

Bromate Formation Differences between Ozone Side-Stream-with-Degas and Diffuser Transfer Systems

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Abstract

The Regional Municipality of Halton serves approximately 480,000 residents with treated surface water from Lake Ontario. The Region's three water treatment plants use ozone for primary disinfection and taste and odour removal. Two plants have diffusers for ozone transfer and one has side stream injection with degas. The Burlington Water Purification Plant (BWPP) and Oakville Water Purification Plant (OWPP) have similar treatment processes other than ozone transfer. The BWPP has diffusers for ozone dissolution and the OWPP uses side-stream-with-degas. The ozone systems began operation in 2004 and 2007 at Burlington and Oakville, respectively.

Bromate is often detected at the BWPP albeit typically below the 10 µg/L regulatory limit. When bromate greater than 10 µg/L was detected the disinfection treatment target was lowered from "enhanced disinfection" to "optimized disinfection" in order to maintain compliance with both disinfection and disinfection-by-product regulations. Conversely, non-detect to minimal bromate has been produced since startup of the ozone side-stream-with-degas facility at the OWPP. It is unclear why there is a difference in bromate formation between the plants. Bench- and full-scale special studies have been conducted and more are planned to determine what might be causing the difference in bromate formation. Of special importance is the very low water temperatures (<5 °C) involved at both plants. Published research data concerning bromate formation is typically based on warmer water temperatures. An explanation of the bromate formation issues and findings from the special studies will be presented in this paper.

Key words: Ozone transfer; bromate; CT; hydroxyl radical; bromide; diffusers; side-stream injection

Background

Both Region of Halton's (Ontario, Canada) Burlington Water Purification Plant (BWPP) and Oakville Water Purification Plant (OWPP) have ozone contactors located between Actiflo sedimentation and gravity filters. Ozone system design criteria are shown in Figure 1. The BWPP has longer detention time (35.7 min design) and bubble diffusers for ozone transfer. The OWPP has 20-min detention time basins and side-stream-with-degas for ozone transfer. Both plants treat water from Lake Ontario with intakes located 15 km apart. Five year average values for selected source water quality parameters are shown in Figure 2. Most concentrations are similar in range but the OWPP intake is periodically influenced by stream runoff. Stream runoff impact is reflected in some differences such as 30-µg/L bromide at the OWPP and 38-µg/L at the BWPP. Water quality is similar most of the year when stream runoff is low.

Ozone Design Criteria			
	BWPP	OWPP	
Water Flow	300	120	MLD
Applied Ozone Dose	1.83	4.00	mg/L
Production per Generator	550	480	kg/day
No. Units Operating	1	1	#
No. Units Standby	1	1	#
Ozone Concentration	10	10	%wt
No. of Basins	4	2	#
No. Diffusers in First Cell	48	NA	#
No. of Cells	12	10	#
Total Volume Each Contactor	1.857	0.833	ML
Design HDT per Contactor	35.7	20.0	min

Parameter	Units	BWPP	OWPP
Alkalinity	mg/L	93.4	92.4
Bromide	µg/L	38	30
Colour TCU	TCU	3	2
Dissolved Organic Carbon	mg/L	1.9	2.0
Nitrate + Nitrite Nitrogen	mg/L	0.40	0.44
Nitrate Nitrogen	mg/L	0.40	0.43
Nitrite Nitrogen	mg/L	0.01	0.02
Organic Nitrogen	mg/L	0.2	0.2
pH	Units	8.16	8.08
Total Ammonia Nitrogen	mg/L	0.04	0.05
Total Dissolved Solids	mg/L	170	175
Total Hardness	mg/L	124	125
Total Kjeldahl Nitrogen	mg/L	0.3	0.3
Turbidity	NTU	1.53	1.551

Figure 1 Ozone design criteria

Figure 2 Source water quality – 5-yr average

Full-Scale Bromate Operating Data

Selected operating data were evaluated for years 2008 thru 2011 particularly in regard to those that potentially might impact bromate formation. Figure 3 displays trends in raw water bromide and treated water bromate concentration obtained from monthly regulatory reports. Tests were conducted by a private laboratory. Minimum detection limit for the test procedure is 3 µg/L. Results reported for data “< 3 µg/L” are displayed as 1.5 µg/L on the charts, with consideration that actual values range between non-detect and 3 µg/L.

Raw water bromide concentration was generally between 30 and 40 µg/L for both plants, except during stream run-off events at Oakville when concentration was 50% lower. Treated water bromate at the BWPP was often at or above the detection limit and periodically >10 µg/L. Potential operational impacts resulting in higher bromate at Burlington are discussed later in this paper. Treated water bromate at the OWPP was often below detection, sometimes at detection and never >10 µg/L. These lower bromate concentrations occurred even when raw water bromide is in similar range as Burlington.

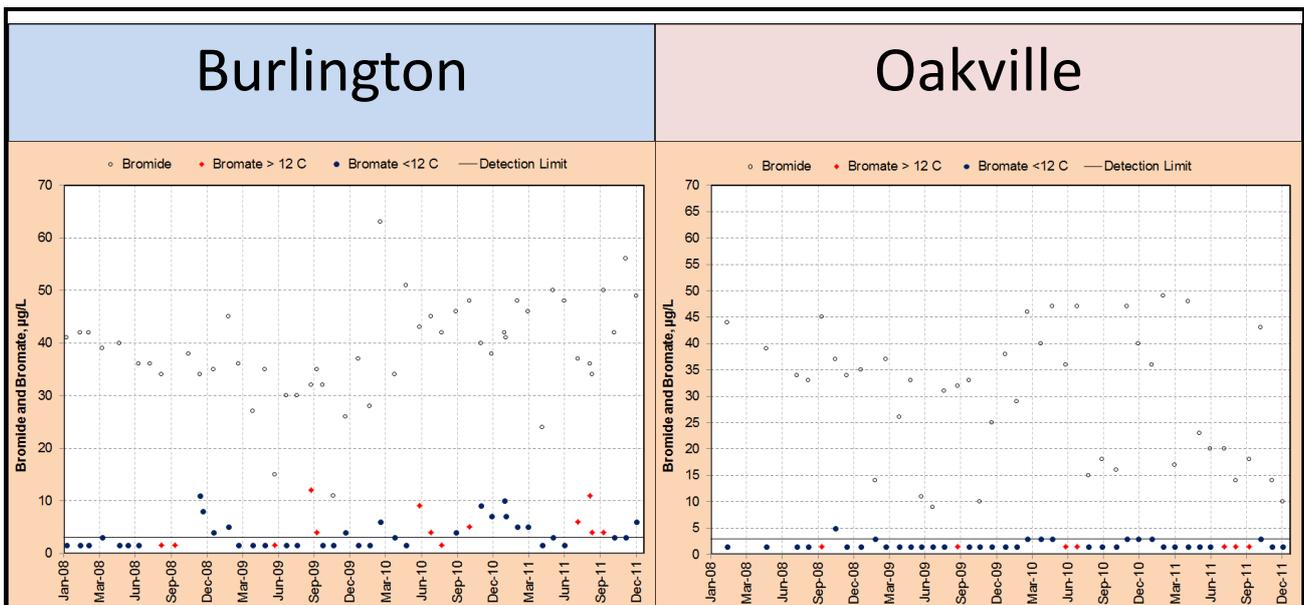
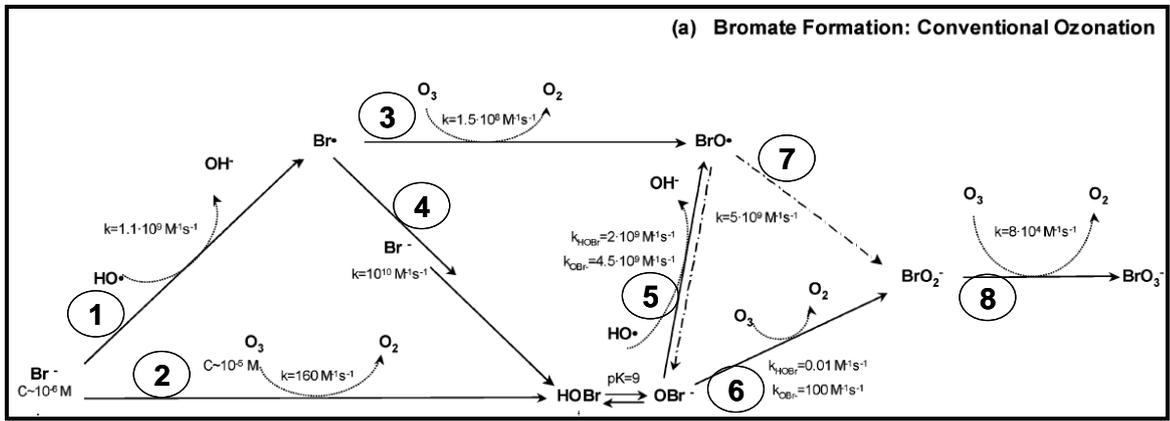


Figure 3 Raw water bromide and treated water bromate concentrations

Bromate formation occurs with ozone as a result of many reactions. A model outlining the complex pathway by ozone and hydroxyl radicals (HO*) is shown in Figure 4 (von Gunten and Hoigné, 1994 and Buffle et al. 2004). A complete description of all chemical reactions can be found in the indicated references. Reactions are numbered for reference purposes only and do not indicate priority order. Of particular note is the role of HO* in reactions 1 and 5 and ozone exposure (Ct) in reactions 2, 3, 6 and 8. It is anticipated that water-quality or operating characteristics that increase either HO* or Ct will result in an increase in bromate formation for a given concentration of influent bromide.



Numbers are for reference purposes only.

Figure 4 Bromate formation with conventional ozonation (Buffle et al., 2004)

Figure 5 displays bromate data relative to operating water temperature for both plants. Water temperature ranged between 2 and 23 °C at both plants. Temperature alone does not appear to be the sole factor in bromate formation difference between the two plants. The BWPP formed bromate at both low and high water temperature. The OWPP had limited to no bromate formation at either low or high water temperature.

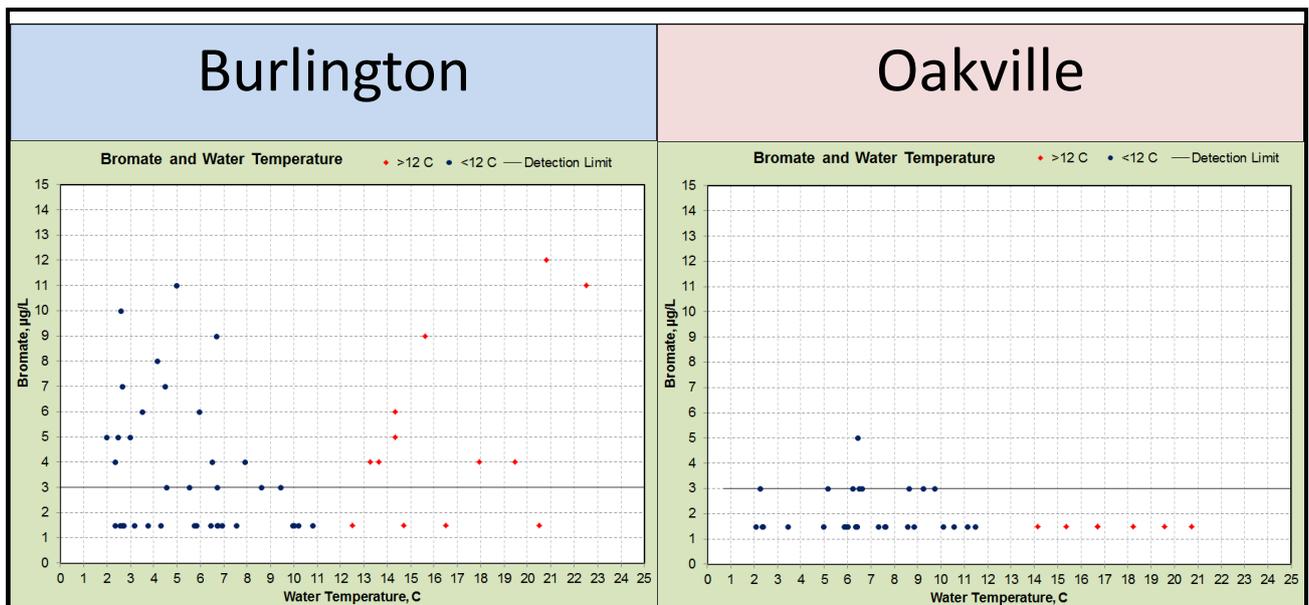


Figure 5 Water temperature effect on bromate formation

Figure 6 shows bromate data compared to applied ozone dose. At the BWPP bromate concentration is higher as ozone dose increases. The bromate concentration is near or above 10 µg/L at an ozone dose >2.0 mg/L. Between 1.5 and 2.0 mg/L applied dose at Burlington bromate concentration

ranged between non-detect and 11 µg/L. At Oakville, bromate concentration is typically non-detect and reached 5-µg/L on one occasion. The range of 1.5 to 2.0 mg/L ozone dose at Burlington likely increased both HO* and Ct, which is expected to contribute to an increase in bromate. The lack of bromate formation at Oakville for similar ozone dosages is unexplained and does not appear to be related to ozone dose alone.

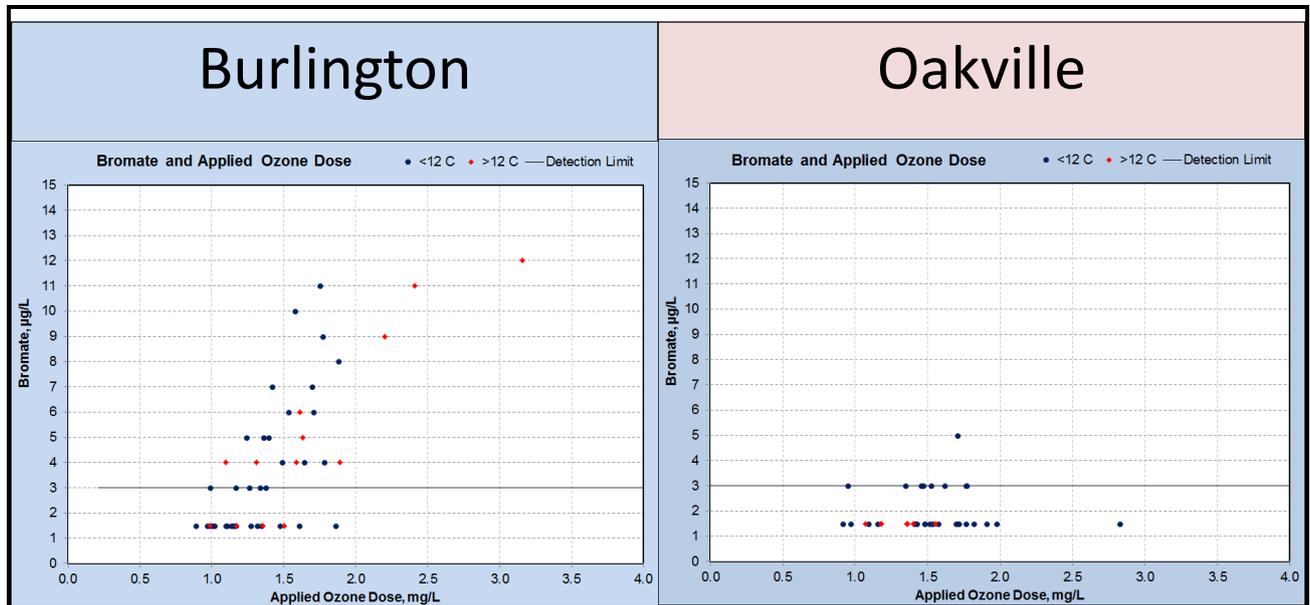


Figure 6 Applied ozone dose effect on bromate formation

Ozone dose creates ozone residual after ozone demand reactions are satisfied. Since water quality and pre-ozone treatment processes are similar at both plants, ozone demand reactions are expected to be comparable. Figure 7 shows bromate data compared to initial ozone residual, which is defined as the residual at the beginning of the disinfection “reaction zone” following ozone addition. At the BWPP bromate is formed at initial residuals ranging between 0.4 and 0.8 mg/L. At Oakville bromate is non-detect at initial residual <0.6 mg/L and either non-detect or at detection limit between 0.6 and 0.9 mg/L. One data point at Oakville reached 5-µg/L at an initial residual of 0.95 mg/L. Initial residual alone does not explain the difference between bromate formation at Burlington and lack of bromate at Oakville. However, initial residual alone also does not fully define ozone exposure, Ct, since contact time is also a component.

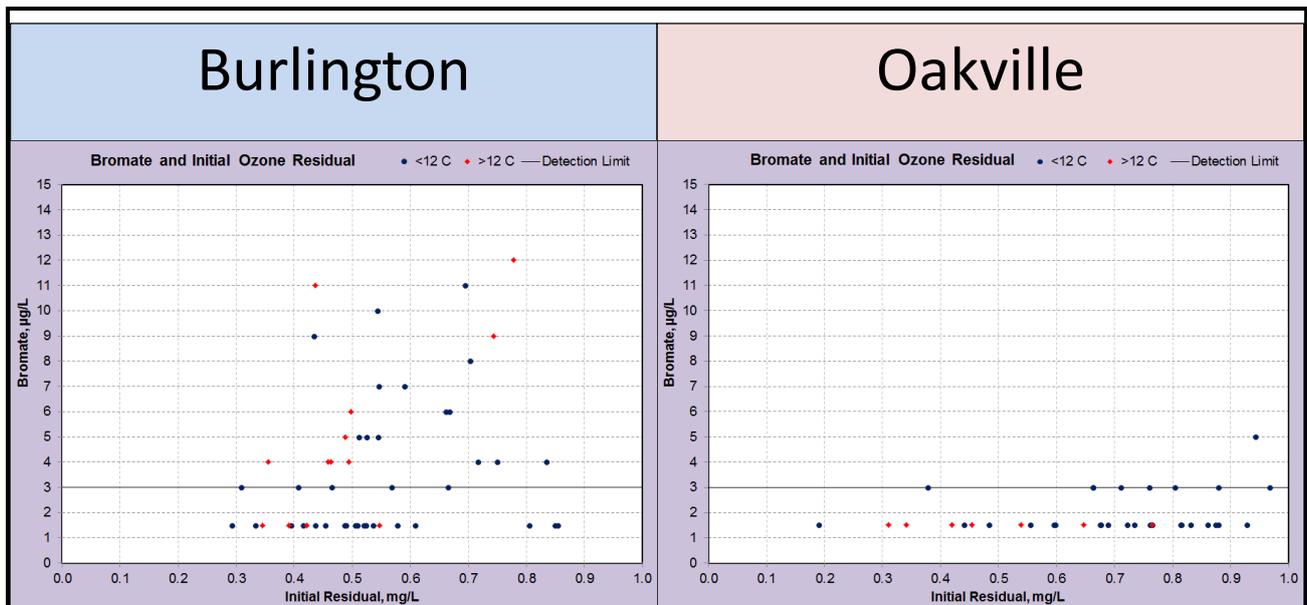


Figure 7 Initial ozone residual effect on bromate formation

It is expected that bromate formation will intensify with increased ozone exposure (Ct). An increase in bromate concentration was observed at the OWPP with bromate concentrations at or slightly above the detection limit when Ct was >13 mg-min/L, as shown in Figure 8. Bromate was formed at Burlington at similar Ct, but also was formed when Ct was much lower and between 7 and 13 mg-min/L.

What about the rate of ozone reaction? Figure 9 incorporates ozone exposure with ozone reaction due to water temperature by comparing bromate formation with Crypto log inactivation credit. Bromate concentration at Burlington was at or slightly above 10 µg/L at >2-logs Crypto inactivation with “warm” water temperature. With “cold” water temperature bromate at Burlington was also formed when Crypto log inactivation ranged between 0.7- and 1.3-log. However, bromate was not detectable or barely detectable at Oakville for similar Crypto log inactivation values. Two items are noted from these data. One is that ozone exposure (Ct) and ozone reaction (log inactivation) do not explain differences in bromate formation between Oakville and Burlington. The second is that further research is needed to confirm whether or not water temperature affects the rate of bromate formation such as noted at Burlington.

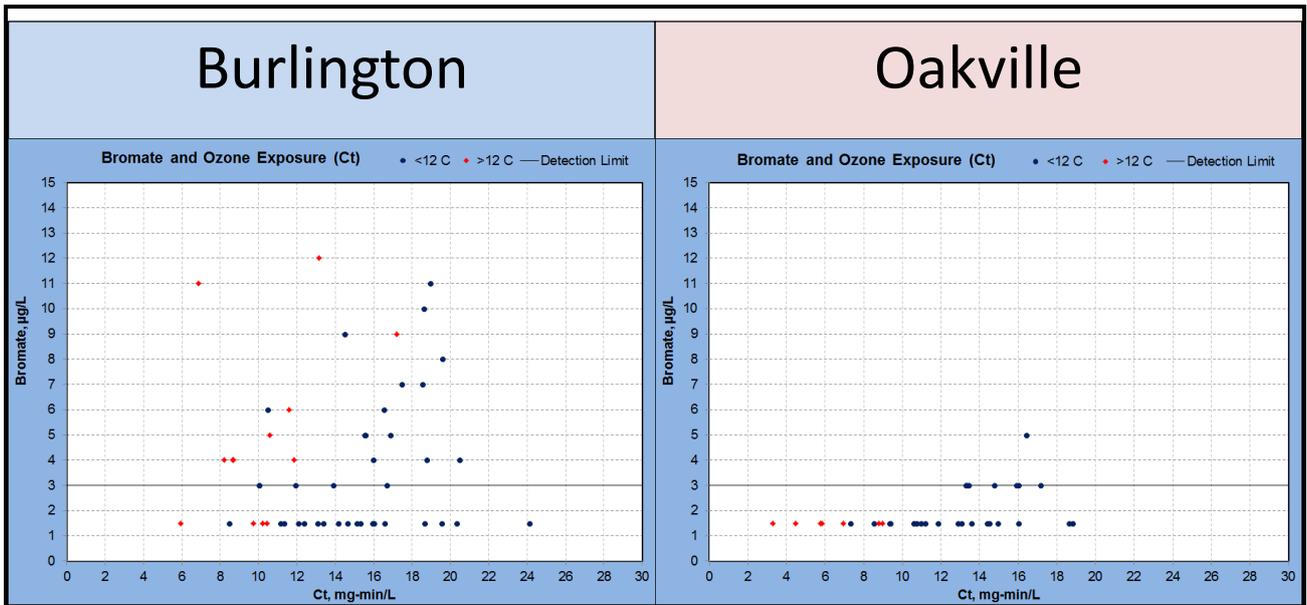


Figure 8 Ozone exposure (Ct) effect on bromate formation

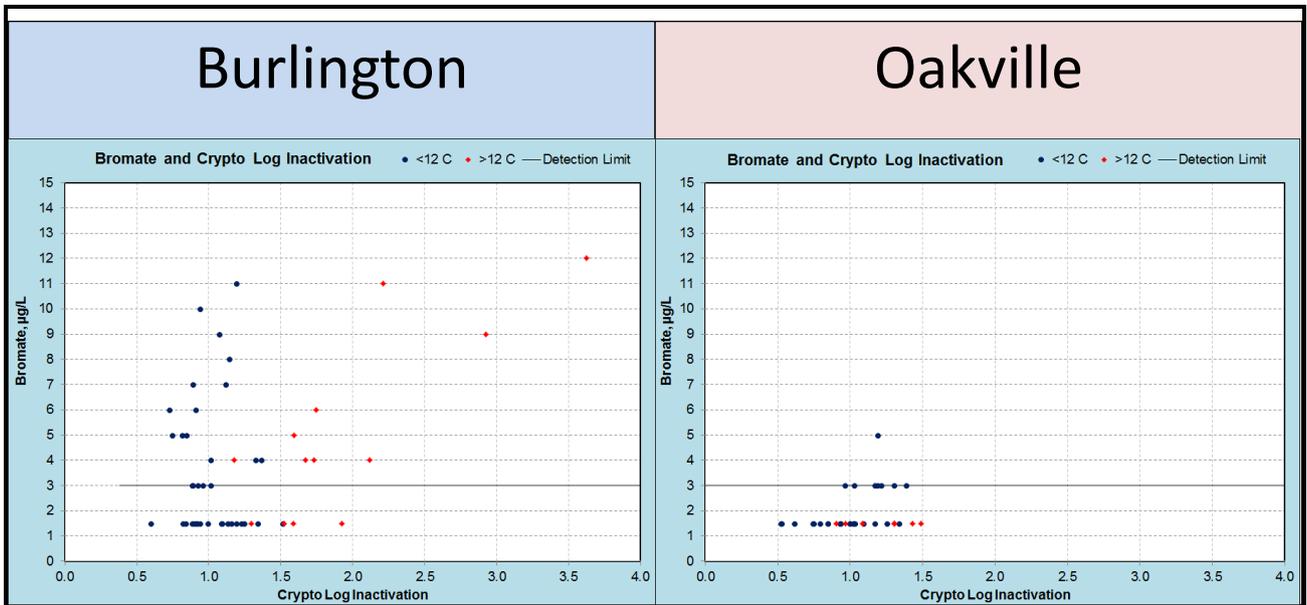


Figure 9 Crypto log inactivation (disinfection reaction) effect on bromate formation

A reaction or reactions other than ozone exposure appears to be contributing to bromate formation at Burlington. Two operating differences exist between the plants. One difference is detention time in the ozone contactor and the other is type of ozone dissolution; namely bubble diffusers and side-stream-with-degas. Figure 10 displays ozone contactor detention time compared to bromate formation. It is the case that ozone contact time has been much lower at the OWPP than at the BWPP. Contactor detention time was mostly between 15 and 40 min at Oakville and between 40 and 130 min at Burlington. Due to this difference a bench-scale study was commissioned at the University of Colorado to determine whether or not detention time was the sole factor in enhancing bromate formation at Burlington. If detention time alone was the cause then perhaps number of contactors in service could be minimized at Burlington to reduce contact time.

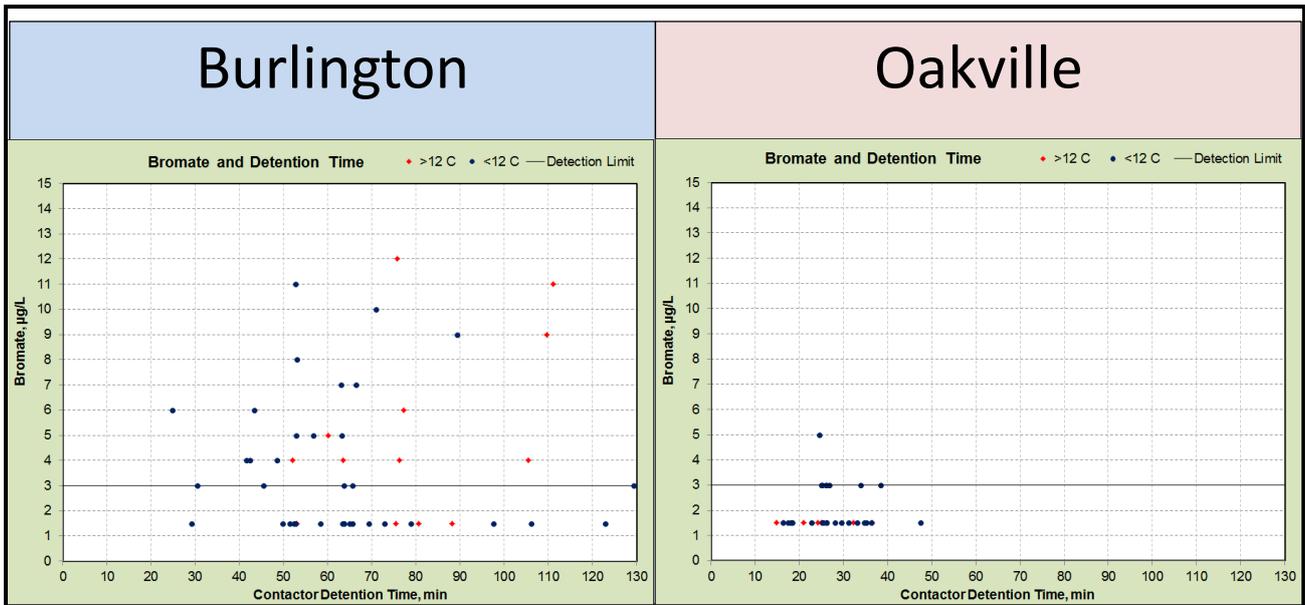


Figure 10 Ozone contact time effect on bromate formation

Bench-Scale Special Study Results

A bench-scale special-study test at the University of Colorado was conducted on Actiflo process effluent from the BWPP using a bench-scale “solution” ozone test (Rakness, 2005). Ozone gas was bubbled into distilled water stock solution until ozone residual developed to about 40 mg/L. A selected volume of stock solution was added to temperature-controlled (3, 12 and 20 °C) sample volume to achieve a target ozone dose that was projected to reach approximately 2-logs Crypto inactivation credit. Side-by-side tests were conducted at long and short contact times reflective of contactor detention times at Burlington and Oakville. The goal was to determine if bromate formation would be higher during longer contact-time operation for similar levels of disinfection. A summary of test results is shown in Figure 11. In four of the six tests Crypto log inactivation was at or slightly above 2-logs but was much lower in two tests.

Parameter and Ozone Test #	Temp (°C)	Ozone Dosage (mg/L)	HDT Actual (min)	Bromide (µg/L)	Bromate (µg/L)	Alkalinity (mg/L as CaCO ₃)	pH (units)	Ct (mg-min/L)	Crypto Log
Actiflo Effluent				41		93	7.82		
1	3	1.67	40		11			30.8	1.62
2		1.20	125		4.5			40.5	2.12
3	12	1.43	40		13			18.3	2.22
4		1.13	100		8			16.1	1.96
5	20	1.60	10		8.8			8.4	2.14
6		1.31	20		5.3			3.9	0.99

Figure 11 Summary of Bench-scale test results

Special study test results for 3 °C are shown in Figure 12. Crypto log inactivation was 2.12-log in the 125-min contact time test and 1.62-log in the 40-min test. It was expected that bromate would be greater in the 125-min test that had greater ozone exposure but the opposite was true. Bromate concentration for the 125-min test was 4.5 µg/L and 11 µg/L for the 40-min test. It is unclear why this difference occurred.

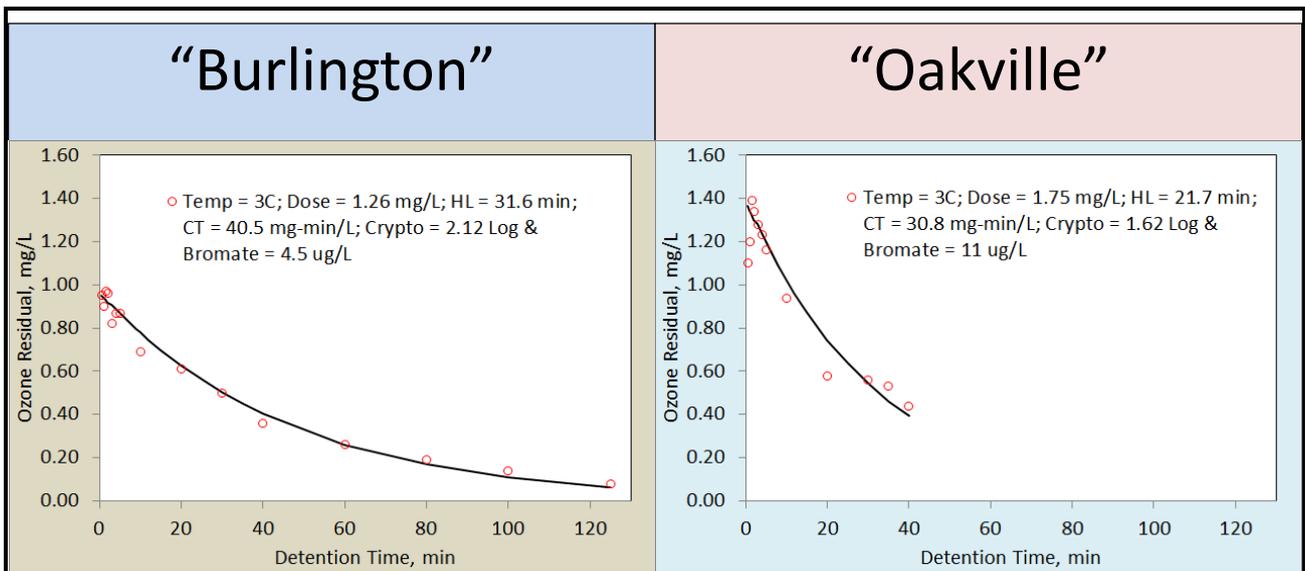


Figure 12 Bench-scale ozone contact time effect on bromate formation at 3 °C

Figure 13 displays residual profile information for the 12 °C special study test. Crypto log inactivation was similar for both detention-time tests at 1.96- and 2.22-log for the 100-min and 40-min test, respectively. Bromate concentration was 8- μ g/L in the 100-min test and 13- μ g/L for the 40-min test. Here again longer detention time did not “increase” bromate formation, which is different from the hypothesis that longer detention time might have an impact based on the full-scale operating results discussed earlier.

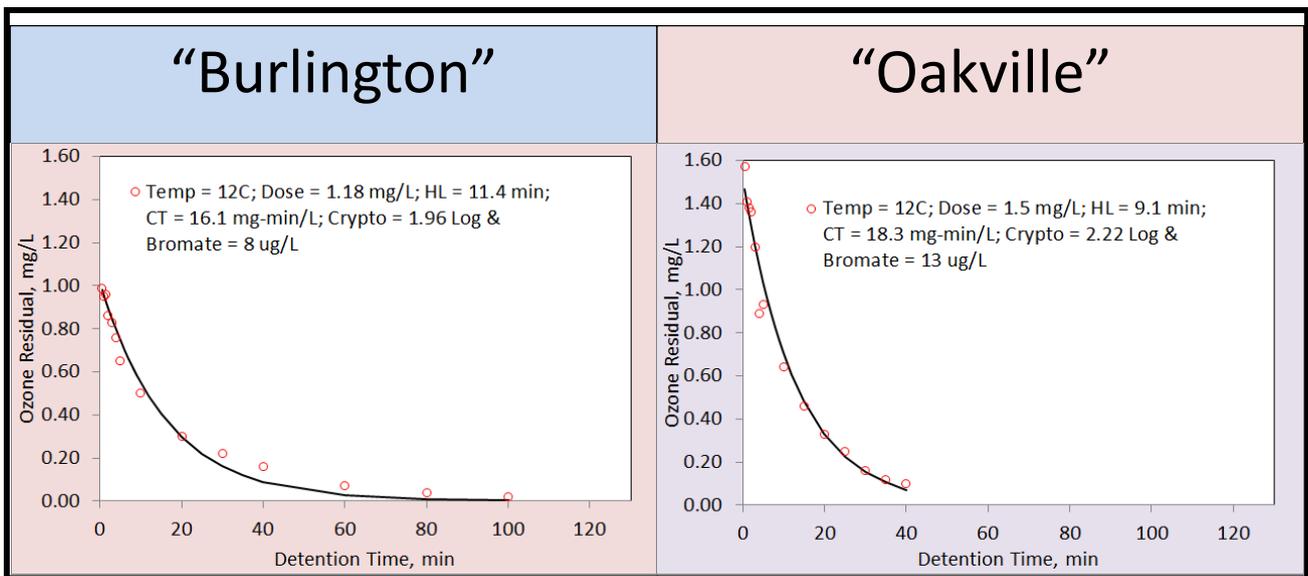


Figure 13 Bench-scale ozone contact time effect on bromate formation at 12 °C

Residual profile data for the 20 °C special study test is shown in Figure 14. Crypto log inactivation was quite a bit different at 0.99-log for the “long” 30-min detention-time tests and 2.14-log for the “short” 10-min test. Bromate concentration in this test was lower for the long-detention-time test at 5.3- μ g/L but this test also had lower Crypto log inactivation. Bromate concentration was 8.8- μ g/L in the short-detention-time test. Since these data points have large discrepancy in Crypto log inactivation it is not possible to assess effect of contactor detention time.

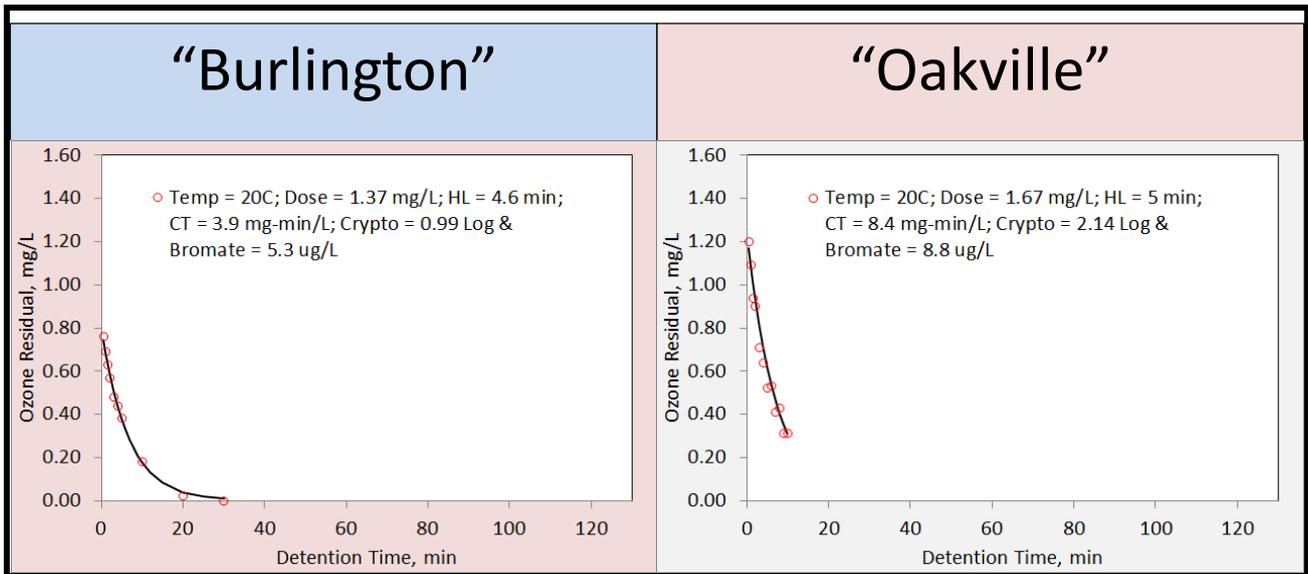


Figure 14 Bench-scale ozone contact time effect on bromate formation at 20 °C

Bromate concentration, independent of detention time, is compared with Crypto log inactivation credit in the lower chart of Figure 15. As expected, bromate generally increases with greater ozone exposure depicted by Crypto log inactivation credit. The lower bromate concentration (4.5- $\mu\text{g/L}$) at 3 °C and elevated Crypto log inactivation is unexplained. The upper chart displays bromate concentration relative to contact time. From these data points it appears that bromate formation is not affected by detention time.

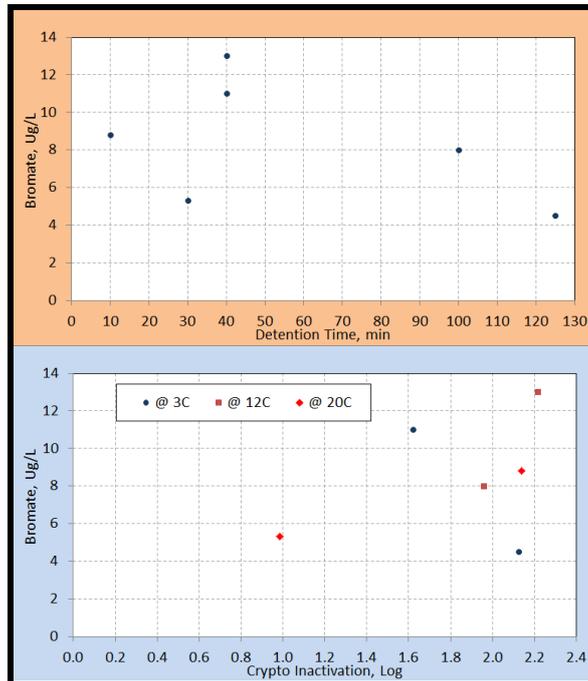


Figure 15 Bench-scale ozone bromate formation versus Crypto Log Inactivation & Detention Time

The results of the bench-scale tests were inconclusive with respect to the hypothesis that elevated bromate concentration at Burlington was due to longer detention time at that plant. Additional full-scale data were collected to further evaluate differences in bromate formation at Burlington and Oakville.

Full-Scale Special Studies

Burlington-Oakville comparative special studies were conducted on February 22 and March 2, 2012. Bromate at Burlington was 5- $\mu\text{g/L}$ on February 22 and was non-detectable at Oakville. However, operating parameters were dissimilar, such as contactor detention time, pH, and Crypto log inactivation. On March 2, 2012 contactor hydraulic detention time at both plants was similar at 25-min. Inlet bromide concentration was similar at 42- $\mu\text{g/L}$. Disinfection performance was also similar at 0.5-log Crypto inactivation. Measured bromate concentration at Burlington on March 2 was 4.5- $\mu\text{g/L}$ and was not detectable at Oakville. These data indicate that bromate is formed at Burlington and not at Oakville even when operating conditions are similar.

Summary of Test Results					
Parameter	Units	Wednesday, February 22, 2012		Friday, March 02, 2012	
		Burlington	Oakville	Burlington	Oakville
Contact Flow	MLD	58.8	57.2	83.4	57.3
Ozone Inlet	pH	8.12	7.31	8.32	7.75
Temperature	C	3.91	4.00	4.92	3.15
Ozone Dose	mg/L	1.40	0.79	0.87	1.46
Contact HDT	min	39.2	22.9	27.4	25.7
Raw Bromide	ug/L	47.6	40.2	42.4	41.6
Ozone Inlet Bromide	ug/L	46.8	46.2	42.2	44.2
Ozone Outlet Bromate	ug/L	5	<3	4.25	<3
Crypto Log Inactivation	Log I	0.63	0.28	0.53	0.48
CT value	CT	14.2	4.4	9.4	8.3

Figure 16 Full-scale ozone bromate formation at comparative detention time

Ozone residual quenching at the BWPP is implemented using sodium bisulfite; whereas calcium thiosulfate is used at the OWPP. It was considered that type of quenching agent might be causing the differences in bromate formation between the two plants. A special study was conducted on May 28, 2012 to determine if quenching agent had impact on bromate formation. The table in Figure 17 summarizes results. Bromate formation at Burlington was 3- $\mu\text{g/L}$ with both quenching agents and was non-detectable at Oakville also with both quenching agents. This test verified, as expected, that the type of quenching agent does not affect measured bromate concentration.

In addition to sampling the contactor effluent at Oakville a sample was collected directly at the effluent of the side stream degas vessel. It was anticipated that bromate might exist at this location since ozone dose and ozone residual are extremely high within the side stream pipe, albeit contact time is very short. In the side stream effluent the bromide concentration was measured at 39- $\mu\text{g/L}$ and bromate concentration was non-detectable.

Parameter	Burlington WPP	Oakville WPP	Oakville Side Stream Effluent	Units
Quenched with Sodium Bisulfite				
Bromide	24	36	39	$\mu\text{g/L}$
Bromate	3	<3	<3	$\mu\text{g/L}$
Quenched with Calcium Thiosulfate				
Bromide	31	34	39	$\mu\text{g/L}$
Bromate	3	<3	<3	$\mu\text{g/L}$

Figure 17 Full-scale ozone bromate formation at comparative quenching agents

Another special study was conducted at Oakville on July 4, 2012. In this study Crypto disinfection was 1-log inactivation credit, water temperature was 9.3 C, ozone dose was 0.97 mg/L, initial ozone residual was 0.63 mg/L, Ct value was 10.4 mg-min/L, and contactor detention time was 25.7 minutes. Bromide concentration was 29 $\mu\text{g/L}$. Bromate was measured at the contactor effluent as well as in the effluent of the side-stream-with-degas unit as it enters back into the main plant flow. In all cases bromate was non-detectable. The reason for conducting this additional special study at Oakville was to assess the potential impact of coagulant on bromate formation. For the past couple of years the BWPP was using Poly Aluminum Chloride (PACl) for coagulation. Up until July 2012, the OWPP was using aluminum sulfate but then switched the process over to PACl. This last special study demonstrates that the use of PACl as a coagulant appears to not influence the rate of bromate formation.

Discussion and Summary

The Regional Municipality of Halton has bubble-diffuser ozone dissolution at their Burlington Water Purification Plant (BWPP) and side-stream-with-degas ozone dissolution at their Oakville Water Purification Plant (OWPP). Bromate regulatory-compliance data is collected monthly. The BWPP has experienced elevated bromate concentration on occasion. The OWPP has experienced negligible or non-detectable bromate formation most of the time. Comparative analysis of operating data was performed to determine potential reasons for different bromate formation at the two plants since raw water quality is similar. The following operating parameters were effectively ruled out as the potential cause: water temperature, applied ozone dose, initial ozone residual, ozone exposure (Ct), Crypto log inactivation credit, ozone contact time, quenching agents and upstream coagulants that are used to enhance sedimentation. Bench-scale tests at variable water temperature were conducted to evaluate potential effect of contactor detention time on bromate formation. Data indicated no effect of detention time. The only reason that appears to be the cause or reason for bromate formation at the BWPP and not at the OWPP is the ozone dissolution system. The BWPP has bubble diffusers for ozone dissolution and the OWPP has side stream with degas. It is unclear why this would occur. Could it be due to localized bromate formation that occurs at an advanced rate at the gas-liquid interface of the bubble? It is recommended that additional studies be conducted to identify potential reasons.

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