Effectiveness of ozone/membrane pairing for the production of drinking water from surface water

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The pairing of ozone and membrane technologies offers a cost-effective solution for the production of drinking water from surface water. The synergistic combination of ozone and a UMF-type membrane facilitates the operation of both technologies and enables the production of water that complies with Québec regulations for drinking water quality. Moreover, the pairing of these two processes is in line with sustainable development criteria: it requires no chemicals (no coagulants, very low frequency of chemical washing) and produces wastewater that requires no special treatment or disposal (no sludge), unlike other technologies that have been certified for the treatment of raw water of comparable quality. Results obtained for the Québec Drinking Water Treatment Technologies Committee (CTTEP) demonstrate that these two technologies, when used in conjunction with one another, can adequately treat raw water that is highly loaded (maximum turbidity of 130 NTU; maximum total organic carbon level of 7.2 mg/L) and heavily contaminated with pathogenic microogranisms (up to 20,000 CFU/100 mL fecal coliforms in meeting the log removals required for viruses, Giardia cysts and Cryptosporidium oocysts). Other results confirm the treatment chain's effectiveness in completely eliminating cyanobacteria and cyanotoxins. The synergetic pairing of just two simple and highly effective processes is promising for the future of the drinking water treatment sector, where standards are high and costs are ever-increasing.

1. Introduction

The production of drinking water from surface water requires effective technologies to achieve compliance with the regulatory requirements in force in Québec (Gouvernement du Québec, 2005). Ozone/membrane pairing (i.e., the DaguaFlo-IV process) was recently certified by the Québec Drinking Water Treatment Technologies Committee (CTTEP) for use as a complete treatment process (with final chlorine or chloramine disinfection) for a full-scale facility (Gouvernement du Québec 2007a and 2007b).

Ozonation is recognized for its disinfectant and oxidizing action in the treatment of surface water. Ozone effectively inactivates bacteria, viruses and Giardia cysts (MDDEP, 2006). Molecular ozone oxidizes organic matter via the same chemical mechanisms as chlorine, and thus minimizes the formation of chlorination by-products, such as trihalomethanes (Doré, 1989). Ozone also destroys organic micropollutants (e.g., cyanotoxins), tastes and odours (MDDEP, 2007).

Ozone-resistant ultra-microfiltration membranes with a small pore size are complementary to ozonation. Membranes with a pore size of less than 1 µm can filter turbidity, bacterias, *Cryptosporidium* oocysts and *Giardia* cysts. This pore size also prevents cyanobacterias from passing into the effluent (MDDEP, 2007).

Thus, the pairing of ozone and membrane technologies enables compliance with the stringent regulations in force, at the microbiological, particulate and organic levels. However, like any other treatment process, this application has limits with respect to the quality of the surface water it can treat, as specified below.

2. Materials and methods

Results are presented from two pilot-scale tests: a certification trial presented to the CTTEP (Niquette, 2007a) and testing for the removal of cyanobacteria and cyanotoxins (Niquette, 2007b). Both studies were conducted using the same treatment process, i.e., the DaguaFlo-IV, and the results were compiled by laboratories accredited by the Québec government.

In the process (see Figure 1), the raw water first passes through a 400 µm self-cleaning pre-filter. Gaseous ozone is generated on-site by an air compressor, an oxygen generator and ozone generators, and is injected into the water line using a Venturi-type injector.

The water and ozone remain in contact in the reaction tank for 4.6 minutes in order to achieve the required disinfection and colour-removal performances. Turbidity is then removed via ultra-microfiltration membranes.

Finally, the treated water is stored in a tank, to be pumped to the municipality via the distribution network.

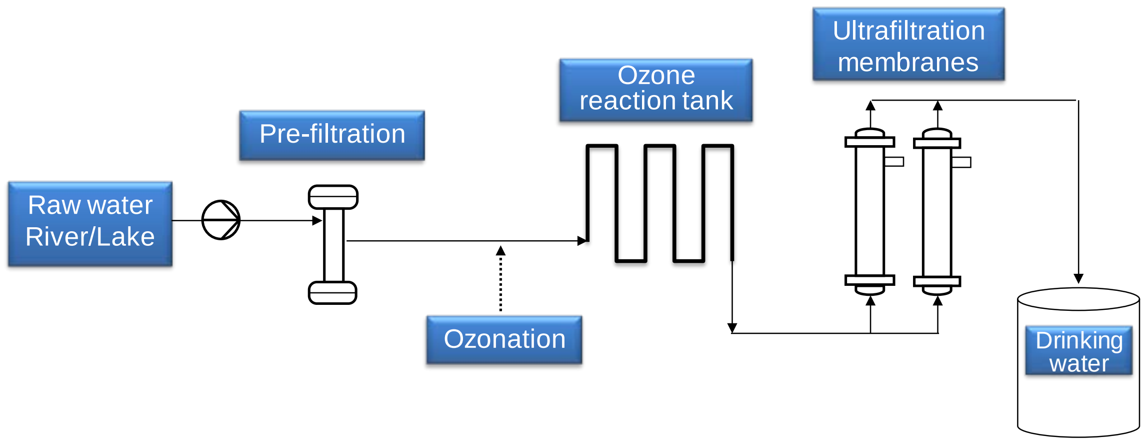

Figure 1: Description of the DaguaFlo-IV process

The ozone generators were developed by Dagua Inc. and use ceramic plate technology. Ozone is generated from oxygen in the ambient air using an electrical plasma discharge. The ozone concentration at the generator outlet is 8% wt. ozone. A Venturi-type injector is used to inject ozone under pressure into the water. With a rate of ozone gas dissolution into water of more than 90%, the injection process patented by Dagua is notably more efficient than an atmospheric pressure system with diffuser injection (40% to 70% efficiency).

Ensuring operator safety is a key design priority. An ambient ozone detector is connected to the programmable logic controller (PLC) to detect any ozone leaks, should an accident occur. In the event of an accidental leak, the PLC is set to automatically shut down the process and transmit an alarm to plant operators via pager. As well, the ozone transport pipes are assembled with a minimum of joints to reduce the potential for leakage.

Ease of operation is another design focus of the ozone/membrane technology. With automatic, PLC-managed filtration and backwash operations as well as continuous water quality monitoring, the DaguaFlo process requires approximately 30 minutes of operating time per day. The absence of chemical handling combined with remote telemetric monitoring and control also minimize operating time and contribute to the ease of operation.

During the DaguaFlo-IV certification trial, raw water was drawn from the Yamaska River at the municipality of Farnham, Québec. The pilot process was monitored from March 12, 2007, to June 20, 2007, inclusive. The parameters listed in Table 1 were measured during the testing by an accredited laboratory, at intervals determined by the CTTEP sampling protocol (MENV and MAMM, 2004).

Trihalomethanes produced by chlorination were evaluated following a chlorination similar to that used upstream of a distribution network (SDS-THM; APHA *et al*., 2005). The incubation conditions for the SDS-THM after chlorination were, as recommended by the CTTEP (MENV and MAMM, 2004): *in situ* pH and temperature; incubation time of 24 ±1 h; free available residual chlorine after 24 h of 0.5 ±0.2 mg/L. The method for determining SDS-THM also applies for chloramine disinfection (APHA *et al.*, 2005). To abide by the spirit of the CTTEP (MENV and MAMM, 2004) and the *Guide de conception des installations de production d'eau potable* (especially section 10.4.3, volume 2; MDDEP 2006), the proposed conditions for the application and incubation of the chloramines for SDS-THM measurement were as follows : *in situ* temperature; 24-h. incubation time; pH of 7.2 (to ensure monochloramine formation); monochloramine concentration of 2 mg/L ±0,2 mg/L with a chlorine to ammonia mass ratio of 4/1 (mg Cl_2/mg NH_3).

During the testing for cyanobacteria and cyanotoxin removal, raw water was drawn from Waterloo Lake near the municipality of Waterloo, Québec. The pilot test was conducted between August 30 and October 4, 2007. The analytical parameters measured during the monitoring were total organic carbon (TOC), cyanobacteria and cyanotoxins. TOC was measured using Laboratoire SM Method ILCE-059. Cyanobacteria were analysed using Géostar Inc. Method GN478-CYA1 1.0. The cyanotoxins measured by the Centre d'expertise en analyse environnementale du Québec (Method MA403 – Microcys 1.0) were: microcystin-LR, microcystin-RR, microcystin-YR and anatoxin-A. Microcystins are hepatotoxins and anatoxins are neurotoxins. Hepatotoxins and neurotoxins are produced by cyanobacteria that are commonly present in surface water supplies and thus seem to be most relevant for water supplies (Health Canada, 2002).

Parameters	Raw water (# of samples)	Treated water (# of samples)	Backwash water prefilter (# of samples)	Backwash water membrane (# of samples)
pH (on-site)	13	13		13
Temperature	13	13		13
Fecal Coliforms	13	13		
Total Coliforms	13	13		
HPC	13	13		
True Color	13	13		
Total organic carbon	13	13		3
Dissolved organic carbon	13	13		3
Turbidity	13	13		3
Suspended solids			3	3
UV Absorbance -254 nm	6	6		
Ammonia	3	3		
Nitrite	3	3		
Nitrate & nitrite	3	3		
Chlorine demand	3	3		
Total alkalinity	6	6		
Calcium	6	6		
Hardness	6	6		
Total iron	6	6		3
Total manganese	6	6		3
Dissolved solids	3	3		3
Total solids	3	3		3
Conductivity	3	3		
SDS-THM (free chlorine)	6	6		
SDS-THM (chloramine)				
Bromate		3		
Bromide	3			
Toxicity (trouts)			1	1
Toxicité (daphnids)			3	3

Table 1: Parameters analysed

3. Results

3.1 Certification trial for the ozone/membrane process (DaguaFlo-IV)

Organic matter in raw water drawn from the Yamaska River is mostly dissolved and is oxidized by the DaguaFlo-IV process. In fact, 76.8% to 100% of the total organic carbon (TOC) is composed of dissolved organic carbon (DOC). The maximum concentration of TOC in the raw water is 7.2 mg/L, and the maximum DOC concentration is 5.5 mg/L. Membrane filtration has little effect on TOC since organic content is mostly in a dissolved form, as mentioned above. The ozonation stage is used to oxidize organic matter and reduce the potential for trihalomethane formation.

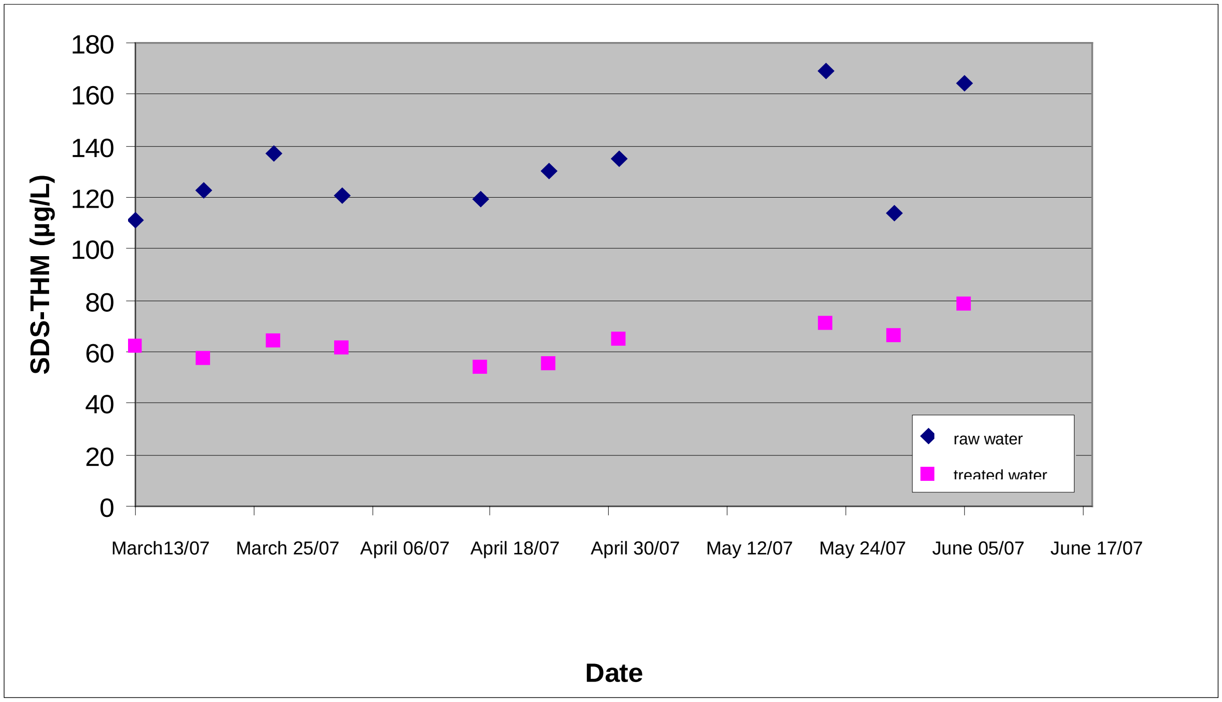

Figure 2: Variations of SDS-THM concentrations

Figure 2 shows that SDS-THM concentrations in the raw water from the Yamaska River, averaging at 132.3 µg/L, are reduced to SDS-THM concentrations in treated water that are consistently below the 80 µg/L limit set out by the *Regulation respecting the quality of drinking water* (Gouvernement du Québec, 2005).

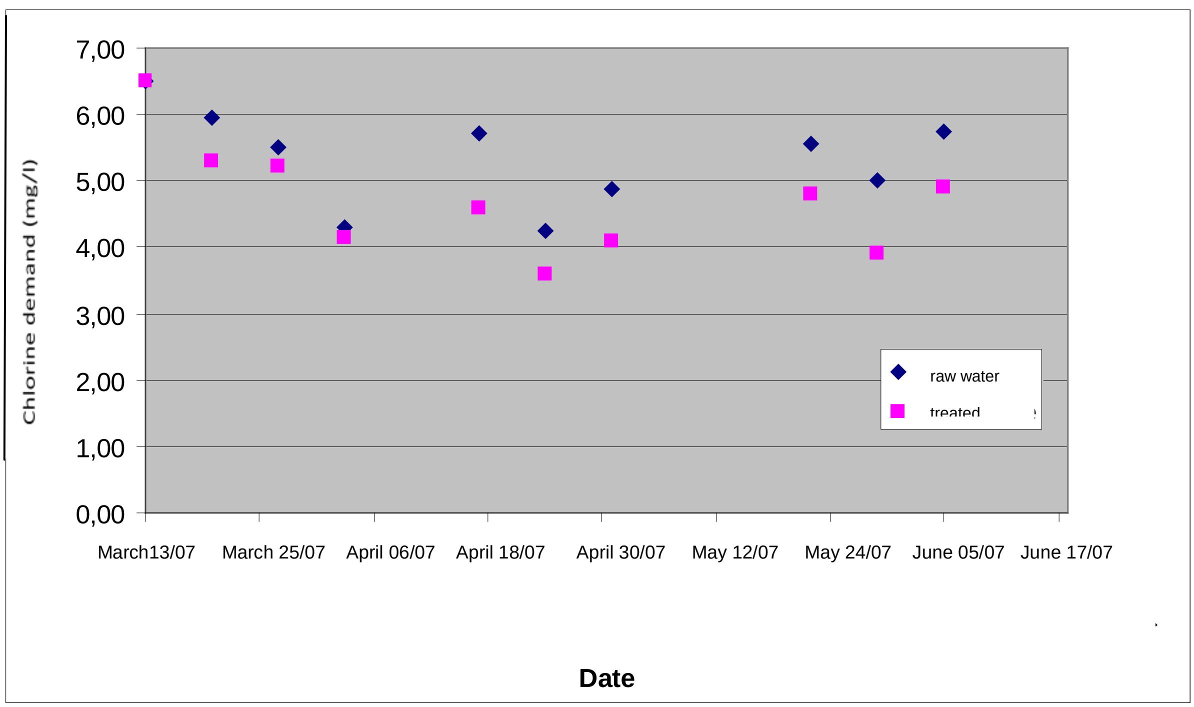

Figure 3: Variations of chlorine demand

Figure 3 demonstrates that chlorine demand is also reduced by the process. SDS-THMs formed through the addition of monochloramines are minimal in both the raw water and the treated water (less than 8 µg/L). Results obtained during the test period demonstrate that the DaguaFlo-IV process significantly reduces colour to values that regularly approach the detection limit of the analytical method used (2.0 TCU) and are well below the 15 TCU limit recommended by the federal government (Government of Canada, 1999). The raw water 254 nm UV absorbance is significantly decreased by the oxidizing action of ozone.

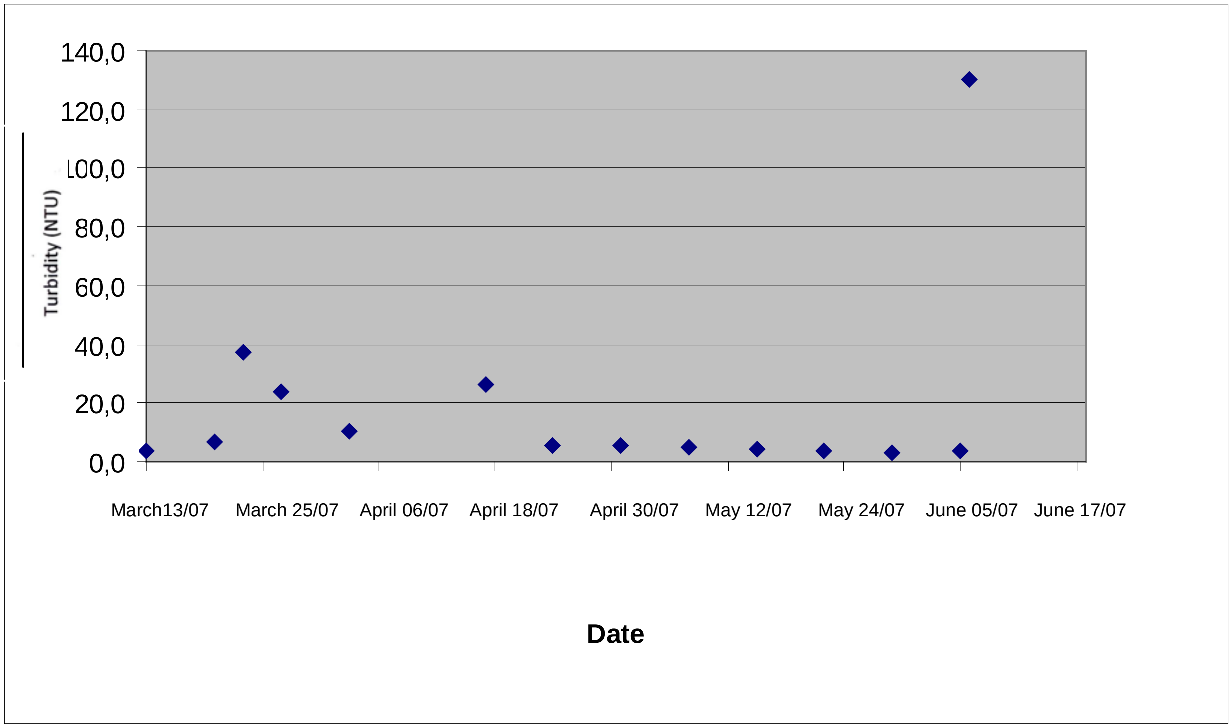

Figure 4: Variations of raw water turbidity

Figures 4 and 5 show, respectively, the raw water and treated water turbidity values measured by the accredited laboratory. Despite a turbidity point of 130 NTU measured in the raw water on June 6 and a 37 NTU point measured in the raw water on March 23, the membrane process consistently maintained below the 0.1 NTU turbidity standard (Figure 5), as prescribed for membrane filtration (Gouvernement du Québec, 2005).

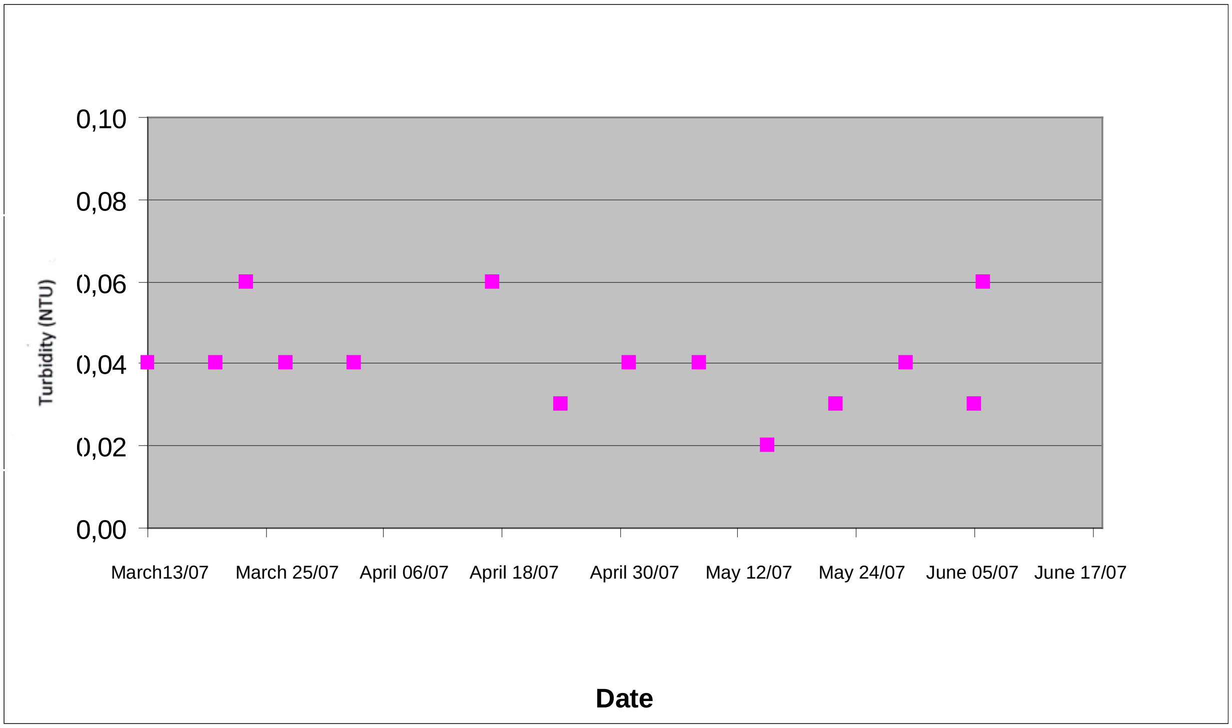

Figure 5: Variations of treated water turbidity

An average ozone residual of 1.0 mg/L at the ozone process effluent was targeted to ensure a CT value enabling the ozone/membrane technology to meet the most stringent surface water disinfection criteria (MDDEP, 2006). However, bromate levels measured at the process effluent were very low (≤ 1,8 µg/L) and did not exceed the 10 µg/L standard (Gouvernement du Québec, 2005). The temperature of the raw water ranged from 0.7 to 20.1°C, and the treated water ranged from 1.9 to 20.8°C during the official monitoring of the pilot project. The pH remained close to neutral.

The pilot process eliminates the presence of fecal coliforms, in spite of the high levels recorded in the raw water (too numerous to be counted in the water, which was considered “wastewater” by the accredited laboratory). It is therefore well-adapted to highly contaminated water (up to 20,000 CFU fecal coliforms/100 mL). The same high level of total coliforms was recorded in the raw water, with no coliforms detected in the process effluent. As well, no HPC bacteria present in the raw water were observed in the treated water.

The ozone-resistant membrane used by the process required no chemical cleaning during the three-month monitoring period, due to the presence of residual ozone in the treated water and the backwash water. If an acid/base backwash was conducted, the water would be then neutralized to a pH of 7.0 for safe discharge into the natural environment. No other potentially harmful product is discharged into the environment, as the backwash water from the centrifugal separator and the membrane have concentrations of suspended matter below 20 mg/L, and thus comply with the requirement for discharge into the environment (MENV, 2006). This finding was confirmed by the toxicity tests conducted on the backwash water, which showed no mortality to trout and daphnids. Moreover, as the DaguaFlo-IV process uses no coagulants, total aluminum concentrations (< 3 mg/L) and total iron concentrations (< 5 mg/L) in the backwash water comply with the corresponding standards (MENV, 2006).

3.2 Removal of cyanobacteria and cyanotoxins

Cyanobacteria and cyanotoxin removal testing was carried out in conditions presenting a heavy load of organic matter, with the raw water TOC ranging from 9.2 to 13.5 mg/L.

Table 2 shows the cyanobacteria removals achieved by the DaguaFlo-IV process during the monitored period. Average cyanobacteria concentrations at the process outlet were reduced to levels below the detection limit of the analytical method used.

Cyanobacteria		
Date	***Raw water***	***Water after membrane and ozone***
	CFU/100 ml	*CFU/100 ml*
Aug. 30-2007	*96*	*<1*
Sept. 5-2007	*80*	*<1*
Oct.4-2007	*60 000*	*<1*

Table 2: Average cyanobacteria concentrations in raw water and treated water

Table 3 shows the cyanotoxin removals achieved by the DaguaFlo-IV process during the monitored period. Cyanotoxin concentrations at the process outlet were reduced to levels below the detection limit of the analytical method used.

Microcystine-LR		
Date	**Raw water**	**Water after membrane and ozone**
	ug/l	ug/l
Aug. 30-2007	1.5	<0.04
Sept. 5-2007	0.65	<0.04
Oct.4-2007	0.37	<0.04

Microcystine-RR		
Date	**Raw water**	**Water after membrane and ozone**
	ug/l	ug/l
Aug. 30-2007	15	<0.03
Sept. 5-2007	6.0	<0.03
Oct.4-2007	2.6	<0.03

Microcystine-YR		
Date	**Raw water**	**Water after membrane and ozone**
	ug/l	ug/l
Aug. 30-2007	1.1	<0.02
Sept. 5-2007	0.47	<0.02
Oct.4-2007	0.28	<0.02

Anatoxin-A		
Date	**Raw water**	**Water after membrane and ozone**
	ug/l	ug/l
Aug. 30-2007	<0.02	<0.02
Sept. 5-2007	<0.02	<0.02
Oct.4-2007	<0.02	<0.02

Table 3: Cyanotoxin concentrations

4. Discussion

The DaguaFlo-IV ozone-membrane process is a proven treatment chain for the purification of loaded surface waters, as shown by an excerpt from the technical assessment sheet (Gouvernement du Québec, 2007a) based on the pilot study results (Table 4). The use of ozone (with the tested CT) in combination with the accredited membrane (Gouvernement du Québec, 2007b) removes pathogenic microorganisms at levels that are sufficient for the treatment of the most contaminated surface waters (up to 20,000 CFU fecal coliforms/100 mL; MDDEP, 2006).

1 Celsius

DISINFECTION [log removal required]	*Crypto*	*Giardia*	VIRUS
Log required			
2 000 - 20 000	**2**	**6**	**7**
200 - 2 000	2	5	6
20 - 200	2	4	5
< 20	2	3	4
Disinfection logs	**3,37**	**7,56**	**9,40**

disinfection design	ozone
CT available	4,23
[C] residual (mg/l)	1
hydraulic efficiency T_{10} /T	0,92
T(minutes)= Vu/Qhmax	4,60
volume V_u (m^3)	0,493
Qhmax (m3/h))	6,43
average flow (gpm)	28,3
average daily flow (m3/d)	154,3

nactivation log]=CT available/CT required/[lo	*Crypto*	*Giardia*	Virus
ozone	0,17	4,36	9,40
membrane	3,20	3,20	0,00
sub-total	3,37	7,56	9,40

	CT value (mg.min/L) for a 90% inactivation (1 log)		
Temperature (Celsius)	*Crypto (pH 6@9)*	*Giardia (pH 6@9)*	*Virus*
<1	25,6	0,97	0,45
2	23,3	-	-
3	21,2	-	-
5	17,5	0,63	0,30
7	14,5	-	-
10	10,9	0,48	0,25
15	6,7	0,32	0,15
20	4,2	0,24	0,125
25	2,6	0,16	0,08

Table 4: Results for the removal of pathogenic microorganisms

During the pilot test, it was demonstrated that by maintaining an ozone residual of 1.0 mg/L in the reaction tank for 4.6 minutes at a hydraulic efficiency of T_{10}/T of 0.92, the combined ozone-membrane process complies with the removal logs required for viruses, *Giardia* and *Cryptosporidium*, for heavily loaded water with a fecal coliform concentration below 20,000 CFU/100 ml.

A membrane filltration made of polyvinylidene fluoride (PVDF) and having a pore size of 0.1 µm complements ozonation. Its small 0.1 µm pore size screens turbidity, bacteria, Cryptosporidium oocysts and Giardia cysts (Gouvernement du Québec, 2007a and 2007b). At less than 1 micron, the pore size also prevents cyanobacteria from passing into the effluent (MDDEP, 2007). Moreover, the PVDF material resists ozone. The presence of ozone on the membrane promotes self-cleaning efficiency and even limits the need for chemical washing.

The ozone/membrane combination is a cost-effective treatment solution for heavily loaded surface water in a sustainable development context that integrates economic, environmental and social considerations. Ozone is manufactured on site from oxygen in the ambient air (minimizing transportation demand), using an ozone generation process that has been optimized to reduce energy use and operating costs. Given that the ozone generation process produces minimal by-products while achieving significant benefits through the removal of pathogenic microorganisms, the quality of the treated water that is produced has a positive social impact. The presence of ozone residual on the membrane minimizes energy requirements for washes and reduces costs related to sewer discharge. Chemical cleaning of the membrane becomes almost optional. Accordingly, the sewer discharge requires no special treatment or disposal (Gouvernement du Québec, 2007a), further minimizing resource requirements. Pathogenic microorganism removal credits also allow for final chlorination to be replaced by the application of chloramines, reducing the social impact on health of trihalomethanes in the distributed water supply. Unlike other processes that have been accredited for the treatment of raw water of similar quality, the ozone-membrane solution requires no coagulant or coagulation adjuvant, for reductions in labour, sludge disposal and operating costs.

5. Conclusion

The paired ozone/membrane technology functioned very well during the test periods, despite the heavy load of organic matter in the raw water that was treated. High standards were achieved for the removal of turbidity and pathogenic microorganisms. As well, the ozonation and membrane filtration process completely eliminated all cyanobacteria and cyanotoxins.

The DaguaFlo-IV treatment chain used in the tests achieves outstanding compliance with the latest requirements for the treatment of raw water drawn from heavily loaded surface waters. The technology also meets the key economic, environmental and social aims of a sustainable development context. For municipalities, ease of operation is assured through the use of only two main processes and their corresponding control systems. From a health perspective, all regulatory requirements and standards are met.

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