribution.

The filtration rate for the biosand filters is 0.35 m/h and the rate for the BAC filters is 0.70 m/h (>30 min contact time). Much like the Osage WTP design, an air diffuser is installed in the sand filter to aid in backwash, and aeration of BAC filters in enabled by a recirculation system that recycles non-chlorinated water back into BAC filters at 0.6 m^3/h. Treated water is chlorinated and stored in

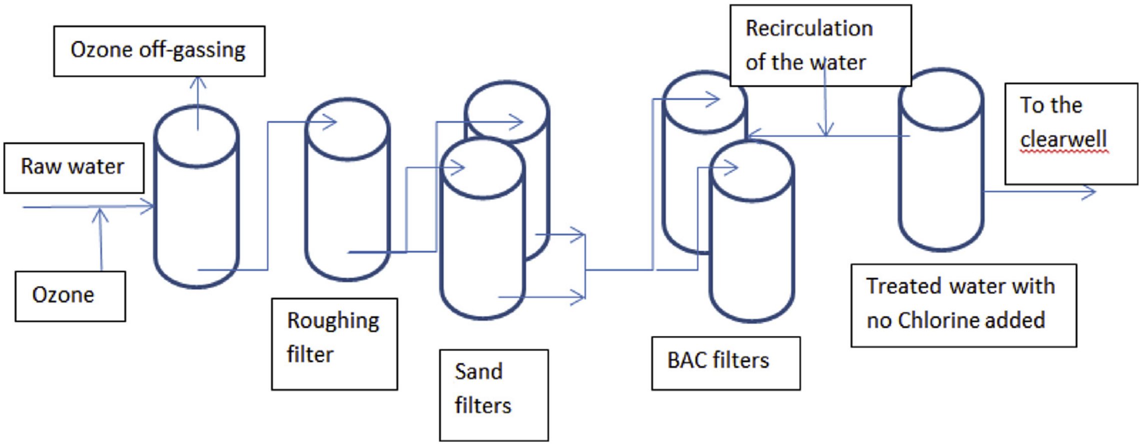

Fig. 2. Schematic of the Benson WTP treatment train.

tanks prior to distribution. Raw water is automatically pumped into the WTP from the dugout when the water level in the roughing filter drops below a set minimum. From the roughing filter water is delivered to the remainder of the filters by gravity flow. Four ozone generators (VMUS-04) are installed, each capable of generating up to 7 mg/L of ozone per unit at 6 L/min of oxygen. At full operating capacity the applied ozone dose is 17 mg/L and the average ozone contact time is approximately 60 min. The established practice for filter backwash is that the roughing filter is backwashed every 10–14 days, sand filters once per month and BAC filters every 1–3 months depending on raw water turbidity.

2.2. Water sampling and chemical analyses

Seasonal samples were collected in approximately two-month intervals throughout 2012 from both communities. For unionized ammonia analyses, water samples were collected in white 250 mL plastic bottles and preserved with 5 mL of 10% sulfuric acid (H_2SO_4). For the remainder of the chemical tests, samples were collected in white 2 L plastic bottles. Water samples for total coliform (TC) and *E. coli* testing were collected in clear 250 mL sterilized plastic bottles containing sodium thiosulphate. The samples were kept cool with ice packs in coolers for transport from the communities and refrigerated prior to analysis. Water sample analyses were performed at the Saskatchewan Disease Control Laboratory (Regina, SK), and included analyses for conductivity, pH, total alkalinity, phenol alkalinity, bicarbonate, carbonate, hydroxide, chloride dissolved, fluoride dissolved, sulfate dissolved, calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), total hardness, total dissolved solids, total suspended solids, turbidity, total Kjeldahl nitrogen (TKN), nitrate-N (NO3-), ammonia (NH3), total nitrogen (N-total), total phosphorous (P-total), ortho-phosphorous (P-ortho), DOC, chlorophyll *A*, biochemical oxygen demand (BCOD), chemical oxygen demand (COD), 24 metals, THMs, total coliforms (TC), and *E. coli*. Raw water samples collected in spring and fall were also analysed for cyanide and phenoxy herbicides at the Saskatchewan Research Council laboratory in Saskatoon, SK.

2.3. Statistical analysis

ProUCL 5.0.00 statistical software for environmental data sets (US EPA, 2013) was used to compare raw water quality and ozone performance in the treatment at the two communities. Non-parametric statistical Mann-Kendal trend analysis ($p < 0.05$) and non-parametric statistical two samples Wilcoxon–Mann-Whitney test for independent samples ($\alpha = 0.05$) were used in the analysis of raw and treated water data.

3. Results

3.1. Trends in water quality at sample sites

TDS, COD, turbidity, pH, total alkalinity, specific conductivity, DOC, chlorophyll *A*, total nitrogen and total phosphorous (Table 2) in Osage water were compared against those of Benson water in order to determine if there were any significant differences between two sources. Non-parametric statistical two samples Wilcoxon–Mann-Whitney test for independent samples ($\alpha = 0.05$) revealed that water quality at the Osage dugout is significantly different from raw water quality at the Benson. The same parameters were analysed to determine if significant changes occurred in the source water. Non-parametric statistical Mann-Kendal trend analysis ($p < 0.05$) was used to determine if any significant changes occurred in the raw water quality at both communities in 2012. The analysis of Osage data shows that TDS and total alkalinity have increased significantly through 2012. Results of the chemical analyses of the water samples collected from the Osage dugout show higher concentrations of other parameters in the time period between spring runoff in 2012 through the end of the sampling period in early 2013 (Table 2, Osage). Total nitrogen was observed to be constantly at or above 1 mg/L during the sampling period, whereas phosphorous concentration fluctuated between 0.81 mg/L in July 2012 and 0.35 mg/L in March of 2013. In general, the availability of phosphorous is a limiting factor in blue-green algae growth. Chlorophyll *A*, a biomolecule essential for photosynthesis in plants and cyanobacteria, was measured at its lowest concentration in April 2012 at 9.95 mg/m^3 and highest of 64.27 mg/m^3 in February 2012. In April 2012, temperatures were below seasonal and the dugout remained covered with ice and snow.

Benson raw water data shows that there is significant increasing trend with $p < 0.05$ in the turbidity in 2012. Chemical analyses of raw water collected from Benson also highlight elevated concentrations of many parameters between spring runoff in 2012 through the end of the sampling period in early 2013 (Table 2, Benson). The values for TDS, COD, total alkalinity (TotalAlk), specific conductivity and DOC increased steadily between April 2012 and March 2013. The concentration of total phosphorous ranged between 0.24 mg/L to 1.26 mg/L for the given sampling period, while total nitrogen remained steady and well above 2 mg/L throughout sampling. Chlorophyll *A* showed steady incline from April to November 2012, increasing from 9.97 to 112.64 mg/m^3.

Turbidity of raw source water in Benson began to increase significantly in November 2012 resulting in the issuing of a Precautionary Drinking Water Advisory (PDWA) by the provincial regulators for the community from that point through the conclusion of field research in April 2013. In December 2012, the turbidity of treated water exceeded the regulatory limit of 1.00 NTU. At that time, the WTP was shown to be incapable of sufficiently removing turbidity to within regulatory requirements. In response to the PDWA and associated potential health hazards in the community posed by elevated turbidity concentrations, an additional series of samples was collected between February and April 2013 to conduct a series of raw water settling experiments, with the final water sample collected on April 2, 2013 containing a measured turbidity of 19 NTU (Table 2). Because of this approach to better understanding the turbidity challenges that forced the PDWA, it was possible to note that the characteristics of settled colloidal matter changed over time, with that contained in March samples being heavier and larger than that in the February samples. After two months of settling, the colloidal matter in the February samples had not yet fully settled.

Since colloids can be mobilized when low ionic strength water mixes with high strength water, it is possible that seepage and mixing of ground water with surface water had caused colloidal displacement. Another possibility is that under-ice convection occurred. As the biodegradation of organic matter occurred on the bottom of the dugout, sediments slowly warmed due to bacteriological metabolism. In turn the water warmed as well (3–5 °C) on the bottom creating a temperature difference between the upper and lower layers of water. Eventually, the temperature difference is sufficiently high that under-ice convection occurs, disturbing the sediments and colloids on the bottom of the dugout (Terzhevik and Golosov, 2012) and dispersing them throughout the water column.

3.2. Alkalinity

Total alkalinity of Osage raw water significantly increased in 2012 ranging between 127 and 204 mg/L as $CaCO_3$. In the months of February, September and November of 2012, carbonate concentrations were low when pH of the raw water was above 8.2, but not

Table 2
Selected parameters for the quality of raw water in Osage and Benson in year 2012–13.

Date	TDS (mg/L)	COD (mg/L)	Turbidity (NTU)	pH	TotalAlk (mg/L as $CaCO_3$)	Specific cond (μS/cm)	DOC (mg/L)	Chlorophyll *A* (mg/m^3)	Total-N (mg/L)	Total-P (mg/L)
Osage										
06-Feb-12	453	34.3	4.6	8.3	150	599	13.9	64.27	1	0.41
30-Apr-12	341	32.1	2.8	8	127	427	13.1	9.95	1	0.38
17-Jul-12	414	39.5	12	8.2	150	528	12	56.18	1.5	0.81
19-Sep-12	459	39.9	8.2	8.6	176	579	12.2	37.12	1	0.52
20-Nov-12	516	38.7	4	8.5	204	654	14.2	38.7	1.4	0.38
18-Mar-13	606	40.6	2.6	7.9	234	743	15.7	13.58	1.8	0.35
Benson										
06-Feb-12	853	76	1.8	7.9	447	981	33.7	16.3	3	0.24
30-Apr-12	599	59.7	1.6	8.1	285	706	25.8	9.97	2.4	0.28
17-Jul-12	739	86.7	3.5	8.7	352	858	31.6	22.92	3	1.28
19-Sep-12	741	82.3	5.6	9.2	372	879	30.4	38.39	2.9	1.07
20-Nov-12	737	86.1	8.9	9.1	367	884	32.9	112.64	2.8	0.86
02-Apr-13	923	98.7	19	8.4	418	1052	35.6	6.79	3.9	1.26

detectable in water samples collected at the roughing filter where the pH measured around 7.7. Overall, changes in total alkalinity through the treatment train were less than 4 mg/L as $CaCO_3$ (Table 3, Osage). Total alkalinity of Benson raw water measured in February 2012 was 447 mg/L as $CaCO_{3.}$ In April of that year total alkalinity dropped to 285 mg/L as $CaCO_3$ due to recharge by spring melt runoff and increased steadily through the year to reach 366 mg/L as $CaCO_3$ by November. Minimal changes were measured in total alkalinity levels through the filters at less than 7 mg/L as $CaCO_3$ (Table 3, Benson). In February and April pH of the raw water was 7.9 and 8.1, respectively, and therefore bicarbonate alkalinity was equal to total alkalinity in the water during those sampling periods (Table 3, Benson).

Through analysis of the concentrations of bicarbonate and carbonate alkalinity for the remaining months of the year, it was possible to demonstrate consumption of carbonate alkalinity alongside production of bicarbonate alkalinity, as well as fluctuations in pH, as shown for those samples collected in Benson (Fig. 3). Mann-Kendall trend test analysis shows significant decrease in carbonate alkalinity through the treatment train in months of September and November in 2012.

3.3. DOC removal and THMs

Although ozone concentration was not directly measured across the treatment train at Osage, the effect of ozone and its radicals can be observed by proxy with respect to the decrease in DOC achieved through the filters and, particularly as associated with significant DOC removal achieved in the roughing filter. The DOC in the raw water ranged between 12 and 15.7 mg/L as measured in July 2012 and March 2013, respectively (Fig. 4a; Table 4).

Table 3
Changes in total alkalinity (TotalAlk) in mg/L as $CaCO_3$ through the Osage and Benson WTP throughout the sampling period. Values for sand and BAC filters for the facility at Benson are presented as the average of each filter pair.

Site	Date	Raw	Roughing filter	Sand filter	BAC filter	Treated (post-Cl)
Osage	06-Feb-12	150	148	154	153	151
	30-Apr-12	127	118	129	131	125
	17-Jul-12	150	154	158	151	151
	19-Sep-12	176	174	176	173	173
	20-Nov-12	204	202	205	205	202
Benson	06-Feb-12	447	445	447	448	458
	30-Apr-12	285	278	271	284	292
	17-Jul-12	352	352	356	346	341
	19-Sep-12	372	372	373	369	367
	20-Nov-12	367	366	364	360	364

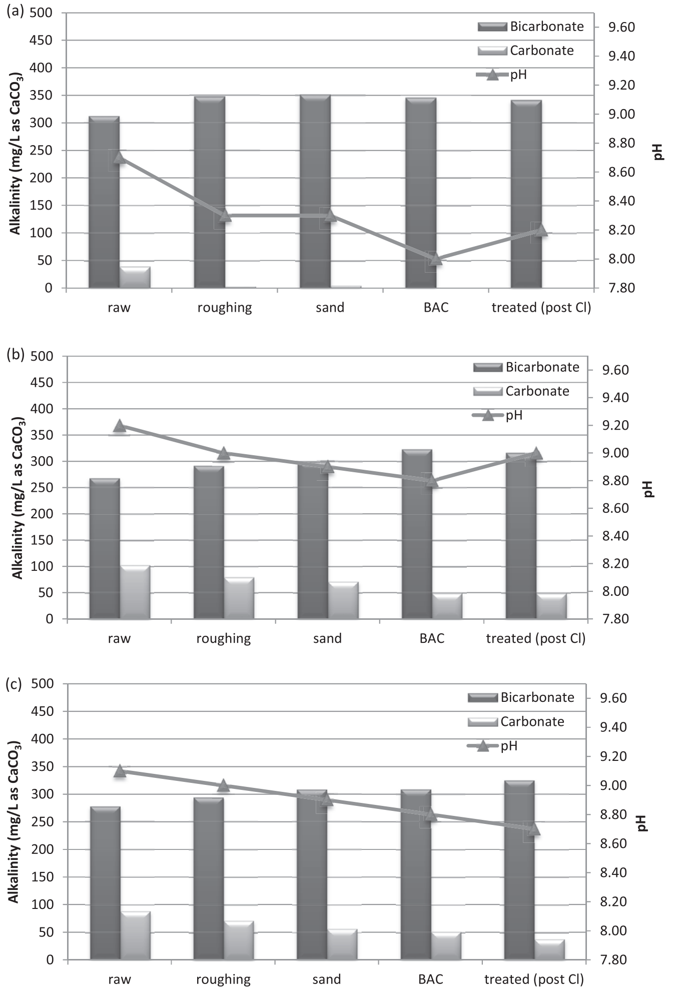

Fig. 3. Total alkalinity and pH in water samples collected at Benson in 2012 during (a) July, (b) September, and (c) November. Total alkalinity is shown as bicarbonate and carbonate alkalinity on the primary axis, and pH values on the secondary axis.

The overall reduction of DOC in the Osage WTP ranged from 35 to 53% with the lowest reduction measured in November and highest in September 2012. Based on the water quality data, the roughing and sand filtration systems alone reduced DOC by 27–43% (Table 4, Osage). The results demonstrated that oxidation of more than half of the organic matter occurred prior to biological filtration. Thus, it can be posited, that the DOC is removed not only via direct ozone contact, but also through the presence of ozone radicals in the water. The DOC analysis (Table 4) of Osage water shows that when analysing a single treatment effect there is a significant reduction in DOC concentration in water collected at the roughing filter. Further down the treatment train, there is no significant change in DOC concentration in water that has passed through the sand or BAC filter, possibly indicating that the ozone has decomposed and that no significant oxidation of pollutants by hydroxyl radicals is evident. However, through analysis of both the modular (individual filters) and cumulative effects (across the WTP treatment train) of ozone from raw water intake through produced potable water across the roughing, sand and BAC filters, the results clearly demonstrate significant water quality improvement through roughing filter. Since the designed-purpose of a roughing filter (aka preliminary filter) is to reduce the initial turbidity in raw water (Logsdon, 2008), the additional benefits achieved for DOC removal are important considerations for both operation and optimization efforts. It is essential for water quality engineers and operators to optimize roughing filter performance as a fundamental component for production of high quality, safe drinking water in such WTP designs.

The analysis of a single treatment effect on DOC at Benson shows that there is no significant change in DOC concentration in water at the roughing filter, suggesting no substantive oxidation after ozone injection. There was also no significant change in DOC in water collected at the sand filter. Significant changes were noted in water at the BAC filter, but that is most likely due to new activated carbon media that was replaced in July. Overall DOC reduction before BAC media replacement was between 20 and 34%. Post-media replacement overall reduction increased to 59%. Recognizing that changes in raw water chemistry and environmental conditions (e.g., temperature, oxygen content) also occurred between February and July, not all of the improvements in DOC removal efficiency can be attributed to the presence of fresh AC in the filter. In April 2013 DOC reduction through the treatment returned to 29% (April 2013) where DOC in the raw water was 35.6 mg/L while that in the treated potable water was 25.4 mg/L (Table 4, Benson). These values provide an indication of activated carbon exhaustion, as lower adsorption ability is exhibited and overall DOC removal by the end of the treatment train dropped to 29%.

The results of these analyses indicate that DOC may be recalcitrant in some filter modules across the WTPs, but do no elucidate the transformations of biodegradable and non-biodegradable DOC. Although the results indicated that oxidation may have a limited impact on total [DOC], it is possible that molecular changes occurred that were not captured through the analytical techniques applied. This may be important for future research, as well as for

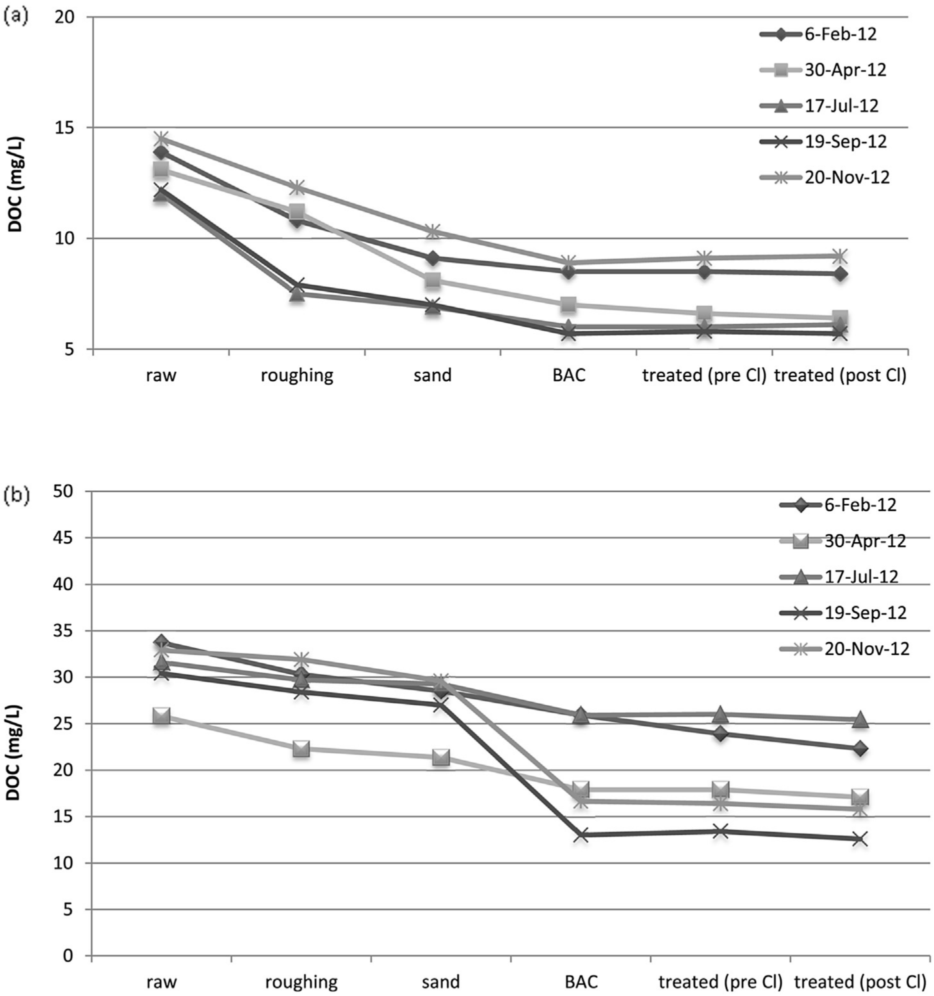

Fig. 4. Changes in DOC (mg/L) removal occurring through the treatment train in (a) Osage and (b) Benson. Results of analysis on water samples collected at the raw water entry before the ozone injection, roughing filter after the de-ozonation tank, sand filter, bacteriologically activated carbon filter (BAC filter), treated water with no chlorine (treated pre Cl) and treated water disinfected with chlorine (treated post Cl).

Table 4
Dissolved organic carbon (DOC) concentration (in mg/L) through treatment processes in samples collected between February 2012 and March 2013 at Osage and February 2012 to April 2013 at Benson.

Date	Raw	Roughing filter	Sand filter	DOC removed[a]	BAC filter	Treated (pre Cl)	Treated (post Cl)	Total DOC removed[b]
Osage								
06-Feb-12	13.9	10.8	9.1	35%	8.5	8.5	8.4	40%
30-Apr-12	13.1	11.2	8.1	38%	7.0	6.6	6.4	51%
17-Jul-12	12.0	7.5	6.9	43%	6.0	6.0	6.1	49%
19-Sep-12	12.2	7.9	7.0	43%	5.7	5.8	5.7	53%
20-Nov-12	14.2	12.3	10.3	27%	8.9	9.1	9.2	35%
18-Mar-13	15.7	12.8	10.3	34%	8.9	9.0	9.1	43%
Benson								
06-Feb-12	33.7	30.3	28.5	15%	25.9	23.9	22.3	34%
30-Apr-12	25.8	22.3	21.35	17%	17.9	17.9	17.1	34%
17-Jul-12	31.6	29.7	29.25	7%	25.9	26	25.4	20%
19-Sep-12	30.4	28.4	27	11%	13	13.4	12.6	59%
20-Nov-12	32.9	31.9	29.6	10%	16.65	16.4	15.8	52%
18-Mar-13[c]	35.6	nd	nd	nd	nd	nd	25.4	29%

nd: no data.
[a] DOC removed from raw through roughing and sand filters is provided in %.
[b] Total DOC removed (%) represents the reduction in [DOC] from raw water to treated (post chlorination) water.
[c] March 2013 data at Benson is only available for raw and post-chlorination treated water.

those involved with the design and operation of WTPs, since biodegradable DOC is more readily degradable in the subsequent biofiltration filter.

Total THMs measured in treated potable water at the Osage WTPs was below the regulatory limit of 100 μg/L. Chemical analyses showed THM concentrations of less than 100 μg/L between February 2012 and March 2013 at Osage (Fig. 5a) and above 100 μg/L during the same period at Benson (Fig. 5b). At Benson, THMs samples were primarily collected at the WTP with only 2 samples collected in the distribution system, despite the data indicating that THM formation continued through distribution system. In February and April 2012, the THMs in the distribution system were higher than that at the WTP outflow (Table 5).

An additional set of samples was collected in the Osage system (18-Mar-13) to establish the extent to which pre-chlorination affected raw surface reservoir water quality. Because ice cover remained intact during this sampling period, the impact of recharge and surface flow interaction with the surrounding environment had been limited for all samples collected between October 2012 and March 2013. The DOC for March 2013 were 15.7 mg/L in raw water and 9.1 mg/L in treated potable water; THMs in treated potable water were 57.9 μg/L.

3.4. Manganese, sulfate, chlorophyll A and chemical oxygen demand

Saskatchewan water supplies tend to be naturally high in iron, manganese, sulfate, and arsenic. Each community's raw water supply contained iron concentrations consistently below 0.1 mg/L. Inflow manganese concentrations in raw water were as high as 0.24 and 0.22 mg/L in Osage and Benson, respectively (Table 6).

Sulfates were consistently present in the raw water samples and were highly stable across the roughing and sand filters, with no statistically relevant removal of those compounds. Sulfate concentrations in raw, roughing filter, and sand filter samples ranged between 90 and 140 mg/L in Osage and 70 and 125 mg/L in Benson. Similarly neither total nitrogen nor phosphate concentrations were notably reduced through the treatment trains of either community's WTP.

At Osage, the COD in raw water samples ranged between 30 and 40 mg/L; in Benson, COD fell approximately between 60 and 100 mg/L.

Although the COD removal efficiencies were higher in spring than summer, fall and winter sampling periods, the COD in the spring samples (February and April) was also lower in the raw water intake (Table 2). From the results of a Wilcoxon–Mann-Whitney test for COD, where $\alpha = 0.05$, and evaluating both a single treatment effect and cumulative effect across the treatment train, the data show that COD removal at both communities follows the same pattern as DOC removal at the respective communities. These individual effects were analysed for raw water versus roughing filter, roughing filter versus sand filter, and sand filter versus BAC filter. Cumulative effect was evaluated with raw water quality as the baseline for comparison, such that statistical treatments were applied to data related to raw versus roughing filter, raw versus sand filter, and raw versus BAC filter. In the evaluation of single treatment effect at the Osage WTP, only the raw water versus roughing filter change in water quality results (per DOC and COD) were significant; all results were significantly positive for the cumulative effect in all categories. For Benson, only the sand filter versus BAC filter change in water quality results (per DOC and COD) were significant; the cumulative effect results indicate that there was no significant change in water quality from raw water through roughing filter, but statistically significant changes were noted for the remaining two cumulative effect assessments comparing raw water quality to that from sand and BAC filters.

The concentration of chlorophyll *A* was not detectable in the samples collected after the sand filter at Osage, except in July 2012 (Table 7). At Benson, chlorophyll *A* was not as readily removed and was detectable in most samples, with the exception of those collected in April 2012. On two occasions (February and July 2012), chlorophyll *A* persisted through the entire WTP, including being detected in the treated post-chlorination water.

4. Discussion

Based on the results of water chemistry analyses during the sampling period, the Osage WTP appeared to be performing well within regulatory compliance. Removal efficiencies achieved through the treatment train indicated that the WTP was performing within design expectations and in response to seasonally changing raw water quality. Regardless of intake DOC, the WTP consistently achieved 30–50% removal. The presence of DOC alone in the treated water does not necessarily present health risks. However, the combination of DOC and oxidizing disinfectants such as chlorine results in the formation of disinfection byproducts such

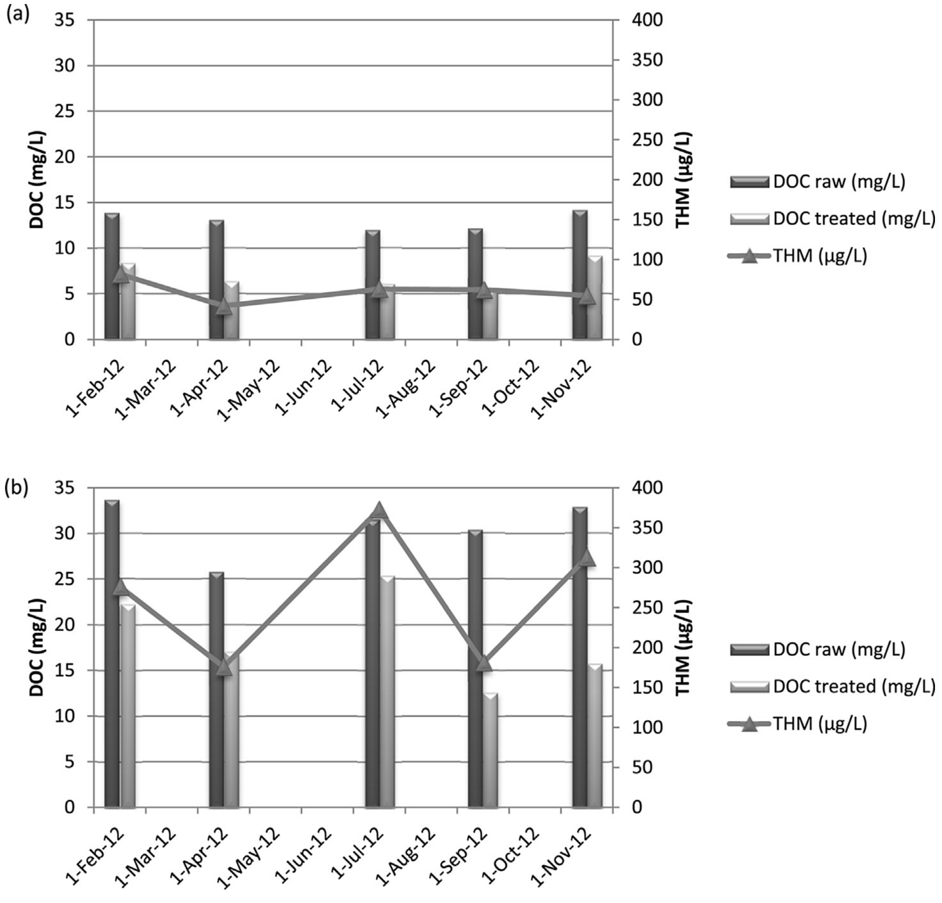

Fig. 5. Comparison of DOC concentration in raw and treated water in (a) Osage and (b) Benson.

Table 5
Trihalomethanes (THMs) concentrations (µg/L) in water samples collected at the Osage and Benson water treatment plant and distribution system between February 2012 and March 2013.

Trihalomethanes (THMs) (µg/L)				
Date	Osage		Benson	
	WTP	End of distribution system	WTP	End of distribution system
6-Feb-12	81.7	63.4	276	375
30-Apr-12	41.9	43.1	176	191
17-Jul-12	62.9	nd	373	nd
19-Sep-12	62.2	nd	181	nd
20-Nov-12	54.9	56.9	313	nd
18-Mar-13[a]	57.9	69.7	nd	nd

nd: no data.

[a] March 2013 data at Benson is not available for THMs.

Table 6
Manganese concentration in raw water and water collected after the roughing filter at the Osage and Benson water treatment plants.

Manganese (mg/L)				
Date	Osage		Benson	
	Raw	Roughing	Raw	Roughing
6-Feb-12	0.02	<0.01	0.07	0.01
30-Apr-12	0.06	0.02	0.02	0.03
17-Jul-12	0.24	0.19	0.22	0.14
19-Sep-12	0.21	0.05	0.08	0.05
20-Nov-12	0.05	<0.01	0.07	0.03

as THMs, HAAs, and/or NDMAs that are potentially carcinogenic (Health Canada, 2006). Excess DOC also interferes with other disinfection methods such as ultraviolet light irradiation and ozonation, while simultaneously encouraging the growth of microorganisms.

Because a batch chlorination event occurred during the research in Osage, it was possible to evaluate the efficacy of such approaches for maintaining low THM production. This practice likely oxidized the majority of NOM in the raw water source at that time and may have supported low [NOM] throughout the months during with the reservoir is isolated for the surrounding environment due to ice cover. Since THMs are volatile, the warmer day and cooler night temperatures experienced in October enabled density-driven

Table 7
Chlorophyll *A* (mg/m^3) levels measured though the treatment at Osage and Benson water treatment plant in period from February 2012 to November 2012.

Date	Raw	Roughing filter	Sand filter	BAC filter	Treated (pre Cl)	Treated (post Cl)
Osage						
06-Feb-12	64.27	1.42	BDL	BDL	BDL	BDL
30-Apr-12	9.95	1.84	BDL	BDL	BDL	BDL
17-Jul-12	56.18	1.36	0.83	0.48	BDL	BDL
19-Sep-12	37.12	0.94	0.47	BDL	BDL	BDL
20-Nov-12	38.70	1.36	BDL	BDL	BDL	BDL
Benson						
06-Feb-12	16.30	2.71	0.92	0.44	0.41	0.47
30-Apr-12	9.97	1.84	–	–	–	–
17-Jul-12	22.92	7.17	2.97	0.95	0.47	0.48
19-Sep-12	38.39	3.25	0.47	0.34	0.47	–
20-Nov-12	112.64	70.30	6.44	4.6	–	–

(–) below detection limit.

mixing of the reservoir, enabling THM evaporation prior to the advent of ice-cover conditions. The change in [THMs] from WTP to end of distribution system is also very small, indicating that conditions are not favourable for the production of THMs during distribution to consumers.

The evidence points to good outcomes for reducing THMs, but is not clear whether this increased haloacetic acid and *N*-nitrosodimylthamine formation, and how it may have impacted the microbiology of the reservoir water and surrounding ecosystem. Nonetheless, the positive impact of batch chlorination, at least in the short term, appeared evident.

The Benson WTP faced challenges through the sample period, including some deviations from the regulatory requirements. DOC concentrations in potable water were not observed at levels below 12.6 mg/L and the THM concentration in all 2012 samples exceeded acceptable threshold levels.

From a regulatory perspective in SK, THM concentrations must be evaluated at farthest point in the distribution system. However, by measuring [THMs] at the WTP, evidence of the presence of THMs in the treated potable water can be determined prior to entering the distribution system. Comparison of values for [THMs] at the WTP outflow and that at the farthest point in distribution system provides insight to both regulators and WTP operators as to where the greatest THM formation occurs and allows for consideration of the conditions that can be optimized to reduce total THMs across the system. Results of measurements of [THMs] at the Osage WTP and at the end of the distribution system indicate that no samples exceed the regulatory limit. In Benson, the raw water DOC ranged from 25.8 to 35.6 mg/L, and removal of DOC ranged from 20 to 59%. Considering the very high total alkalinity concentrations of more than 400 mg/L as $CaCO_3$ and the high initial DOC concentration, this represents a significant DOC removal efficiency for the Benson WTP. However, the remaining DOC in the treated water remains too high to meet THM regulations.

The Benson WTP operated under a PDWA from December 2012 to May 2013 due to the high turbidity in the treated water. The raw water was saturated with colloidal materials that the WTP filters were unable to adequately remove. In general, turbidity in treated water does not present a health risk to the public. However, excessive turbidity is often linked with both high probability of excess microbial contamination and unacceptable taste and odor in potable water. Depending on the water source and quality of the water, turbidity particles can serve as either transportation vectors of potentially pathogenic microbes that cause gastrointestinal illnesses and/or as safe harbour from chlorination and other disinfection techniques (Health Canada, 2012).

In Benson, the significant fluctuations in raw source water quality appear to be correlated with a lack of source water protection systems at the raw surface water source. Since colloids can be mobilized when low ionic strength water mixes with high strength water, it is possible that seepage and mixing of ground water with surface water is at least partially responsible for the observed colloidal displacement. Another possibility is that under-ice convection occurred. As biodegradation of organic matter occurs on the bottom of the dugout, sediments slowly warm due to bacteriological metabolism. As the lower layers of water warm (3–5 °C) a temperature differential between the upper and lower layers of water is created that induces an under-ice convection event. In such a case, the sediments and colloids are disturbed on the bottom of the dugout (Bengtsson, 2012) and dispersed throughout the water column.

These fluctuations in raw water quality in Benson may be better managed and minimized through both implementing a larger buffer zone (source water protection) and potentially by placing adequate pre-treatment within the WTP at particular times of the year during which turbidity and [DOC] tend to be highest. A revision to the treatment train making use of dual media up-flow roughing filters will reduce turbidity since flow of heavier particles is restricted. The further benefit of this design makes effective use of gravity settling such that heavier particles are removed in the roughing filter and not transported further through the WTP processes. Turbidity levels and efficiency of the Osage WTP to manage those turbidity-causing materials were not of primary concern in Osage and, thus, were not deemed to be a significant treatment challenge in the community.

Based on the results of this research, ozone performance appears to be more efficient at Osage than Benson. However, these results are most likely related to lower raw source water quality at Benson translating into lower WTP performance. The surface water dugouts in both communities are located in agricultural fields and are recharged by runoff, which contributes contaminants from both natural and anthropogenic processes to the raw water sources. Since the Benson surface water reservoir does not employ berms or buffer zone and is a collection reservoir for spring meltwater that has traveled through an additional 50 km of agricultural fields containing active oil wells, the risk for negative impacts on raw surface water quality in that community is much higher than observed in Osage.

One measure for evaluating the oxidative power and efficiency achieved by ozonation of the two WTPs is through detection and quantification of Chlorophyll *A* through and after BAC filters. The results indicate that the Benson WTP lacks oxidative power in comparison to that experienced in the Osage WTP. Further evaluation with respect to impacts of total alkalinity and COD on hydroxyl radical availability for oxidation was noted in Benson where total alkalinity was significantly higher than that observed in Osage.

Even though the ozone generators produced the same oxidative power in Benson as in Osage, ozone employed in Benson did not have the same mechanism or pathway of reaction due to the presence of carbonate and bicarbonate ions. High COD values consume significant concentrations of oxygen in order to oxidize a variety of organic compounds. This high oxygen demand impacts ozone efficacy (Table 8). It is also highly probable that in the addition to the high total alkalinity high COD concentration in the Benson raw source water created synergistic or additive ozone scavenging resulting in reduced DOC removal in the ozone-assisted biofiltration design. In addition, low removal rates of manganese and sulfate concentration suggest that these did not significantly impact on initial ozone consumption in either WTP. The agreement of the DOC and COD results suggest that due to the high alkalinity, bicarbonate and carbonate in particular, oxidation by ozone is stunted and therefore its effects seem to be insignificant, occurring very slowly.

To improve ozonation efficiency and oxidative power, installation of ozone generators in series across the WTP treatment train would enhance efficacy of targeted organic contaminants such that water containing an ozone residual from one tank is receiving a boost of ozone as it enters the next tank. Because of the smaller flow volumes required in small rural communities, parallel systems that can handle higher flows are not required. Series filtration designs are considered more beneficial in WTPs as there are more opportunities for filter-water interaction to enhance contaminant removal (Sánchez et al., 2006). Making use of emerging technologies, such as ozone injectors that minimize the diameter of the ozone bubbles to maximize the surface area and oxidation potential, is also recommended for improving ozone dosage and efficacy in a modular potable water treatment design that use ozone-assisted biofiltration.

The BAC filter performance, which is affected by oxygen concentrations in the treatment train, also differed between the two communities. The amount of DOC removed in the BAC filter at Benson in February, April and July 2012 was as much as 4 times higher than in Osage. The effluent [DOC] in Osage was significantly lower despite the less efficient removal rate in that WTP, at 0.6, 1.1 and 0.9 mg/L. Although the data suggest higher removal efficiency of DOC at Benson, not only was potable water quality lower due to the poorer quality water input, but those BAC filters also feature larger surface area for reactions and interface chemistry than those in Osage. Because of the design differences and significantly different water quality entering each plant, it is not possible to directly compare the two. However, it is clear that the Benson WTP removes a large proportion of the DOC entering the plant but that this removal is insufficient for achieving potable water quality that minimizes THM production.

Based on the analytical results for measurement of chlorophyll *A*, phosphorous, and nitrogen concentrations, both of the surface water impoundments used for raw water intake in the community of Benson can be classified as nutrient-rich, if not eutrophic (Janus and Vollenweider, 1981). The results of water quality analyses and WTP performance indicate a need for more proactive solutions for safeguarding raw source water quality. In particular, given the location of the Benson impoundment, that system is particularly vulnerable to both overland flows and cumulative downstream impacts of spring melt and agricultural and oil exploration activities upstream of the reservoir. Enhancement of the source water protection systems can be achieved through the incorporation of buffer zones along both the dugouts as well as implementation and preservation of buffers along the source creek to reduce negative impacts from agricultural and oil well operations on raw water quality. Additional strategies may include stream bed improvements and redevelopment of the reservoir base material. For instance, creating a stream-bed that forces water to cascade through the bed not only adds the advantage of increased aeration and subsequent beneficial chemical and biological reactions, but also minimizes sediment deposition in the reservoir, reducing levels of turbidity and DOC. The raw water in both communities would further benefit from the presence or expansion of powerful aeration unit(s), such as air diffusers, capable of aerating water throughout the water column.

Table 8
Percent of COD removed from raw water infused with ozone through sand filtration.

Date	COD removal post-sand filtration (%) Osage	Benson
6-Feb-12	64%	22%
30-Apr-12	69%	20%
17-Jul-12	47%	15%
19-Sep-12	41%	16%
20-Nov-12	47%	16%

Based on the data collected from two very small rural community ozone-assisted biofiltration, it was possible to identify design optimization opportunities to improve produced potable water quality, as well as to handle changes in raw water quality intake. For instance, by designing the treatment train in series rather than in parallel, the system can operate under steady flow conditions at all times allowing for higher contaminant removal capacity (Sánchez et al., 2006). Use of water meters or valves to ensure steady flow for all filters is highly recommended. The data further highlights the impacts of high total alkalinity and salinity, pH, the presence of carbonate and phenol alkalinity, and the ionic strength of raw source water on the effectiveness of ozone. Thus, by routinely monitoring these parameters, WTP operators can adjust ozonation and ozone dosage rates to ensure sufficient DOC degradation under increased hydroxyl radical scavenging conditions.

Through visual inspection of turbidity in settling tests from Benson, it was noted that improved monitoring and system response to high turbidity loading and the presence of fine colloidal materials is required. Through the analysis of logged data, the ideal operating parameters for treating water of this inflow quality can be achieved within the existing WTP design. The required change is in the operation of the plant during those periods. Monitoring of the inflow DOC, DOC removal percentage, ozone dosage, and COD range is recommended to ensure safe and adequate potable water treatment performance. The removal of DOC can serve as a proxy for governing the performance status of the WTP, which relies on ozone dosage and affects THM production. By monitoring ozone dosage, a proxy for the type of alkalinity and ionic strength is possible in coordination with DOC removal efficiency. Monitoring both DOC removal percentage and ozone dosage provides a WTP operator with sufficient data to determine adequate ozone dosage to reduce [DOC] and minimize potential disinfection byproducts formation. The literature suggests that ozone dosages between 0.5 and 2 g of O_3/g of DOC initially present in order to reduce DOC, and consequently DBP formation (Gottschalk et al., 2010). If greater than 2 g of O_3/g of DOC initially present is required, then benefit-cost and system sustainability analyses should be completed prior to full-scale WTP installation. Seasonal differences in ozone doses will also affect cost-effectiveness and system sustainability. Monitoring the range of COD in raw source water and throughout the treatment train provides a good indicator of ozonation performance. While COD of the water demonstrates demand for ozone, it is not an indication of DOC removal. COD reduction can provide evidence that DOC transformation has occurred whereas DOC reduction confirms mineralization and removal of organic compounds from the treated water.

The results of these field research activities provide important information and guidance for engineers and operators responsible for optimizing performance and operation of small-scale WTPs in rural areas for which high quality surface water is not available. Such conditions for WTPs design and operation in which low flows and intermittent consumption patterns create significant performance and potable water production challenges that are often not reflected or captured in the laboratory context.

5. Conclusions

The performance of two small ozone-assisted biofiltration WTPs to produce potable water under a variety of seasonal, field conditions was completed as a method for improving rural population access to safe drinking water. The overall analysis of the water quality parameters demonstrate that WTP performance is hindered by high alkalinity and ionic strength of the water, high organics loading (DOC) and turbidity (particularly that of an extremely fine colloidal nature). The presence of high carbonate and bicarbonate alkalinity was noted to inhibit ozone contact and interaction with DOC. In turn, the overall treatment train was proved incapable for adequately removing DOC. The results further point to the likelihood of incomplete DOC oxidation to biodegradable DOC that could be readily biodegraded in the BAC filters. The results suggest that, to maximize organics oxidation, the ozone dosage must be determined based on [DOC] and administered based on the presence of alkalinities.

The current WTP designs and source water impoundments at each community do not fully address the seasonal water quality needs and challenges, as reflect by the issuing of a Precautionary Drinking Water Advisory during the research period. The water quality in the surface impoundments is susceptible to both seasonal fluctuations and land use impacts from proximate agricultural lands since overland runoff and other flows contribute to the raw water sources.

This field research provides evidence that a single water treatment design can not necessarily produce identical treatment results for two similarly sourced surface water sources. Differing strengths of diverse water parameters will ultimately require differing approaches and changes to improve operational performance. If those small, but demonstrated significant, differences are taken in consideration at the time of WTP design, there can be significant achievements in cost savings related to on-site upgrades, reduced operator and community frustration, and lessened likelihood of regulatory infractions and permit suspensions.

Acknowledgments

The authors thank Sam Ferris, Executive Director, Environmental and Municipal Services at the Water Security Agency of Saskatchewan, as well as the Saskatchewan Ministry of Environment for supporting this research through funding and laboratory analyses. The authors further gratefully acknowledge financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) to McMartin (DWM 288137-15) and Stavrinides (JS 386654-10) and the Canada Foundation for Innovation (CFI) to Stavrinides (JS 28591).

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