

NOM removal: evaluating five process alternatives to alum coagulation

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ABSTRACT

Bench-scale experiments were conducted to evaluate disinfection by-product (DBP) precursor removal by coagulation with alum and ferric sulfate (FS), intermediate ozonation (IO_3), powdered-activated carbon (PAC), ion exchange resin (IX), and spiral-wound nanofiltration (NF). The effect of source water quality on process performance was also assessed on six source waters. Overall, NF offered the best performance in terms of dissolved organic carbon (DOC) removals along with lower DBP concentrations in every tested condition except for DOC-rich waters (13–15 mg/L). Conventional treatment coupled with recirculated PAC adsorption (Actiflo® Carb) was the process configuration providing the most consistently low DOC (less than 2 mg/L), facilitating DBP regulation compliance. IX/alum and alum/ IO_3 reduced DBP concentration to a lesser extent, but proved to be more efficient than conventional treatment with alum alone. In terms of effluent DBP concentration, FS outperformed alum at higher coagulant dosages, whereas alum offered a superior performance at lower dosages. Finally, this investigation shows the relevance of conducting treatability assays to identify the most suitable treatment alternative for DBP control.

Key words | coagulation, disinfection by-products, ion exchange resin, nanofiltration, ozonation, powdered-activated carbon

INTRODUCTION

Chlorine is the most widely used disinfectant in the water industry as it can efficiently inactivate a broad range of pathogens at low cost and provides a measurable residual concentration in distribution systems. However, free chlorine reacts with natural organic matter (NOM) and generates potentially carcinogenic disinfection by-products (DBPs). As regulations become stricter, many utilities using chlorine as secondary disinfectant are reviewing their DBP control strategy to achieve regulatory compliance.

Coagulation is widely used in North America, due to its relatively low cost and efficiency to remove DBP precursors and turbidity. Coagulation efficiency is driven by numerous factors including raw water alkalinity, pH and turbidity, mixing conditions, and NOM properties such as molecular weight distribution, charge density, solubility, and functional groups (Pernitsky & Edzwald 2006). In contrast with

conventional treatment used to minimize filter effluent turbidity, coagulation optimized for NOM removal (typically through pH adjustment) may lead to greater removals of DBP precursors (Bell-Ajy *et al.* 2000). Owing to the limitation of using alum under very low pH conditions, many utilities have elected to use ferric-based coagulants. However, alum was reported to remove dissolved organic carbon (DOC) more efficiently at relatively low dosages ($<0.5 \text{ mM Al}^{3+}$ or Fe^{3+}) while ferric sulfate (FS) tends to outperform alum at higher dosages (Edwards 1997). The gain in NOM removal provided by FS thus remains highly site specific.

Intermediate ozonation (IO_3), i.e., ozonation following coagulation and settling, can also be used for DBP control. Ozone preferentially reacts with humic substances (mostly by electrophilic substitution and oxidation reactions), which

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results in substantial color and UVA_{254} removal and significantly lower DBP concentrations (Reckhow *et al.* 1986). IO_3 was reported to decrease DBP formation potential over a wide range of source waters (United States Environmental Protection Agency 2001). Yet, IO_3 performance proved to be specific to the water characteristics and ozonation conditions (Singer *et al.* 2003). Reported decreases in trihalomethane (THM) and haloacetic acid (HAA) concentrations by IO_3 evaluated on nine source waters were more variable than coagulation. In some cases, IO_3 even generated greater DBP concentrations (Singer *et al.* 2003).

Adsorption of DBP precursors on activated carbon is most commonly achieved using granular-activated carbon filters rather than powdered-activated carbon (PAC). However, investigations conducted on various surface waters have shown that the use of PAC subsequent to coagulation results in greater DOC removals than coagulation alone (Szlachta & Adamski 2009). Nevertheless, for dosage below 10 mg PAC/L, the performance may be limited considering the operating costs (Carrière *et al.* 2009). To increase performance, a high concentration recirculating PAC contactor has been developed and is commercialized as the Actiflo[®] Carb process. The PAC concentration in the contactor may vary from 1 to 5 g/L and recirculating the PAC increases its residence time, a benefit which translates into lower operating costs.

Over the last decade, other processes such as ion exchange (IX) and nanofiltration (NF) have also emerged as viable solutions to increase the removal of DBP precursors. For example, magnetic IX resin (MIEX[®]), a strong base anion exchange resin, has been shown to improve DOC removals compared to coagulation and to significantly reduce total trihalomethane (TTHM) and five haloacetic acid (HAA5) concentrations (Molczan & Szlachta 2011). The DOC removal efficiency of such resins depends on the IX dosage, NOM characteristics, pH, and sulfate concentrations which compete for active sites (Boyer & Singer 2005). Regarding NF, spiral-wound modules are commonly used for NOM removal. Direct spiral-wound NF assays (without pre-treatment) on nine source waters revealed that DBP precursor removal was specific to the water quality as the observed high DOC rejection was associated with highly variable permeate THM yields ($\mu\text{g THM/mg C}$) (de la Rubia *et al.* 2008). Consequently, spiral-wound NF may also be impacted by water quality as well as operating conditions.

Although, many investigations evaluated the impact of process performance and source water quality on resulting DBP concentrations, few studies systematically allowed a direct comparison of several technologies tested on various sources waters, especially while including more recent technologies such as MIEX[®], Actiflo[®] Carb, or NF. Such a comparison is of relevance for water utilities aiming to determine the most appropriate technology for DBP control while taking into account the impact of source water quality. The general objectives of this project are: (i) to evaluate the DBP precursor removal efficiency of six processes, namely alum and FS coagulation, IO_3 , recirculated PAC, magnetic IX, and NF; and (ii) to assess the impact of source water quality on process performance using six Canadian surface waters representing a broad range of characteristics.

MATERIALS AND METHODS

General experimental approach

Five treatment alternatives to alum coagulation were assessed in bench-scale experiments in a perspective to allow a direct comparison of NOM removal on different surface waters (Figure 1). The performance of alum coagulation under an optimal coagulation regime was first compared to coagulation with FS. Second, the use of magnetic IX resin (MIEX[®]) as a pre-treatment to conventional treatment was sought. Third, the implementation of IO_3 or a recirculated PAC reactor (Actiflo[®] Carb) after alum coagulation/settling was evaluated. Finally, direct filtration using spiral-wound NF270 (Dow-Filmtec[™]) was tested. Six Canadian surface waters were selected to study a wide range of water qualities. The treatment alternatives were tested in parallel on each given source water upon its reception at the laboratory.

Conventional treatment with alum or FS

Jar test experiments were performed according to the Actiflo[®] ballasted jar test procedure (defined by the supplier) which consisted of a rapid mix (2 min, 300 RPM), polymer/sand injection (2–5 min, 150 RPM), maturation (3–6 min, 150 RPM) followed by a settling period (3 min). To assess dissolved DOC as well as UVA_{254} removal, settled waters were filtered through a

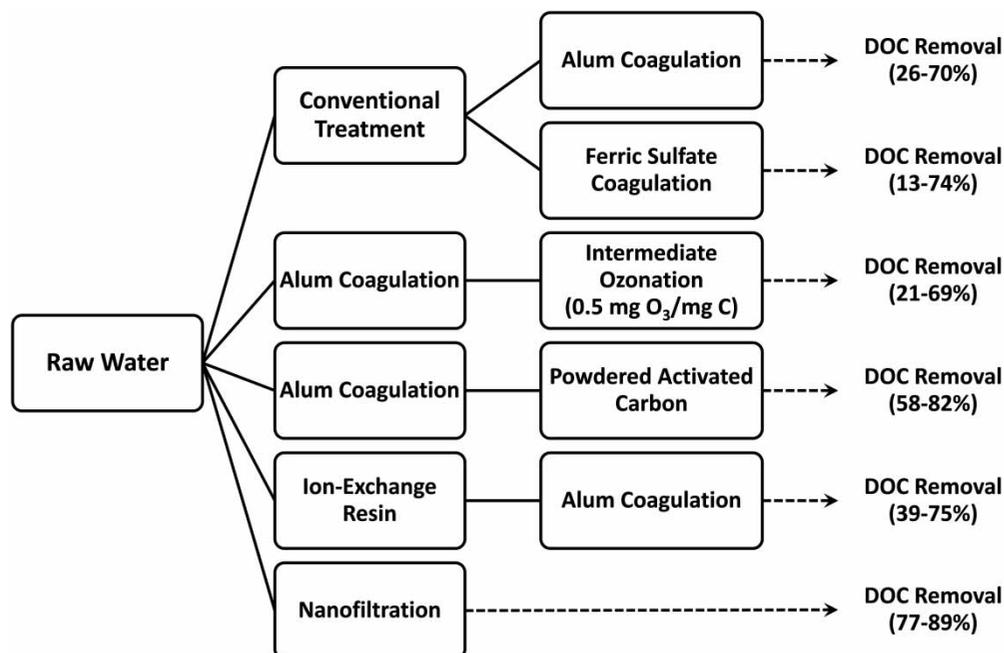


Figure 1 | Schematic diagram of treatment trains assessed in the framework of this investigation and the range of observed DOC removals expressed as a percentage.

pre-washed 0.45 μm PES Supor[®]-450 membrane (Pall). Six alum dosages were tested for each source waters without pH adjustment. Consequently, experiments were conducted under optimized coagulation conditions in contrast with enhanced coagulation (i.e., pH was not adjusted independently from alum dosage). For a given source water, the threshold value proposed by the US Environmental Protection Agency for enhanced coagulation, where a dosage increase of 10 mg dry alum/L improved TOC removal by less than 0.3 mg C/L, was retained as the optimal coagulant dose. Alternatively, the alum dose was considered as optimized if the DOC concentration of filtered effluent was less than 2 mg C/L or if its specific UV absorbance (SUVA) was less than 2.0 L/mg cm. Assays conducted with FS did not aim to find the optimal dosage. Instead, equivalent ferric dosages (in mEq/L) were derived from the optimal dosages found for alum. For example, if the optimized alum dosage is found to be 1.00 mg Al/L, then a ferric dosage of 2.07 mg Fe/L was used.

IO₃

For each investigated source waters, dosages of 0.5 and 1.0 mg O₃/mg C were applied to settled waters produced with alum as described above. Ozonation assays were

performed in Teflon-lid 1.5 L stirred batch reactors in which an ozone stock solution was injected to obtain the desired dosage. The stock solution was produced using a TG-10 ozone generator (ozone solutions) and had a concentration of 60–70 mg O₃/L to minimize dilution in the reactor. Ozone residual measurements were performed with the indigo trisulfonate method, as per Method 4500-O₃ in *Standard Methods* (APHA 1998).

Recirculated PAC

PAC experiments were conducted on settled waters. Source waters were first treated with the previously determined optimal alum dose (as described above). Subsequently, settled waters were used to conduct Actiflo[®] Carb bench-scale simulations which consisted of a rapid mix (7.25 min, 190 RPM), followed by a slow mix (5 min, 140 RPM) and a settling period (5 min). Ten percent of the previously identified optimum alum dose was also added 30 sec prior to the slow mix in order to facilitate PAC settling. Aged PAC (5 d) was added into the rapid mix at a concentration of 3 g/L to simulate the PAC recirculation. The aged PAC (Picahydro MP23, PICA) was obtained as slurry from an industrial Actiflo[®] Carb pilot unit operated

in France. The simulated operating conditions are equivalent to a dosage of 8.5 mg/L of virgin PAC.

IX

Bench-scale MIEX[®] simulations were performed on all raw waters using the multiple loading strategy, as defined by the supplier. In this method, 5 mL resin undergoes multiple treatment cycles. During each treatment cycle, 1 L raw water was mixed at 150 RPM (15 min) and then allowed to settle (30 sec). At the end of each cycle, the treated water was transferred into a collection vessel so that it contained a composite of all treatment cycles. This composite is representative of the treated water that would have been obtained at full scale. DOC removal efficiency was assessed through the use of a performance ratio (mg DOC removed/mL resin) and the highest observed ratio was selected as the optimal resin dose. Subsequently, IX treated waters were coagulated with six alum dosages as described above. The optimal alum dose was chosen according to the same criteria as previously defined for conventional treatment.

Spiral-wound NF

Direct NF assays were performed with raw water using a Sterlitech CF042 cross-flow cell in which a flat sheet NF270 (Dow-Filmtec[™]) membrane had been placed. The process was operated in recirculation at a constant pressure (30 psi), at an initial flux of 20 LMH, and the cross-flow velocity was adjusted to 0.5 m/s. Temperature was kept constant by means of a thermostatic bath. A 1.5 µm 934-AH[™] fiber glass filter (Pall) was used as pre-treatment to prevent particular fouling and to ensure that an industrial

spiral-wound NF process would necessarily include some sort of pre-filtration.

DBP formation and quantification

DBP formation and quantification was only performed with retained optimal conditions of the tested technologies according to the uniform formation conditions test (pH 8.0, residual chlorine of 1 mg Cl₂/L after an incubation at 22 °C for 24 h) to allow a comparison of various source waters (Summers *et al.* 1996).

THMs were isolated by liquid-liquid extraction as per Method 6232B (APHA 1998). HAA extraction was done according to Method 552.2 (United States Environmental Protection Agency 1995). Quantification of both TTHM and HAA5 was performed using a Varian CP-3800 gas chromatograph equipped with an electron capture detector.

Other water quality analysis

UVA₂₅₄, DOC, alkalinity, pH, and turbidity measurements were analyzed in both raw and treated waters (APHA 1998).

RESULTS AND DISCUSSION

Source water characteristics

Table 1 provides a description of the source water characteristics under investigation. DOC spanned a large range which was coherent with the large differences in concentrations of HAA and THM precursors.

Table 1 | Description of investigated source waters

Source water	DOC (mg/L)	UVA ₂₅₄ (cm ⁻¹)	SUVA (L/mg-cm)	Alkalinity (mg/L as CaCO ₃)	pH	Turbidity (NTU)	THM (µg/L)	HAA (µg/L)	THM/HAA
Mille-Iles	6.13	0.19	3.1	47	7.3	20.6	260	163	1.6
St Lawrence	2.93	0.04	1.4	83	7.9	1.0	111	33	3.4
Yamaska	8.67	0.29	3.4	85	7.7	4.1	365	186	1.9
St Maurice	5.95	0.22	3.7	6	6.5	7.5	218	278	0.8
Athabasca	13.47	0.41	3.0	93	7.9	142.7	436	665	0.7
Souris	16.40	0.42	2.6	148	8.0	8.0	513	327	1.6

Retained optimal chemical dosages

The optimal chemical dosages selected in the present study are listed in Table 2. Alum dosages varied from 0.20 to 1.66 mEq/L (20–170 mg dry alum/L). For all source waters, the lowest tested dosage of ozone (0.5 mg O₃/mg C) was always selected as doubling the ozone dose to 1.0 mg O₃/mg C only resulted in low additional UVA₂₅₄ removals (<10%). Similarly, the lowest tested dosage of IX was always selected as optimal as although increasing IX dosages increased DOC removals, on average, as much as 64% of the total performance had been achieved with the lowest dosage. Finally, alum dosage after IX pre-treatment declined on average by 33% (19–60%).

Impact of process type on treatment performance

Performance data were summarized in three figures. Figure 2 presents the calculated UVA₂₅₄ and DOC removals while Figure 3 provides the DBP-UFC and effluent DOC concentrations. Finally, Figure 4 presents DBP yield (expressed as µg THM or HAA/mg DOC) and chlorine reactivity (mg Cl₂/mg DOC). The immediate chlorine demand accounted on average for 25% of the total chlorine consumption and was subtracted from it. Lastly, when considering all source waters and each tested technology, DOC removal (expressed in %) and TTHM or HAA5 precursor removal (also expressed in %) proved to be correlated (TTHM: $r^2 = 0.51$, HAA5: $r^2 = 0.76$).

Coagulation (conventional treatment)

Conventional treatment efficiency with alum and FS proved to be highly variable. UVA₂₅₄ was removed to a greater extent than DOC (Figure 2). This trend was expected as UVA₂₅₄ is used as an indicator of the aromatic fraction of NOM which is readily removed by coagulation (Carrière *et al.* 2009). UVA₂₅₄ and DOC removals by alum ranged from 34 (St Lawrence) to 85% (Athabasca) and 26 (St Lawrence) to 70% (Athabasca), causing effluent DBP concentrations to vary from 58 (St Lawrence and St Maurice) to 203 (Souris) µg TTHM/L and from 17 (St Lawrence) to 73 (Souris) µg HAA5/L. Similarly, UVA₂₅₄ and DOC removals by FS ranged from 30% (St Lawrence) to 88% (Athabasca) and 13% (St Lawrence) to 74% (Athabasca), respectively. This led to variations in effluent DBP concentrations from 43 (Athabasca) to 158 (Souris) µg TTHM/L and from 8 (St Lawrence) to 79 (Souris) µg HAA5/L. For comparison purposes, all DOC removals obtained, with the exception of that of FS in the case of St Lawrence River, are higher than the minimum requirements for enhanced coagulation (as a function of raw water DOC and alkalinity). When considering all source waters, no significant differences in DOC and UVA₂₅₄ removal ($p \geq 0.81$) or TTHM and HAA5 concentrations (Figure 3) ($p \geq 0.23$) were observed among both coagulation strategies. However, when considering individual source waters, FS outperformed alum in terms of TTHM precursor removal in DOC-rich waters as the use of FS reduced treated water TTHMs by 29 ppb (40%) (Athabasca) and 44 ppb (22%) (Souris) compared to alum. In terms of effluent HAA5

Table 2 | Retained optimal chemical dosages used to evaluate DBP precursor removal

Source waters	Alum (mEq/L)	FS ^a (mEq/L)	Ozone (mg O ₃ /mg C)	Recirculated PAC ^b (mg/L)	IX ^c (mL/L)	Alum after IX (mEq/L)
Mille-Iles	0.54	0.54	0.5	8.5	0.5	0.39
St Lawrence	0.20	0.20	0.5	8.5	0.5	0.08
Yamaska	0.64	0.64	0.5	8.5	0.5	0.39
St Maurice	0.39	0.39	0.5	8.5	0.5	0.29
Athabasca	1.57	1.57	0.5	8.5	0.5	1.27
Souris	1.66	1.66	0.5	8.5	0.5	1.18

^aFS, ferric sulfate.

^bRecirculated PAC, powdered-activated carbon: equivalent carbon dosage.

^cIX, ion exchange resin.

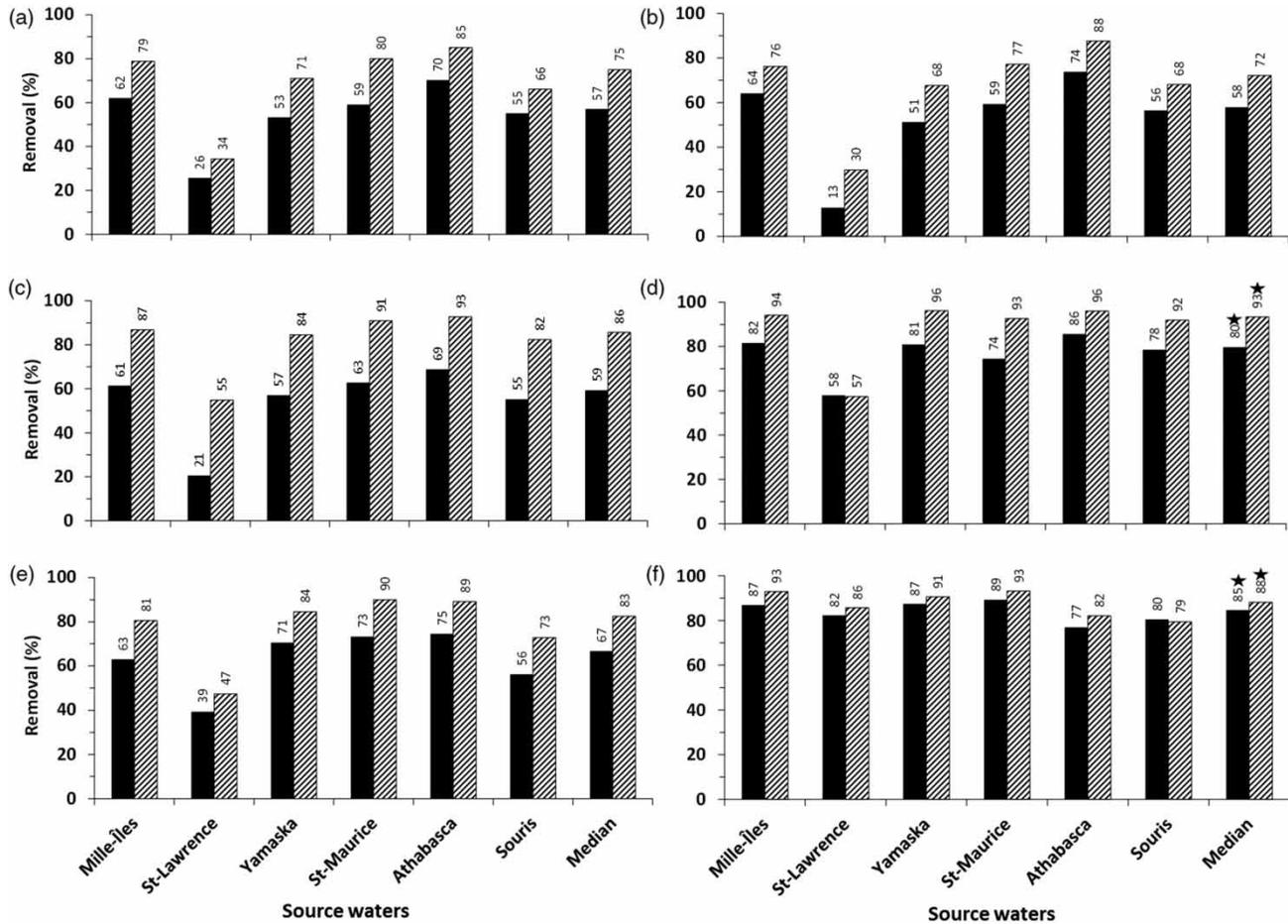


Figure 2 | DOC (solid bars) and UVA₂₅₄ (striped bars) removals for alum coagulation (a), FS (b), IO₃ (c), PAC (d), IX (e), and NF (f). Statistically improved removals in comparison with alum according to results of a Mann-Whitney test ($p < 0.05$) are designated with a star over the bars representing the median values ($n = 6$).

concentrations, the difference between alum and FS was always less than 18 ppb. Similarly, the difference in DOC and UVA₂₅₄ removals between alum and FS was always lower than 10% with the exception of the Athabasca River, where FS resulted in a DOC removal slightly higher (13%) than the one obtained with alum. It must be stressed, that both coagulation strategies led to DOC concentrations higher than 2 mg/L (which is the threshold concentration suggested by the US Environmental Protection Agency to ensure stage 1 regulatory compliance in terms of DBPs) for all source waters (Figure 3); although some DOC concentrations barely exceeded this threshold concentration, such as the Mille-Îles (alum: 2.33 mg C/L, FS: 2.20 mg C/L), St Lawrence (alum: 2.18 mg C/L, FS: 2.58 mg C/L) and St Maurice (alum: 2.44 mg C/L, FS: 2.42 mg C/L). Conversely, the effluent DOC concentration in the case of Souris River

was, for both coagulation strategies, as high as 7 mg C/L. TTHM yield of alum treated waters (Figure 4) exceeded those of FS treated waters by 9–32%. In contrast, the impact of the coagulant type on HAA5 yield (Figure 4) proved to be site-specific. FS yielded significantly lower values than alum in the case of St Lawrence (60%) and Athabasca rivers (53%), while alum resulted in lower HAA5 yield for the Souris (12%), St Maurice (25%), and Yamaska (139%) rivers. Finally, FS yielded lower Cl₂ reactivity values (Figure 4) for all tested source waters (4–91% lower) except for the Mille-Îles River.

The consistently lower THM yield obtained with FS reveals that FS is better suited than alum for lower molecular weight material removal (1–4 kDa) (Matilainen 2007), namely for fulvic acids which are known to generate significant amounts of TTHMs (Sinsabaugh III et al. 1986). HAA5

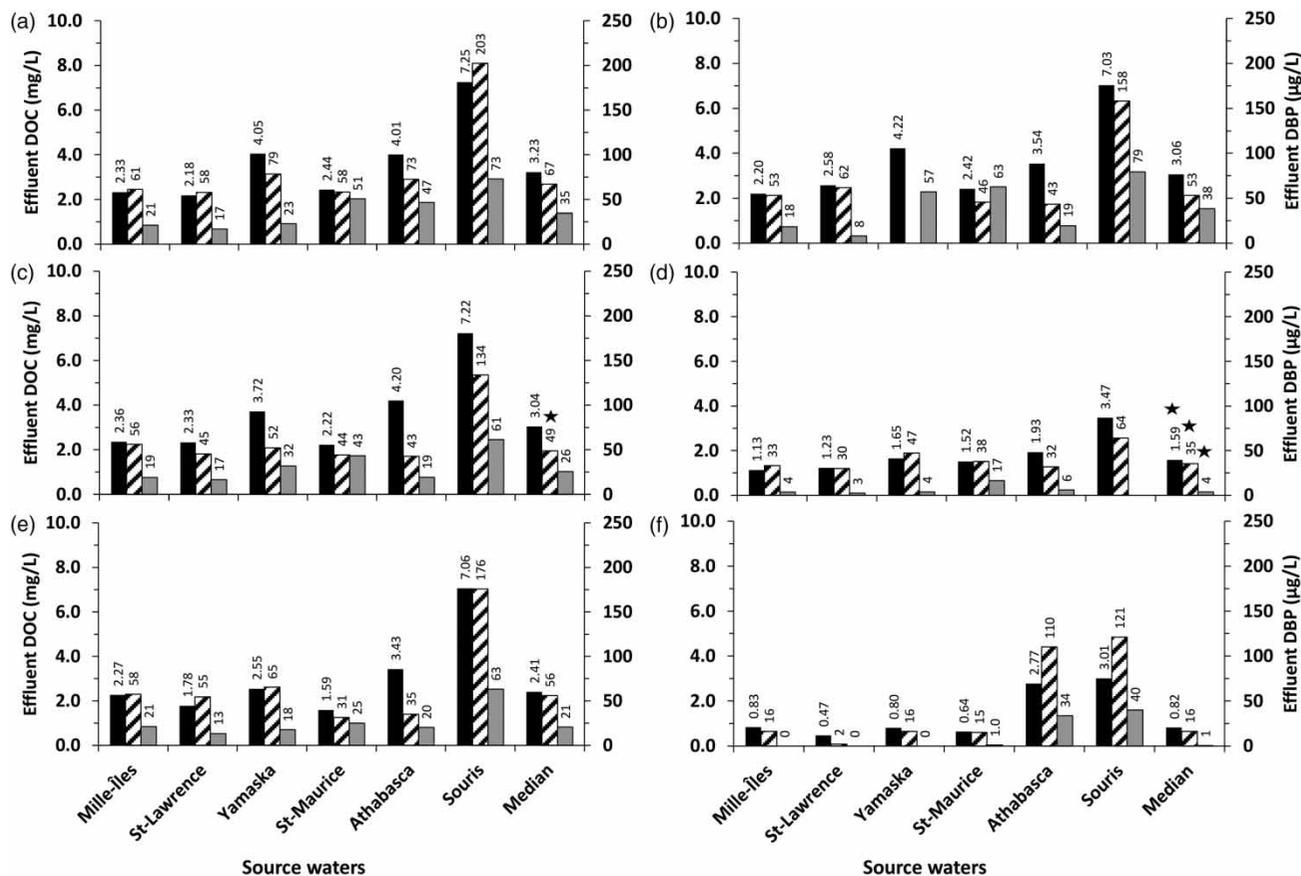


Figure 3 | Effluent DOC (solid bars), TTHM-UFC (striped bars), and HAA5-UFC (gray bars) concentrations for alum (a), FS (b), IO₃ (c), PAC (d), IX (e), and NF (f). Statistically different concentrations in comparison with alum according to results of a Mann-Whitney test ($p < 0.05$) are designated with a star over the bars representing the median values ($n = 6$).

precursor removal of most tested source waters ($n = 4$) did follow this trend, with the exception of the St Maurice and Souris rivers. Observed removal efficiencies were revealed to be highly site-specific, and thus driven by the relative abundance of the different NOM fractions. These observations are concurrent with previous studies which revealed that aluminum- and iron-based coagulants remove different types of DBP precursors (Tubic *et al.* 2013). Consequently, when using equimolar dosages under optimized coagulation conditions, observed performance variability among alum and FS cannot be assessed through bulk DOC analysis as this parameter lacks sensitivity to reflect DBP precursor removal efficiency. Hence, this study reveals that optimized coagulation may, in some cases, result in DOC concentrations close to 2 mg/L. Most importantly, this study reinforces the relevance of conducting treatability assays to accurately determine the most suitable coagulation strategy for DPB control.

IO₃

Overall, no significant differences either in terms of DOC ($p = 0.81$) or UVA₂₅₄ ($p = 0.09$) removals (Figure 2) were observed between IO₃ and conventional treatment (alum coagulation). When considering individual source waters, IO₃ (0.5 mg O₃/mg DOC) had no impact on DOC removals; whereas, it slightly improved UVA₂₅₄ removals in the case of the St Lawrence, Yamaska, St Maurice, and Souris rivers (13–21%). DBP-wise (Figure 3), the use of IO₃ proved to significantly improve the performance of conventional treatment to reduce THM concentration ($p < 0.05$). Nevertheless, this conclusion could not be extended to HAA ($p = 0.47$). While lower HAA5 concentrations were observed for most waters, IO₃ somewhat increased HAA5 concentrations when applied on the Yamaska River (9 µg/L or 40%). Increasing the ozone dose from 0.5 to 1.0 mg O₃/mg DOC did not prove to be beneficial as it offered no

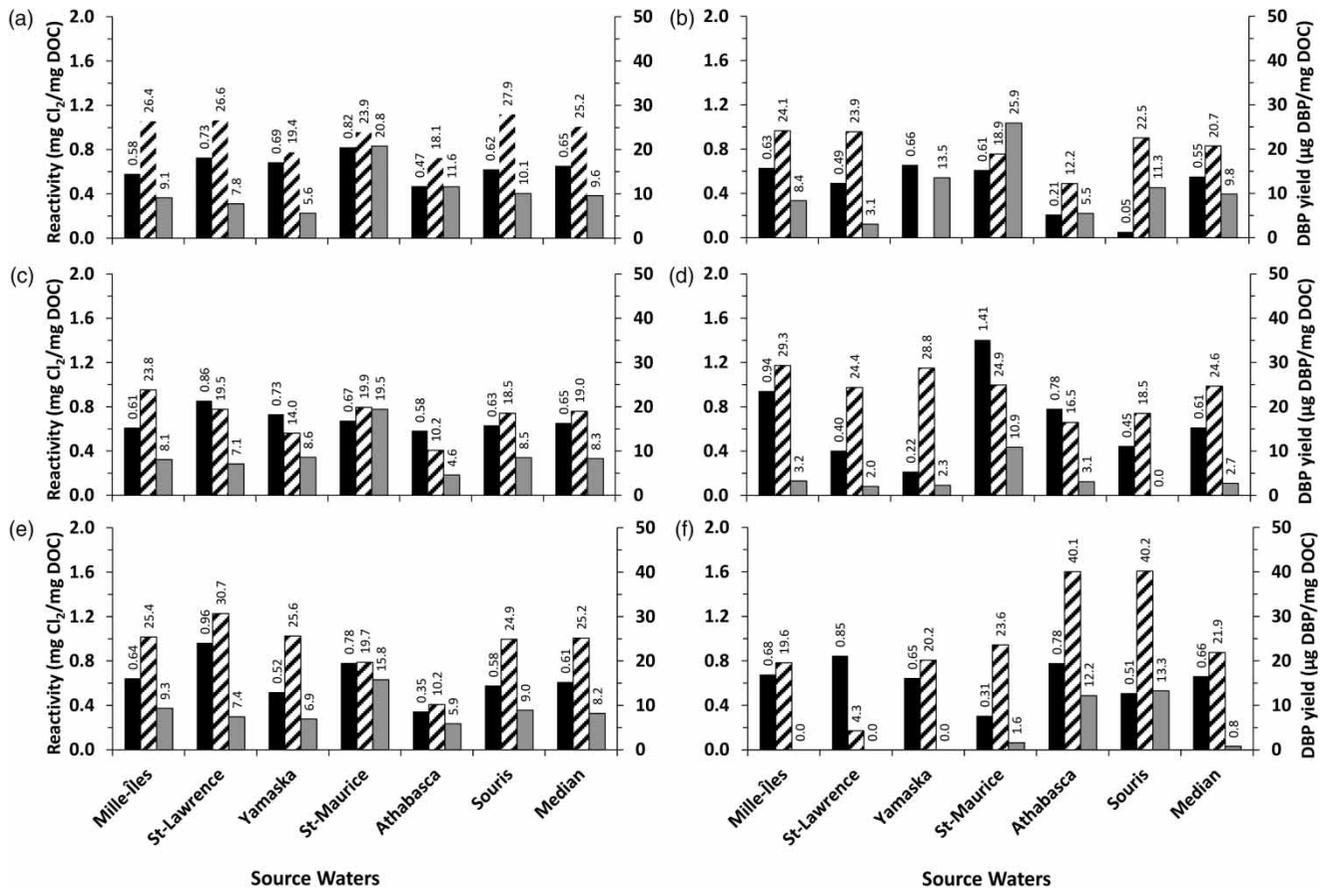


Figure 4 | Chlorine reactivity (solid bars), TTHM (striped bars), and HAAS yields (gray bars) for alum coagulation (a), FS (b), IO₃ (c), PAC (d), IX (e), and NF (f).

additional UVA₂₅₄ or DBP precursor removal (<10%) and in some cases generated greater DBP concentrations. In terms of DBP yield (Figure 4), IO₃ reduced the TTHM yield of most treated waters compared to alum (10–44%). Similarly, IO₃ reduced the HAA5 yield (6–61%) except for the Yamaska River. In contrast, the chlorine reactivity (Figure 4) was generally slightly increased by IO₃ (2–24%) except for the St Maurice River where the IO₃ reduced the chlorine reactivity by 18%. Consequently, UVA₂₅₄ reflects the DBP yield of IO₃ treated waters better than chlorine reactivity.

The low UVA₂₅₄ values obtained subsequent to IO₃ illustrate the ability of ozone to break down remaining aromatic structures and unsaturated carbon-carbon bonds of NOM in coagulated water (Singer et al. 2003). In most cases, UVA₂₅₄ values were lower than 0.035 cm⁻¹, a value that was shown to be a threshold for stage 1 DBP compliance (Edzwald & Kaminsky 2009). Hence, the efficient

cleavage of electron-rich sites may account for the observed low DBP yields. Available results indicate that IO₃ is a more robust treatment process for DBP control than conventional treatment alone as in the framework of this study lower effluent DBP concentrations were observed for almost all investigated source waters. In summary, a dose of 0.5 mg O₃/mg DOC is better suited for all investigated waters, from both DBP control and economic standpoints. Finally, one must keep in mind that superior DOC and UVA₂₅₄ removals by IO₃ could be achieved if this process was followed by biological filtration. This would result in lower DBP concentrations and in more biologically stable waters (Singer et al. 2003).

PAC

Adding a recirculated PAC process to a conventional treatment largely improved NOM removal (Figure 2) and DBP

control (Figure 3). In contrast with alum coagulation, additional DOC removals (15–33%) along with statistically lower DBP concentrations ($p < 0.05$) were obtained while using a PAC age of 5 days (equivalent to a PAC consumption of 8.5 mg/L). In fact, the recirculated PAC process is the only technology that offered DOC concentrations below 2 mg/L for all tested waters (except the Souris River), thereby facilitating regulatory compliance in terms of TTHM and HAA5. However, the resulting PAC treated water DBP yield (Figure 4) proved to be highly site-specific. TTHM yield was found to be less than alum treated water in the case of the St Lawrence (8%), Athabasca (9%), and Souris rivers (34%), while it proved to be higher in the case of the Yamaska (48%) Mille-Iles (11%), and St Maurice (4%) rivers. HAA5 yield was found to be less than alum for all investigated source waters (48–100%). Finally, treated waters from the Yamaska, St Lawrence and Souris rivers showed lower chlorine reactivity (Figure 4) than their alum treated counterparts (Yamaska: 69%, St Lawrence: 44%, Souris: 28%) while higher Cl_2 reactivity was observed in the case of the Mille-Iles (62%) Athabasca (67%), and the St Maurice (71%).

These results suggest that coagulation and PAC adsorption are complementary in terms of NOM fractions removal. Coagulation tends to preferentially remove high-molecular-weight NOM (HMW-NOM), whereas PAC is better suited for the removal of low-molecular-weight NOM (LMW-NOM) (Szlachta & Adamski 2009). LMW-NOM was found to be removed by PAC in the early stages of adsorption (<30 min), while HMW-NOM is removed at a substantially lower rate because of slower diffusion through carbon pores (Najm *et al.* 1998). As a contact time of 12.25 min was used in this study on pre-coagulated water, it is likely that the gains in NOM removal are mostly due to relatively hydrophobic LMW-NOM adsorption onto PAC. The refractory LMW-NOM has been shown to mainly consist of polar, hydrophilic molecules and may still react with chlorine as increased reactivity was reported in some cases in this study, as well as in the literature (Krasner & Scilimenti 2001). Further research is needed to best characterize recalcitrant LMW-NOM and to fully understand the cause of its increased reactivity. Adsorption onto PAC by means of the conditions retained in this study is therefore robust enough to provide, for

most waters, the DOC concentrations required to meet DBP regulatory compliance. Nevertheless, the removal efficiency of DBP precursors of this process may be partially explained by the low PAC age. More research is needed to better determine the relation among PAC age and DBP precursor removal in order to optimize treatment efficiency and minimize operating costs.

IX resin

IX prior to coagulation (0.5 mL/L) induced a 20–60% reduction in the required alum dose (Table 2). When considering all source waters the additional gains in DOC and DBP precursor removals achieved by IX + alum treatment (Figure 2) did not prove to be statistically significant ($p > 0.05$) compared to alum alone. Despite the low gains in NOM removals in comparison with alum, TTHM and HAA5 reductions (Figure 3) were found to be higher in several cases. Specifically, IX/alum treated waters from St Maurice and Athabasca rivers showed higher TTHM precursor removals than their conventionally treated counterparts, which resulted in a reduction of 27 ppb (46%) TTHM for St Maurice River and of 38 ppb (52%) TTHM for Athabasca River. Compared to alum, additional HAA5 precursor removals were obtained in the case of the Yamaska (reduction of 31 ppb or 60%), St Maurice (reduction of 26 ppb or 51%), and Athabasca rivers (reduction of 11 ppb or 46%). IX treated water DBP yield (Figure 4) proved to be highly variable. Adding an IX pre-treatment to alum coagulation resulted in a reduction of the TTHM yield in the case of St Maurice (18%) and Athabasca (44%), while the St Lawrence and Yamaska rivers yielded higher values (15% and 32%, respectively). HAA5 yield proved to be less than conventional treatment in the case of the St Maurice (24%) and Athabasca (49%), it proved to be similar for the St Lawrence, Mille-Iles, and Souris rivers and proved to be superior to the alum treated counterpart for the Yamaska River (23%). Lastly, IX reduced the Cl_2 reactivity (Figure 4) in comparison with alum for the Athabasca (26%) and Yamaska (24%) rivers, had little impact on the St Maurice (5%) and Souris (7%) and increased Cl_2 reactivity of the St Lawrence (33%) and Mille-Iles (11%) rivers.

The fact that superior DOC removals were obtained with substantially lower alum dosages is in agreement with

previous studies that demonstrated that coagulation and IX remove different NOM fractions (Singer & Bilyk 2002). Coagulation preferentially removes more hydrophobic HMW-NOM whereas IX resins are best suited for the removal of highly charged, hydrophilic LMW-NOM (Bolto *et al.* 2002). Although, PAC and IX resins are known to remove molecules of similar weights (Humbert *et al.* 2008), in this study, PAC adsorption outperformed IX due to the fact that a relatively low resin dose was used. As both the resin dose and PAC age influence the relative efficiency of both processes, this trend is only valid for the given experimental conditions. For instance, other authors have reported that with higher resin doses (6–8 mL/L) and different PAC dosages (4–40 mg fresh PAC/L), IX showed higher DOC removals (Humbert *et al.* 2008). These inconsistencies of both IX and PAC dosages explain the conflicting trends observed among the current investigation and previously reported data as these parameters govern the DOC removal capacity of both processes. Finally, this study demonstrates that the removal efficiency of DBP precursors by IX is site-specific, and that for the given resin dose the best performances compared to alum alone were observed for sources waters exhibiting the lowest TTHM/HAA5 ratios (St Maurice: 0.8, Athabasca: 0.7). Thus, for the reasons stated above, IX performance should always be interpreted while bearing in mind that its performance is related to the alum/IX optimization strategy.

NF

Overall, NF proved to be substantially impacted by raw water DOC concentrations. Compared to conventional treatment, direct NF offered significantly greater DOC and UVA₂₅₄ removals ($p < 0.05$) (Figure 2), but offered similar filtered effluent TTHM ($p = 0.22$) and HAA5 concentrations ($p = 0.06$) (Figure 3). NF offered the highest DOC removal for all investigated source waters except the Athabasca River where it was outperformed by the recirculated PAC process. Despite the fact that NF generally offered superior NOM removal, the permeate DOC concentrations were as high as 3 mg C/L for the Athabasca and Souris rivers as opposed to less than 1 mg C/L for the other investigated source waters. Recirculated PAC outperformed NF when used on the Athabasca River (NF: 77%, PAC: 86%) and offered a

similar performance when used on the Souris River (NF: 78%, PAC: 80%). Nevertheless, NF revealed to be, along with recirculated PAC, the best treatment alternative for HAA5 precursor removal as all permeate HAA5 concentrations were relatively low ($\leq 40 \mu\text{g/L}$ or below detection limit). In contrast, TTHM precursor removal proved to be site-specific. Of the tested technologies, NF offered the best TTHM precursor removal for the St Lawrence, St Maurice, Yamaska, and Mille-Iles rivers but resulted in high TTHM concentrations in the case of the Athabasca (110 $\mu\text{g/L}$) and the Souris rivers (121 $\mu\text{g/L}$). Thus, even if permeate DOC concentrations were lower than for PAC treated waters in the case of the Souris River, it did not result in lower TTHM concentrations. For instance, TTHM concentration of the Souris River water was lower when treated with PAC (64 $\mu\text{g/L}$). In addition, permeate TTHM yield of NF treated waters (Figure 4) was found to be lower than that of alum treated waters in the case of Mille-Iles (26%) and St Lawrence (84%), while higher values than alum treated waters were obtained for the Athabasca (121%) and Souris rivers (44%). Similarly, NF of the Souris River resulted in a higher HAA5 yield (32%) than conventional treatment with alum (Figure 4). In comparison with alum coagulation, direct NF of St Maurice and Yamaska waters resulted in similar TTHM and lower HAA5 yields (St Maurice: 92%, Yamaska: 100%) whereas NF of the St Lawrence and Mille-Iles rivers significantly reduced the HAA5 yield (100%). Finally, chlorine reactivity (Figure 4) proved to be decreased by NF as opposed to conventional treatment for the Yamaska (24%) and Athabasca rivers (26%), to be comparable to alum for the Souris and St Maurice, and to be increased by NF in the case of the Mille-Iles (11%) and St Lawrence rivers (33%).

The results of this work are concurrent with previous studies which reported similar DOC removals while using NF270 (68–99%) (Park *et al.* 2005; de la Rubia *et al.* 2008). Despite, the attempt to stir the boundary layer on the membrane surface by means of concentrate recirculation, concentration-polarization seems to occur to such an extent that diffusion of NOM across the membrane was amplified in the case of the Athabasca and Souris rivers (Schäfer *et al.* 2004) due to their high-NOM content. Therefore, direct NF may not be suited for such high levels of organics. The significance of this probable leakage of NOM due to extensive concentration-polarization when

treating DOC-rich waters is portrayed by the highest reactivity assessed in the framework of this study. It is hypothesized that some fulvic acids may have diffused through the membrane and therefore increased permeate reactivity. This suggests that the NOM fraction which diffused through the membrane was more reactive than the NOM residual left in alum/PAC treated waters. Nevertheless, NF used in direct filtration conditions was still the most efficient process to treat low to commonly occurring DOC concentrations (3–8 mg/L). Conversely, when used to treat DOC-rich waters (>13–15 mg/L), NF operating conditions (especially recovery rate and cross-flow velocity) may need to be revisited to minimize the impact of concentration polarization.

CONCLUSIONS

This study evaluated DBP precursors' removal efficiencies of alum and FS coagulation, IO_3 , PAC, IX, and NF, but also assessed the impact of source water quality on process performance using six source waters.

- Recirculated PAC used on pre-coagulated water was the only process to provide sufficient DBP precursor removals to meet regulatory compliance criteria for all investigated source waters.
- The use of NF under direct filtration conditions, while being the most efficient process for low to commonly encountered DOC concentrations in Canada, offered insufficient performance in DOC-rich waters (13–15 mg C/L), thereby highlighting the need to revisit operating conditions to minimize concentration polarization.
- IX and IO_3 offered DBP precursor removal to a lesser extent than NF and recirculated PAC. Increasing ozone dosage from 0.5 to 1 mg O_3 /mg DOC either resulted in similar or even greater DBP formation. The use of a low resin dosage (0.5 mL/L) resulted in a substantial reduction in coagulant dosage (20–60%).
- FS outperformed alum in terms of DBP precursor removals when used for DOC-rich waters, but was outperformed by alum when used in low-DOC waters (≈ 3 mg/L).

In conclusion, results of this investigation highlight the relevance of conducting treatability assay to determine the

best DBP control technology for a given source water quality. Further work should consider characterizing the NOM present in both source and treated waters to better understand the mechanisms involved. Such knowledge would facilitate the comparison of different technologies as well as the identification of the most suitable DBP control strategy for a given source water.

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