

Comparative efficiency of oxidation processes to remove acesulfame in water treatment plants supplied by surface water sources

Jean Sérodes^a, Antoine Grondin^b, Sabrina Simard^a, Geneviève Pelletier^b and Manuel Rodriguez^{IWA id a,*}

^a Urban & Regional Planning, Université Laval, Quebec, Canada, G1V 0A6

^b Civil and Water Engineering, Université Laval, Quebec, Canada, G1V 0A6

*Corresponding author. E-mail: manuel.rodriguez@esad.ulaval.ca

 MR, 0000-0003-2010-6438

ABSTRACT

The effects of oxidizing agents during water treatment on the concentration of an artificial sweetener were evaluated in full-scale conditions. Five drinking water treatment plants (DWTPs) located in a northern environment with high seasonal variations which use different raw water sources and different combinations of oxidants (ozone, chlorine, UV radiation) were investigated through the removal of the artificial sweetener acesulfame (ACE) along their treatment chains. In total, 98 sampling campaigns were conducted at these DWTPs. Raw water (impacted by variable tidal and hydrodynamic conditions), partially treated water within the DWTPs, and fully treated drinking water were sampled during eight months over the period of higher variability of source water quality. Results showed ACE concentrations in raw waters vary on a seasonal basis: higher in winter and summer (when rivers have low water discharges) and lower during spring and fall. Multi-barrier treatment systems under study were effective for the removal of acesulfame due specifically to the effect of ozone and chlorine during oxidation steps, while no removal was observed using physico-chemical (coagulation flocculation, filtration) and UV treatments. Depending on the number of treatment steps that involved ozonation or chlorination and the position of these oxidative processes in the treatment chain, removal of ACE varied from 24% to 90% in the plants under study. The results indicate that increasing oxidant doses would result in better removal of ACE and other contaminants, but these strategies must consider unknown transformation products, potentially with greater toxicological effects than their precursors.

Key words: acesulfame, chlorination, drinking water, removal efficiency, oxidation, ozonation

HIGHLIGHTS

- We examined the role of oxidizing agents when artificial sweeteners are present in water.
- Five drinking water systems were investigated through the removal of acesulfame (ACE).
- Removal of ACE varied significantly depending on the type and the location of the oxidative processes.
- ACE concentrations were unchanged after physico-chemical and UV treatments.
- The doses of ozone were not sufficient to entirely remove acesulfame.

1. INTRODUCTION

Artificial sweeteners are largely used in the food, beverage and pharmaceutical industries (Lange *et al.* 2012). Potassium salt acesulfame (ACE) is one of the most widely used artificial sweeteners. After ingestion by humans, ACE remains largely unchanged when excreted in urine and this compound is therefore abundant in domestic wastewaters. It is considered to be highly resistant to biodegradation in wastewater treatment plants that use activated sludge processes (Buerge *et al.* 2009; Lange *et al.* 2012). Consequently, a large portion of ACE from human consumption reaches natural waters (Van Stempvoort *et al.* 2011). Despite some evidence that ACE can be partially degraded by solar photolysis (Gan *et al.* 2014) or by advanced wastewater treatment processes (Castronovo *et al.* 2017), studies have found that partial degradation of ACE during wastewater treatment results in substantial residual concentrations (Spoelstra *et al.* 2013, 2020; Tran *et al.* 2014; Van Stempvoort *et al.* 2020).

Treated wastewaters are discharged into receiving water bodies that may supply downstream drinking water treatment plants (DWTP). In some cases, water reuse may also be carried out (Eslamian 2016). Due to their chemical stability and high levels found in the environment, ACE and other artificial sweeteners are recognized

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as potential tracers of anthropogenic inputs into natural waters (Richardson & Ternes 2005). Recent research shows ACE and sucralose to be the most chemically stable among artificial sweeteners (Scheurer *et al.* 2009). In addition, these sweeteners exhibit toxicological properties that indicate that even trace quantities ($\mu\text{g/L}$) could be harmful to humans (Weihrauch & Diehl 2004).

Compared to studies conducted on wastewaters and in natural environments, research on the presence of ACE in drinking water treatment processes and in potable water has been very limited (Buerge *et al.* 2009; Scheurer *et al.* 2010; Li *et al.* 2017; Buchner *et al.* 2019). Despite the treatments employed at DWTPs, ACE has been detected in finished drinking water in two studies conducted in Switzerland and Germany (Buerge *et al.* 2009; Scheurer *et al.* 2010). However, the effect on ACE efficiency removal of multiple oxidants (combined or not) used in full-scale DWTPs supplied by surface waters with high water quality variability in their watershed has not been investigated yet.

The aim of this study was to investigate the removal efficiencies of the artificial sweetener ACE by multi-barrier treatment plants that use diverse oxidation strategies and that are supplied by surface waters highly impacted by seasonal variations. For this purpose, ACE removal was studied in DWTPs located in a northern temperate region where seasonal variations may greatly affect the variability of source water quality and operational treatment strategies. DWTPs selected for this study are supplied by watersheds with different natural and anthropogenic characteristics, that use various types of treatment processes and apply variable oxidation and disinfection strategies (ozone, chlorine, UV radiation) at different positions along their treatment chains. Particular attention was given to factors that affect the variability of ACE levels in the source waters. The five DWTPs are all located in the vicinity of Quebec City (Canada) and their source waters originate from three different rivers (Figure 1). The research is based on a robust multiple-point sampling program that was conducted over eight months.

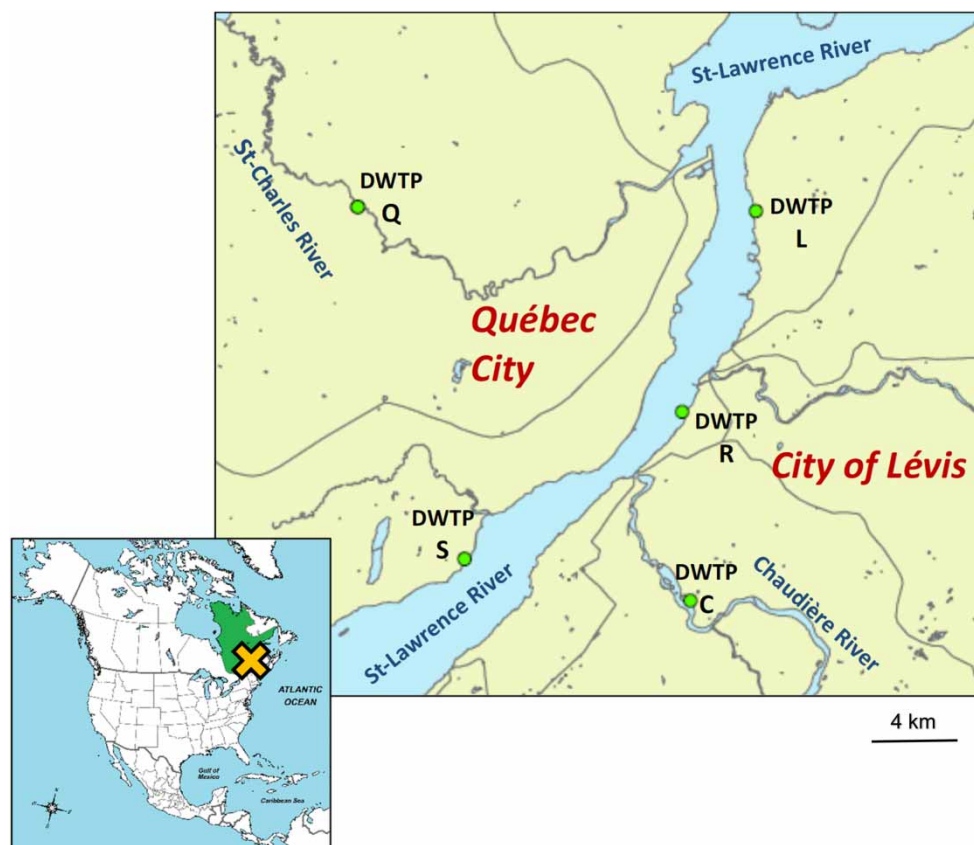


Figure 1 | Location of the DWTPs under study.

2. MATERIALS AND METHODS

The methodology to meet the study objectives was based on the following steps: (1) Selection of DWTPs with different raw water qualities and diverse treatment and oxidation processes; (2) Determination of sampling locations that represent the treatment and oxidation processes within the DWTPs; (3) Identification of representative periods for sampling to consider source water quality and flow variabilities; (4) Field sampling in raw water and the selected DWTPs; (5) Validation of laboratory chemical methods and water quality analysis for each collected sample; (6) Data analysis and interpretation.

2.1. Sampling campaigns and characteristics of the drinking water treatment plants

The five DWTPs examined in this study are supplied by various surface water sources, including St. Charles Lake and River (plant Q), St. Lawrence River (plants S, L and R), and Chaudière River (plant C). Table 1 presents the sampling locations and the main quality source water parameters. It should be noted that plant S is located on the north shore of the St. Lawrence River (on the Quebec City side) while plants L and R are on the south shore (on the Lévis side) (Figure 1). These three DWTPs are located the furthest downstream of the St. Lawrence River and are in a region that is subjected to tidal fluctuations. The effects of the tides in this region are substantial, with daily current reversals at approximately every 6 hours. The water is brackish just a few kilometers downstream from these plants (30 km from plant L and 45 km from plant S).

Table 1 | Characteristics of sampling and raw water quality of the five DWTPs

DWTP	S	L	Q	C	R
Sampling points (N)	6	5	5	6	4
Samplings (N)	9 (×3 tides)	9 (×3 tides)	9	8	9 (×3 tides)
Oxidation steps (N)	3	2	2	3	1
Mean raw water conductivity (µS/cm)	183	218	170	139	220
Mean raw water turbidity (NTU)	7.6	5.4	2.0	5.2	5.4
Mean raw water COT (mg/L)	4.1	4.0	3.6	7.1	4.1

The sampling strategy (number, location, frequency) was based on the number of investigated DWTPs, the characteristics of each DWTP and the relevance of considering the various seasonal conditions of raw water quality and flow variability. The number of sampling sites varied for each DWTP, depending on the number of steps in the treatment chain. However, raw water, partially treated waters after oxidative processes, and finished drinking water were sampled in all DWTPs. Table 2 presents the treatment steps for each of the DWTPs in our study. Because the purpose of this study was to evaluate the removal of ACE at different stages of the treatment process, the focus was on ozonation and chlorination during the pre-treatment, intermediate or final treatments in the chain. Four of the five DWTPs (S, Q, L, C) use both ozonation and chlorination. Plant R uses only chlorination. Three DWTPs (L, R and C) also use UV radiation treatment. Lastly, all five DWTPs implement a final chlorination treatment. There were four sampling points in plant R, five in plants Q and L and six in plants S and C.

Table 2 | Treatment steps of the five DWTPs from entrance to exit of the water (in grey)

DWTP	Pre Oz	Coag-Floc	Sedim	Inter Oz	Inter Cl ₂	Filtr	Post Oz	UV	Final Cl ₂
S									
L									
Q									
C									
R									

Sampling was conducted eight times at plant R and nine times at plants S, L, C and Q, approximately every 4 weeks, from March to October 2019. Each sampling day, raw waters for the three DWTPs on the St. Lawrence

River (S, L, R) were sampled three times, once during high, intermediate and low tides. For logistical reasons, the sampling strategy did not consider the precise travel time of water between its entrance into the DWTP and its exit at the outlet as finished water. At each DWTP, samples were collected within approximately one hour of each other. This is a common sampling strategy that has been applied in numerous studies, such as [Kleywegt et al. \(2011\)](#), [Machado et al. \(2016\)](#) and [Campestrini & Jardim \(2017\)](#), all of which monitored the levels of contaminants in source and finished waters by collecting samples on the same day.

In total, 498 samples were gathered during the eight-month study. Samples were collected in pre-cleaned, 250-mL polypropylene containers with a Teflon lid. They were immediately acidified according to the parameter being measured: five drops of 12.5 g/L ascorbic acid for residual chlorine quenching in all bottles and 2 mL of 10% HCl in the bottle being used for ACE analysis. Samples were then filtered through 0.45- μm Digifilters (SCP Science, Montreal, Canada) to eliminate solid matter particulates and then stored in the dark at 4 °C until extraction. Additional water quality parameters, including total organic carbon (TOC), conductivity and turbidity were analyzed using standard methods ([Rice et al. 2012](#)). These parameters were only measured in raw water.

2.2. Analysis of acesulfame by liquid chromatography (UPLC-MS/MS)

The analytical method was developed by our research team ([Grondin 2020](#)) based on the procedures proposed by [Roberts et al. \(2011\)](#) and [Tran et al. \(2013\)](#). Aliquots of acidified samples (8 mL) were transferred into 10-mL amber vials and spiked with 80 μL of deuterated ACE-D4 internal standard solution, at a concentration of 20 $\mu\text{g/L}$ (TRC, # AM135202). Solid phase extraction was then performed using 10-mg HLB micro-cartridges (ITPS SmartSPE, # 10-WOHLB-T) on a Model 1200 RTC-PAL automated system. To analyze for acesulfame, the micro-cartridges were conditioned with 500 μL of LC-MS grade Methanol Optima (Fisher) followed by 500 μL of HCl solution at 0.08% (v/v, in Millipore C18 water, Nanopure water generated using a Millipore system with a cartridge that eliminates trace contaminants for liquid chromatography (LC-MS)). Next, the samples (3.4 mL) were loaded into the micro-cartridges and the cartridges were washed a second time with 300 μL of HCl solution at 0.08% (v/v). ACE was eluted from the micro-cartridges using 200 μL of methanol. Finally, 467 μL of Millipore C18 water was added to each eluate to obtain a final composition ratio of 70:30 (H₂O: methanol) prior to analysis. For ACE quantification, liquid chromatography tandem mass spectrometry (LC-MS/MS) analyses were performed using an UPLC system (Acquity I-Class, Waters) and a triple quadrupole mass spectrometer (Xevo-TQS, Waters) with an electrospray interface operating in negative mode. Chromatographic retention and separation were achieved using a Waters CORTECS-T3 column (100 mm \times 2.1 mm \times 1.6 μm) with 0.2% (v/v) acetic acid solution (mobile phase A) and 0.2% (v/v) acetic acid in LC-MS grade acetonitrile (mobile phase B) as eluents. The flow rate was set at 0.455 mL/min., with a column temperature of 40 °C. The injected sample volume was 20 μL . The transition masses for ACE were 161.95 Da >78.00 Da, with a cone voltage of 26 V and a collision energy of 22 V, and 161.95 Da >82.1 Da, with a voltage of cone of 26 V and a collision energy of 13 V. For the ACE d4, the transition masses were 165.95 Da >78.00 Da, with a cone voltage of 26 V and a collision energy of 22 V, and 165.95 Da >86.10 Da, with a cone voltage of 26 V and a collision energy of 13 V. The MDL and MQL were 0.003 $\mu\text{g/L}$ and 0.008 $\mu\text{g/L}$, respectively. The recovery rate for ACE was 95%. The uncertainty associated with ACE concentration measurements was $\pm 17\%$.

3. RESULTS AND DISCUSSION

3.1. Temporal variations of ACE concentrations in raw waters

[Figure 2](#) presents the patterns of ACE concentrations during the study period (March to October 2019) for plants S and L, which get their raw water from the St. Lawrence River (ACE concentrations for plant R are not shown because they are similar to plant L). As is typical for the climate in this northern region, in late March, the high water levels seen in spring have not yet occurred and the river flow is near its mean annual value (9,000 m³/s) (www.cehq.gouv.qc.ca). During this period, ACE presented values near 150 ng/L. The following period in April and May was characterized by intense snow thaw with peak river flow (around 12,500 m³/s) and ACE concentrations dropped to their lowest values, below 100 ng/L. From that period to the end of summer, ACE levels continued to increase until maximum values were reached, which ranged from 140 to 180 ng/L.

Despite the similar patterns observed for plants S and L, the concentrations of ACE were systematically different because their water intakes are located on opposite shores of the river ([Figure 1](#)). Plant S is located on the north shore of the St. Lawrence River, which is joined by four major tributaries approximately 100 kilometers

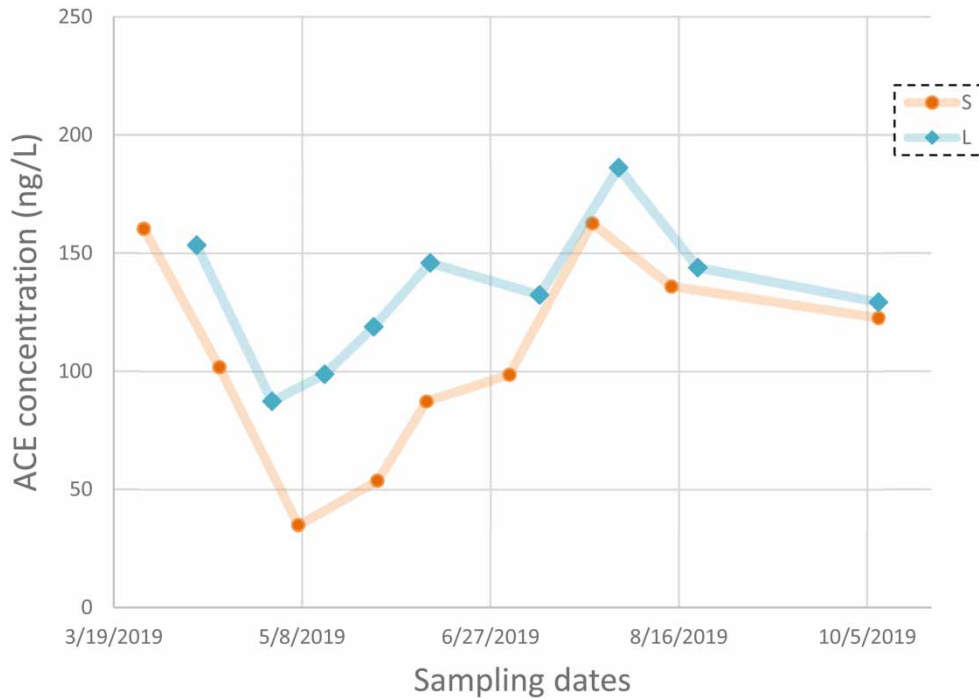


Figure 2 | ACE concentrations in raw water at plants S and L (St-Lawrence River) (Regression coefficient, R^2 , between ACE levels in raw waters of S and L was 0.52).

upstream of the water intake of this plant. These tributaries are less mineralized compared to the St. Lawrence River water. Flows from these tributaries are a fraction of that of the St. Lawrence River, they gradually mix with the St. Lawrence River over many kilometers while tending to stay along the north shore. The water intake of plant S is located along this strip of partially mixed waters, between the main water body of the St. Lawrence River and the north shore tributary waters. Consequently, the mean values of water quality parameters from plant S are different from plants L and R (Table 1). ACE concentrations of raw water entering plant S were systematically 10 to 40 ng/L lower than the concentrations of raw waters that feed plants L and R (Figure 2). Plants L and R are located near plant S, but they are on the south shore where there is no slow mixing of waters because of the absence of large tributaries upstream on that shore.

Plant C receives its water from the Chaudière River (Figure 1). This river has a much lower flow than the St. Lawrence River. The Chaudière River also has a different hydrological regime, with periods of low water in winter and summer, followed by sudden and intense high waters due to snow thaw and rain in spring and autumn. ACE concentrations in the raw water of plant C followed this pattern, with very low levels (35 to 50 ng/L) in the spring and very high levels in summer (up to 220 ng/L) and a mean value of 93 ng/L (Table 3 and Figure 3). Plant Q is located on the St. Charles River, which is very small flow-wise compared to the St. Lawrence River. However, due to the presence of a large lake a few kilometers upstream of the plant Q water intake,

Table 3 | Average dose, efficiency and removal by ozonation steps

Units		ACE in raw water ng/L	Dose Oz.1 mg/L	ACE after Oz.1 ng/L	Efficiency ng/mg	Removal by Oz.1 %	Dose Oz.2 mg/L	ACE after Oz.2 ng/L	Efficiency ng/mg	Removal by Oz.2 %	Removal by ozonation %
DWTP	S	115	0.8	85	38	26	0.77	36	66	58	69
	L	136	np	np	np	np	1.34	32	76	76	76
	Q	77	np	np	np	np	0.92	35	49	55	55
	C	93	np	np	np	np	0.90	26	46	71	71
	R	141	np	np	np	np	np	np	np	np	np

DWTP: Drinking water treatment plant; Oz.1: Pre-ozonation; DWTP C: Oxidative steps are successively inter-chlorination, then post-ozonation, then final chlorination (see Table 2); Oz.2: inter-ozonation for DWTPs L and Q, and post-ozonation for DWTPs S and C; np: not present.

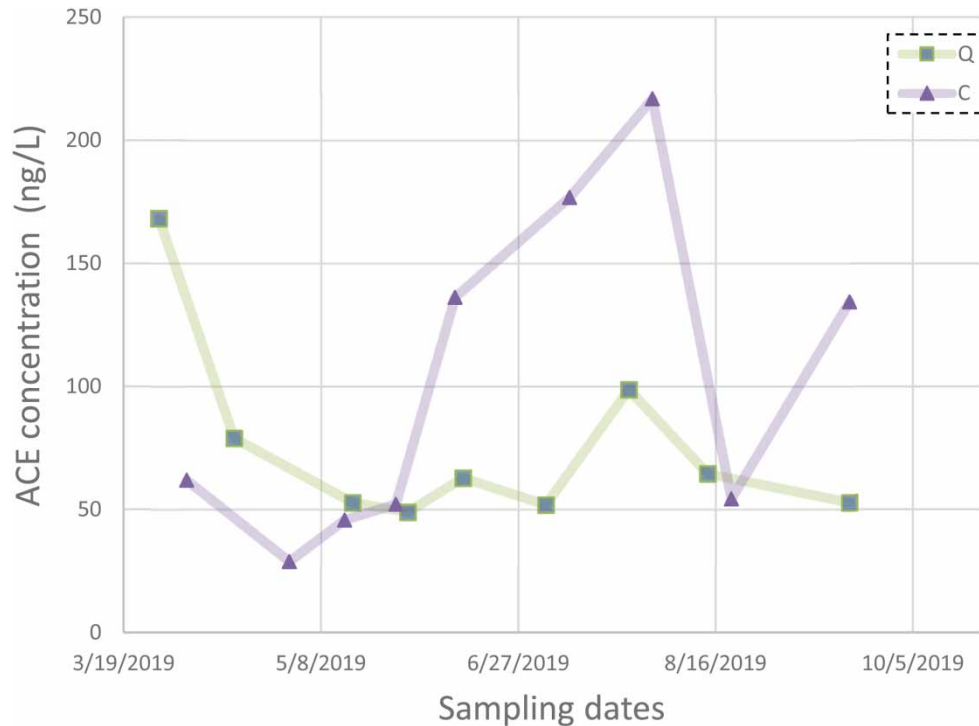


Figure 3 | ACE concentrations in raw water at plants Q and C (regression coefficient, R^2 , between ACE levels in raw waters of Q and C was 0.13).

seasonal ACE patterns for this plant were less variable than that of plant C. The location of plant Q in relation to the lake resulted in less variable water flows and thus ACE concentrations, with a mean value of 77 ng/L (Table 3 and Figure 3).

3.2. Tidal effects on ACE concentrations in the raw waters of the St. Lawrence River

Plants S, R and L are located in a region of the St. Lawrence estuary where tides are extreme, with a tidal range between 4 and 5 m. Although the position of any DWTP raw water intake is fixed, its relative position to the upper water line ‘moves’ towards the shore when the tide falls and ‘moves’ away from the shore when the tide rises. The depth of the intake under the water surface also gradually decreases over 6 hours and then increases over the following 6 hours. Consequently, the raw water quality could change on a daily basis throughout the year. In order to evaluate the influence of these continuous changes of water quality on ACE concentrations, three samples were collected on each sampling day to represent periods of low, intermediate and high tides.

For plants L and R, located on the south shore, no change in ACE concentrations between the three tidal states were observed for any given day (± 5 ng/L). For plant S, located on the north shore, tidal effects were more pronounced due to incomplete mixing between the main water in the St. Lawrence and the north shore tributary waters, as previously described. When the tide is low, more shore water enters the intake of plant S, while at high tide, more of the main water from the St. Lawrence River enters. Consequently, ACE concentrations in plant S were higher during periods of high tide (average 125 ng/L) and lower during periods of low tide (average 100 ng/L).

In summary, these results indicate that seasonal hydrological patterns in the source waters affect the average concentrations and temporal variability of ACE in the raw waters of these three DWTPs. In turn, variable ACE levels will impact the ACE removal efficiency of the various oxidation strategies used in the DWTP treatment chains.

3.3. Efficiency of ozonation for removing ACE

As summarized in Table 2, the five DWTPs in our study have different operational practices. One DWTP has two ozonation steps, three have only one ozonation step, and one plant does not use ozone. Among the four DWTPs that use ozone, plants S, Q, and L apply ozone as the first oxidant in the treatment chain, while plant C applies it

as the second oxidant, (chlorine is the first). Ozone is thus applied either in pre-, inter- or post-treatment in the treatment chains (Table 2), according to the initial design of the plant. The position at which ozone application occurs and doses applied are usually determined by plant operators and managers, based on their expertise. These decisions about ozone application strategies are based on a small number of parameters (e.g., inactivation requirements and water quality parameters such as turbidity, color, natural organic matter indicators, consumer complaints about taste) but not on trace contaminants. It is important to note that ACE is not removed during the physico-chemical steps of treatment (coagulation-flocculation, sedimentation, sand filtration, UV), but is removed only during oxidative steps (ozonation, chlorination).

All data reported in Tables 3 and 4 are the average values from the nine sampling campaigns. Efficiency is defined as the quantity of ACE (ng/L) that is eliminated by one mg/L of ozone, and therefore results are expressed as ng/mg. Removal is defined as the quantity of ACE (ng/L) that is eliminated during the ozonation step compared to the initial value measured at the beginning of this step, and is expressed as a percentage.

Table 4 | Average dose, efficiency and removal by chlorination steps

Units		Dose Cl ₂ .1	ACE after	Efficiency	Removal	Dose	ACE after	Efficiency	Removal	Removal by	TOTAL
		mg/L	Cl ₂ .1		ng/L	ng/mg	%		final Cl ₂	final Cl ₂	ng/mg
DWTP	S	np	np	np	np	1.05	12	23	67	67	90
	L	np	np	np	np	1.20	21	10	34	34	85
	Q	np	np	np	np	1.65	23	7	34	34	70
	C	na	88	na	5	na	26	na	0	0	72
	R	np	np	np	np	1.30	107	26	24	24	24

DWTP: Drinking water treatment plant; Cl₂.1: pre-chlorination; DWTP C: oxidative steps are successively inter-chlorination, then post-ozonation, then final chlorination; np: not present; na: data not available.

Plant S applies two ozonation steps in pre- and post-treatment. The pre-ozonation step occurs at the beginning of the treatment chain before the coagulation-flocculation step. Post-ozonation is applied to clear water, just after filtration through sand filters. Mean values for ACE removal were 26 and 58% for the first and second ozonation treatments respectively, with a mean total of 69% (Tables 2 and 3). Considering that the means of the applied doses are quite similar for the two steps (0.80 mg/L first ozonation and 0.77 mg/L second), ozonation is much more efficient in clear water than in raw water. This is because there is less competition between ACE and other organic substances where suspended solids and some humic matter have already been removed. However, in general for plant S, ACE removal efficiency using ozone (66 ng/mg) was within the average range for DWTPs that use just one ozonation step (from 46 to 76 ng ACE/mg O₃).

Plants L and Q apply only one ozonation step (Tables 2 and 3). In both plants, this step occurs after sedimentation and before filtration. At the point of ozonation, mean ozone doses and ACE concentrations for these two plants were very different. For plant L, the mean ozone dose and ACE concentration were 1.34 mg/L and 136 ng/L, respectively, while at plant Q, they were 0.92 mg/L and 77 ng/L, respectively. Mean ACE removals were 76% for plant L and 55% for plant Q. Removal efficiencies also differed: 76 ng/mg at plant L compared to 49 ng/mg at plant Q. Raw water of the St. Lawrence River (plant L) contains higher concentrations of ACE (Table 3) and is generally considered more polluted than the St. Charles River (plant Q). These general conditions explain the application of a higher dose of ozone at plant L, which then generates a higher ACE removal efficiency compared to plant Q. Plant Q, which had a mean initial concentration of ACE of 77 ng/L, would have required a higher ozone dose (about 1 to 1.1 mg/L) to achieve the removal efficiency of plant L, because the source waters for these two plants are very different (Table 1).

Finally, plant C employs a totally different ozonation strategy compared to the other plants that use ozone (Tables 2 and 3). Ozone in this plant is applied to filtered water, but is preceded by a chlorination step, which is not the case for plants S, L and Q. This ozonation strategy resulted in an ACE removal of 71%. However, the three oxidation steps (two chlorination steps plus ozonation) together presented a global removal of only 72% because of the low removals of the two chlorination steps (5 and 0%, respectively). On the other hand,

plants L and Q apply only one chlorination step at the end of the treatment chain and achieved 70 and 85% total ACE removal (Table 3). Unfortunately, because the chlorine dosages applied at plant C were not available, it was not possible to compare them with the dosages at plants L and Q.

As indicated in Table 3, the four DWTPs that use ozone had mean total doses of ozone that varied from 0.8 to 1.34 mg/L. Differences in DWTP design, together with the different ozone demands (not measured in the study), led to ACE removal efficiencies by ozone that varied from 46 to 76 ng ACE/mg O₃. Although it is difficult to conclude which strategy of ozonation is the best, it is evident that higher doses of ozone (plants S and L) result in higher efficiencies: 66 and 76 ng/mg for plants S and L, respectively. Nevertheless, due to the substantial difference between efficiencies of these two plants, we can conclude that it is better to apply a high dose of ozone as the first oxidative step, later in the treatment chain. Plants Q and C apply low doses of ozone (0.90–0.92 mg/L, respectively), which results in lower efficiencies: 49 and 46 ng/mg for plants Q and C, respectively.

These results confirm that ozone is highly efficient at removing ACE, regardless of where it is applied along the treatment chain. Such efficiencies have already been observed both in laboratory conditions (Scheurer *et al.* 2010, 2012; Buchner *et al.* 2019) and in full-scale DWTP conditions (Scheurer *et al.* 2010). However, as demonstrated by these researchers, efficiency is linked to the generation of by-products – some of which are more toxic than the original chemical compound that is removed. For example, among the numerous possible ozonation by-products (OPs), Buchner *et al.* (2019) identified OP 170, OP 168 (names based on molar mass) and various short chain organic acids (formic, acetic, oxalic, and sulfamic acids).

3.4. Efficiency of chlorination at removing ACE

As indicated in Tables 2 and 4, the chlorination practices in plants S, L, R and Q are very similar (plant C is different). These four DWTPs apply chlorination as the final disinfection step, just before treated water leaves the plants. This practice follows the Quebec government regulations for drinking water (<https://www.environnement.gouv.qc.ca/eau/potable/brochure/parties-1-2-3.htm>), which require a minimum concentration of 0.3 mg/L of free residual chlorine in the treated water leaving the plant. At the four DWTPs, mean applied doses were similar during the study period, varying from 1.2 to 1.6 mg/L. Efficiency of the final chlorination step on ACE removal varied from 7 to 26 ng/L ACE per mg/L Cl₂ (Table 4). It is interesting to note that the highest dose of chlorine resulted in the lowest ACE removal efficiency. Trace quantities of ACE towards the end of the treatment process seem to be more difficult to remove than the initial ones.

The process used at plant C includes two chlorination steps. The first one is applied between the sedimentation and filtration steps as inter-chlorination, using a small dose of chlorine (information confirmed by the operator but not available). This inter-chlorination removed, on average, only 5 ng/L of the initial 93 ng/L (Table 4). The final chlorination that follows a highly efficient ozonation step did not remove any ACE. According to the staff at plant C, this strategy is necessary to decrease the bacterial charge, which is very important in the Chaudière River due to agricultural activities on its watershed. Nevertheless, this practice increases the risk of producing chlorinated by-products. Indeed, in a controlled laboratory study, Li *et al.* (2017) identified 10 by-products that resulted from the chlorination of ACE, including sulfamate, mono- and di-chlorinated sulfamate, and regulated THMs and HAAs.

In plant S, the ACE removal efficiency of the final chlorination step was surprisingly high (23 ng/L ACE per mg/L Cl₂) (Table 4). The final chlorination step preceded by two ozonation steps conferred the best performance for overall ACE removal (90%), from a mean concentration of 115 ng/L in raw water to 12 ng/L in finished water.

Finally, plant R is an exception among the DWTPs of the region because it does not use ozone and has only one oxidative step that uses a typical mean dose of chlorine (1.3 mg/L). Consequently, total ACE removal (24%) at this plant was lower than at the other DWTPs.

Among these five different oxidative treatment strategies, it is difficult to identify which practices are the best. However, the strategy used in plant C, with chlorine as the first oxidant, is questionable. Further research that investigates the types and amounts of by-products that are produced is necessary to differentiate between the treatment processes and removal of ACE.

3.5. Efficiency of UV at removing ACE

The role of UV treatment in DWTPs is contributing to inactivate protozoans (*Cryptosporidium* and *Giardia*) and some viruses. Three of the DWTPs (L, R, C) in our study apply UV treatment. Plants L and C applied UV just before the final chlorination step and plant R applied UV after the final chlorination step (Table 2). Mean

doses applied varied from 65 mJ/cm² at plant L to 45 mJ/cm² at plant C. These doses are above the recommended dose in Canada (40 mJ/cm²) (Health Canada 2017). Nevertheless, results show no change in ACE concentrations after UV treatment for the three DWTPs concerned.

Generally, UV light does not induce or favor the formation of by-products, except for bromate and chlorate (Wang *et al.* 2015). As for the effects of UV on ACE removal, Gan *et al.* (2014) showed that ACE could be reduced by sunlight photolysis in natural waters, but with a long period of exposure (half-life of 9 days). In laboratory-controlled conditions, Yu *et al.* (2019) found that some emerging contaminants, including ACE, are easily photodegraded with no additional oxidants, by either low-pressure or medium-pressure UV light. However, a much longer exposure time is needed than the ones found in DWTPs.

4. CONCLUSIONS

- Acesulfame (ACE) concentrations in raw waters varied on a seasonal basis: higher in winter and summer (when rivers have low water discharges) and lower during spring and fall. Plants taking their water from the St. Lawrence River, which is submitted to large-amplitude tides in this region, show acesulfame concentrations which vary rapidly over the course of a day.
- Multi-barrier treatment systems under study are globally effective for the removal of acesulfame, but only during the oxidation steps, while no removal is observed during physico-chemical (flocculation, sedimentation, filtration) and UV steps.
- Acesulfame removal by ozonation varies from 55 to 76% which corresponds to 46 to 76 mg/L ACE per mg/L O₃ applied.
- The location of the ozonation point within the treatment chain (intermediary vs final), together with the levels of applied doses, affect removal efficiencies.
- Chlorination is commonly applied at the end of the treatment chain at relatively moderate doses (1.2 to 1.6 mg/L Cl₂). Indeed, removal of ACE by chlorine is low compared to ozone, ranging from 0% to 34%, except for one plant where 67% removal was observed, likely due to the two ozonation steps that preceded chlorination.
- The cumulative removal of ACE by ozone plus chlorine varied from 24% for the plant using only a final chlorination, to 90% for the plant that applies two ozonation treatments prior to a final chlorination.
- Increasing oxidant doses in order to achieve improved removals of ACE and other contaminants may be relevant. But this may in turn raise questions about the formation of unknown transformation products, potentially with greater toxicological effects than their precursors.

Future research must consider the possible impacts of climate changes on the presence of ACE in source waters and on the oxidation processes and contaminant removal performances by DWTPs. In fact, climate changes will possibly affect the seasonal hydrological patterns of the watersheds where the DWTPs are located, and will influence water flows, pollutant transport times and contaminant dilution in surface water. In addition, the expected changes in local precipitation patterns associated with climate changes will affect the levels of pollutant discharge (including ACE) from wastewater treatment plants to receiving bodies located upstream DWTPs. Furthermore, expected increases in water temperature associated with climate changes will affect the kinetics of the oxidation processes and thus the contaminant removal performances of DWTPs.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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