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MWRA's Experience With Disinfection By-Products

By Windsor Sung, Ph.D., P.E.*

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Abstract

The formation of regulated THM4 in chlorinated MWRA water can be described by simple empirical models. The 2 most important parameters are UV-254 absorbance of raw water, and the amount of chlorine dosed. HAA5 can undergo degradation in the distribution system, and can be described by including in addition, the level of nitrite and nitrate as well as temperature. The levels of THM4 and HAA5 decreased almost 10 fold when MWRA used ozone instead of chlorine to meet primary disinfection requirements in late July, 2005. The running annual averages (RAA) for THM4 and HAA5 are now less than 6 and 8 ppb, respectively. The level of aldehydes increased with ozonation. Aldehydes are currently un-regulated, and it also undergoes degradation in the distribution system.

Introduction

Massachusetts Water Resources Authority (MWRA) supplies un-filtered surface water to over 2 million customers in the metropolitan Boston area. Table I gives a brief summary of the chronology of the various treatment schemes. The 2 major drinking water regulations behind these changes were the surface water treatment rule and the lead and copper rule. In terms of disinfection MWRA went from a simple chloramination prior to 1996 to chlorine/chloramination between 1996 and 2005 to the

present treatment of ozone/chloramination. Figure 1 shows the level of the 4 regulated trihalomethanes (Bromodichloromethane, Bromoform, Chloroform and Dibromochloromethane) observed at one location in the distribution system during this time period. In addition, changes in pH targets to meet the lead/copper rule also increased the level of THM4 produced. The change in pH probably decreased the level of total haloacetic acids (HAA) produced. MWRA also studied the formation of DBP known to be favored by ozone (aldehydes and keto-acids) with University of Massachusetts, Amherst prior to the start-up of the John Carroll Water Treatment Plant (JJCWTP) in late July, 2005 and continues to monitor the formation and changes in aldehyde levels in the distribution system. Weekly process control samples were collected from locations that reflect treatment changes and extreme detention times. Before the JJCWTP, MWRA can only add chemicals through shafts down to the deep rock tunnels. Chlorine was first added at the Wachusett Reservoir located near Clinton to the west of Boston. The location called Lab is in Marlborough and is collected prior to the addition of corrosion control chemicals. It reflects only the impact from chlorine and about 5 hours of contact time. Additional locations in between reflect the impacts from the corrosion chemical addition (change in pH), and subsequent chloramination. The location called Entry is in Medford and reflects the full treatment effect. Site A is in Marblehead, located at the eastern edge of Massachusetts and reflects extreme travel time (longer than 10 days during the winter). Site B is in Quincy, located to the southeast of Boston and reflects average travel time (3 to 5 days).

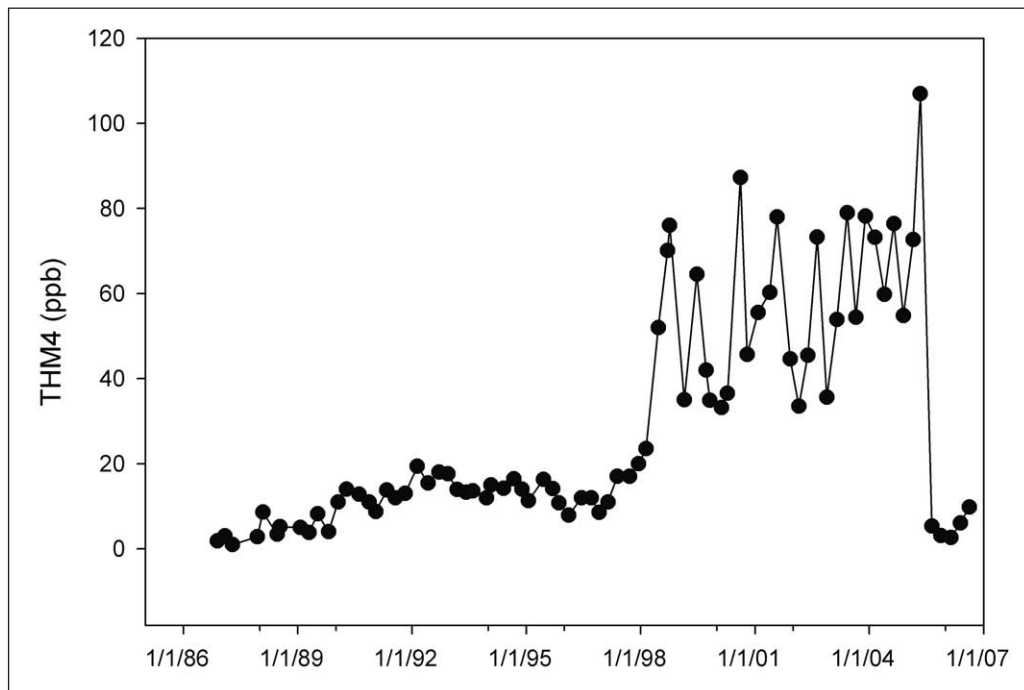
*Program Manager, Chemistry, Massachusetts Water Resources Authority, Southborough, MA

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Table I. Chronology of MWRA Treatment Changes

<i>Time</i>	<i>Treatment Provided</i>	<i>Water Quality Concern</i>
Prior to 1970	Chloramination	Disinfection
1970 to 1980	Sodium Hydroxide and Fluoride	Lead corrosion and dental health
1990 to 1996	Change in chloramination practice	Measurable residual at entry
1997	Soda ash addition Sodium hypochlorite addition Separation of chlorine and ammonia	Lead corrosion Acclimation of aqueduct Total coliform in distribution system
1998	Sodium hypochlorite dose increased Target pH raised to 9	Inactivation of <i>giardia</i> Lead corrosion
1999 to 2005	Alkalinity targets increased from 30 to 40 mg/L as CaCO ₃ , target pH increased from 9 to 9.5	Lead corrosion
2003 to 2005	Sodium hypochlorite dose increased to accommodate for construction activities	Balance of pathogen inactivation and DBP formation
2005	Ozone in place of chlorine for primary disinfection	Inactivation of <i>giardia</i> and <i>crypto</i>

Figure 1. THM4 level at a location in metropolitan Boston



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Methods

MWRA collected weekly samples for THM4 and HAA5 analyses in 1998 when sodium hypochlorite was added in sufficient dose to meet the required CT for *giardia* inactivation. This is in addition to the quarterly compliance monitoring. Sampling locations were chosen to isolate the effects from chlorine addition, increase in pH and chloramination. Weekly samples were also collected for nitrite and nitrate analysis to investigate the extent of nitrification in the distribution system. Analytical methods follow either published EPA methodology or Standard Methods. Early monitoring results allowed predictive models to be developed so that competing water quality requirements such as the lead and copper rule could be quantified in terms of impact on DBP levels¹⁻³.

Sample taps were flushed prior to sampling by opening the tap and flushing until the water temperature stabilized (usually about 10 min.). Standard laboratory quality control included method blanks, fortified blanks, fortified samples and sample duplicates with each batch of 20 or fewer samples for all analyses.

Trihalomethanes (THM). Samples were collected in duplicate 40 mL glass vials pre-treated with 2 drops of 10% sodium thiosulfate as the de-chlorinating agent. Samples were analyzed by EPA Method 524.2 on a Hewlett Packard (HP) mass selective detector equipped with a HP model 6890 gas chromatograph and OI Analytical model 4560 sample concentrator with DPM-16 Multi-sampler.

Haloacetic acids (HAA5 and 6). Samples for haloacetic acids were collected in duplicate 60 mL amber VOA vials that were pre-preserved with 0.6 mL of a 1% ammonium chloride solution. Samples were analyzed following the procedures in EPA Method 552.2. Dual column Agilent 6890 GC equipped with dual G2397A micro-ECDs were used for this project.

Aldehydes. Samples were collected, in duplicate, in 40 mL amber vials and sealed with PTFE®-lined screw caps. 20 mg of ammonium chloride (to react with any free chlorine that could lead to the formation of target analytes) and 20 mg of copper sulfate pentahydrate (to inhibit any biological decay of target analytes) were added to the sample bottles as dry solids prior to sample collection. Samples were analyzed by modification of EPA Method 556. Dual column Agilent 6890 GC equipped with dual G2397A micro-ECDs were used for this project. Target compounds included formaldehyde, acetaldehyde, propanal, butanal, pentanal, hexanal, heptanal, octanal, nonanal, decanal, cyclohexanone, crotonaldehyde, benzaldehyde, glyoxal (ethanedial) and methyl glyoxal (2-oxopropanal).

Combined nitrate/nitrite. Samples analyzed for combined nitrate/nitrite were collected in 500 mL or 1 L plastic bottles that were pre-preserved with 6 M H₂SO₄. Samples were analyzed by Skalar Sanplus Autoanalyzer following EPA method 353.2.

Sampling Locations

Weekly process control samples were collected from locations that reflect treatment changes and extreme detention times. Before the JJCWTP, MWRA can only add chemicals through shafts down to the deep rock tunnels. Chlorine was first added at the Wachusett Reservoir located near Clinton to the west of Boston. The location called Lab is in Marlborough and is collected prior to the addition of corrosion control chemicals. It reflects only the impact from chlorine and about 5 hours of contact time. Additional locations in between reflect the impacts from the corrosion chemical addition (change in pH), and subsequent chloramination. The location called Entry is in Medford and reflects the full treatment effect. Site A is in Marblehead, located at the eastern edge of Massachusetts and reflects extreme travel time (longer than 10 days during the winter). Site B is

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in Quincy, located to the southeast of Boston and reflects average travel time (3 to 5 days). The weekly collection frequency was changed to monthly when the JJCWTP became operational and levels of THM4 and HAA5 decreased almost ten fold. MWRA will only collect quarterly compliance samples from June 2007 on. For quarterly compliance purposes, MWRA collects from 16 different locations in Arlington, Belmont, Boston, Lexington, Lynnfield, Marblehead, Norwood, Quincy, Stoneham, Waltham and Winthrop. Figure 2 shows the location of these cities in relation to Boston.

Typical data analysis involved the computation of monthly average from weekly samples. Multilinear regression was performed on the monthly data. Once the regression was performed, the individual difference between the regression model result and observed value was squared. The square root of the average sum of square difference is called the standard error of the regression.

Results and Discussion

Figure 3 shows the monthly averaged THM4 level measured at the 3 locations Lab, Entry and Site A from January 2001 to October 2006. Prior to the start-up of JJCWTP the location Lab show the effect from chlorine addition, the Entry location show the effect of pH addition and chloramination, Site A show the effect from the distribution system. JJCWTP consolidated all treatment under one roof and the Lab location became the effluent of the treatment plant. Chloroform is the major component in the trihalomethanes, comprising about 87% of the THM4 prior to ozone and is now 100% of the THM4. Small amounts of bromodichloromethane (BDCM, < 8ppb) were formed when chlorination was practiced. The formation of THM4 with chlorination is well described by power law functions which include UV-254 (surrogate for precursor levels), pH, temperature, chlorine dose and contact time. The details of this modeling effort has been described

Figure 2. MWRA water communities

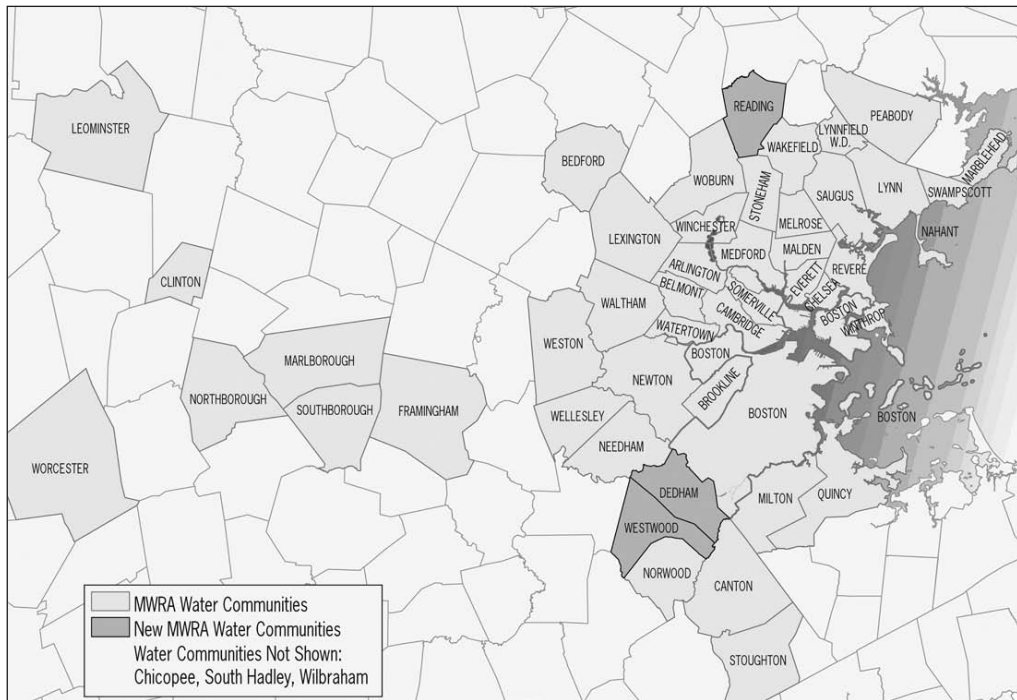
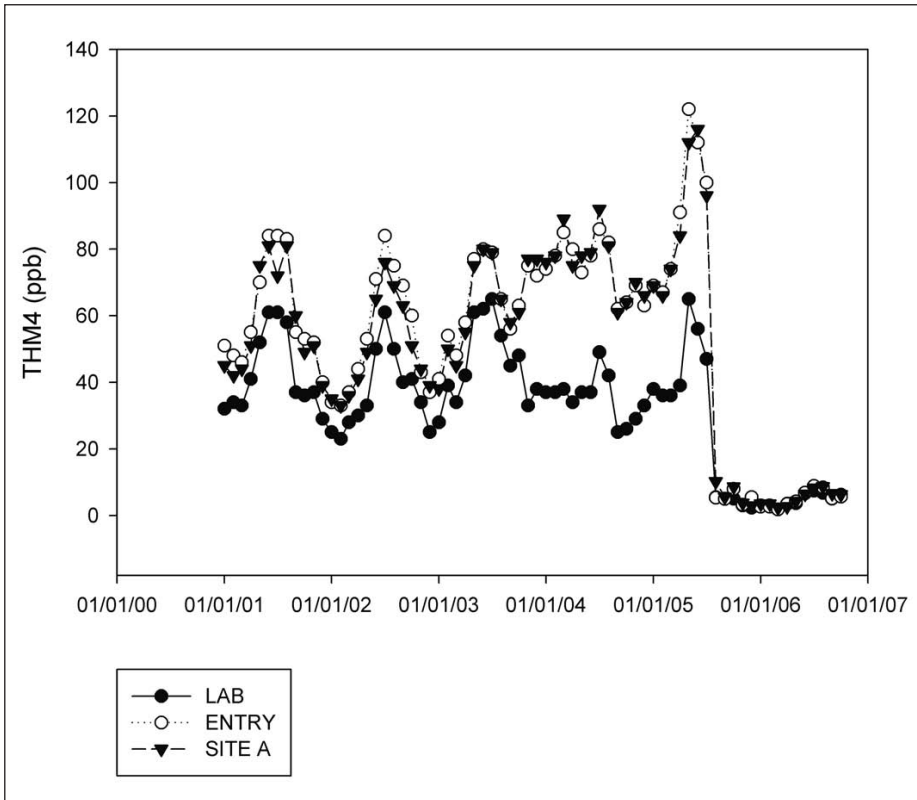


Figure 3. Behavior of THM4



previously.³ For this study, a simple approximation can be obtained by using only the raw water UV-254 absorbance and chlorine dose, the equation is:

$$\text{THM4(ppb)} = 1003.35 \times \text{UV-254} + 13.66 \times \text{Dose} - 13.06 \quad (1)$$

Equation (1) has an r^2 of 0.72 and the standard error is 9.5 ppb. The equation was derived by using the average of THM4 levels from the 3 locations, Entry, Site A and Site B. THM4 levels do not vary greatly between the 3 sites, the average standard deviation as a percentage of the average THM4 level is 4%. UV-254 is the raw water absorbance in Abs/cm and Dose is the chlorine dose at the reservoir in mg/L as chlorine. The difference between the average calculated from the 3 sites (Entry, Site A and B) are essentially the same as that collected from the 16 compliance locations collected quarterly. A linear regression between the result from the 3 sites against the result from

16 sites show that the 3 site average is 1.03 times that of the 16 site average and the r^2 is 0.97. The correlation holds for both chlorination and ozonation conditions. This would not be true for systems using free chlorine as THM4 formation will continue within the distribution system.

Figure 4 shows the monthly averaged HAA5 level measured at the same 3 locations and the same time period. There is little additional formation of HAA after the initial period of chlorine contact. The literature indicates that HAA undergoes biological degradation and that DCAA is preferably degraded over TCAA.⁴⁻⁶ Figure 5 shows the ratio of TCAA over DCAA measured from these 3 locations. The overall average of all the ratios was 1.30 and is close to the ratio of the molecular weight of TCAA over DCAA, which is 1.27. Therefore, about equimolar amounts of dichloroacetic acid (DCAA) and trichloroacetic acids (TCAA) were formed by chlorination. There

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Figure 4. Behavior of HAA5

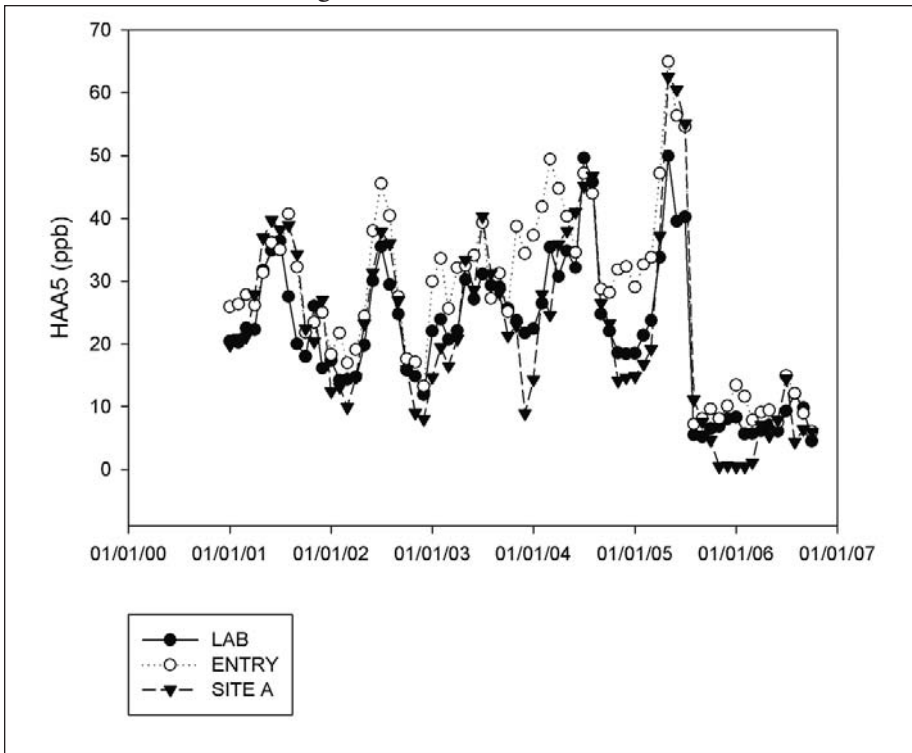
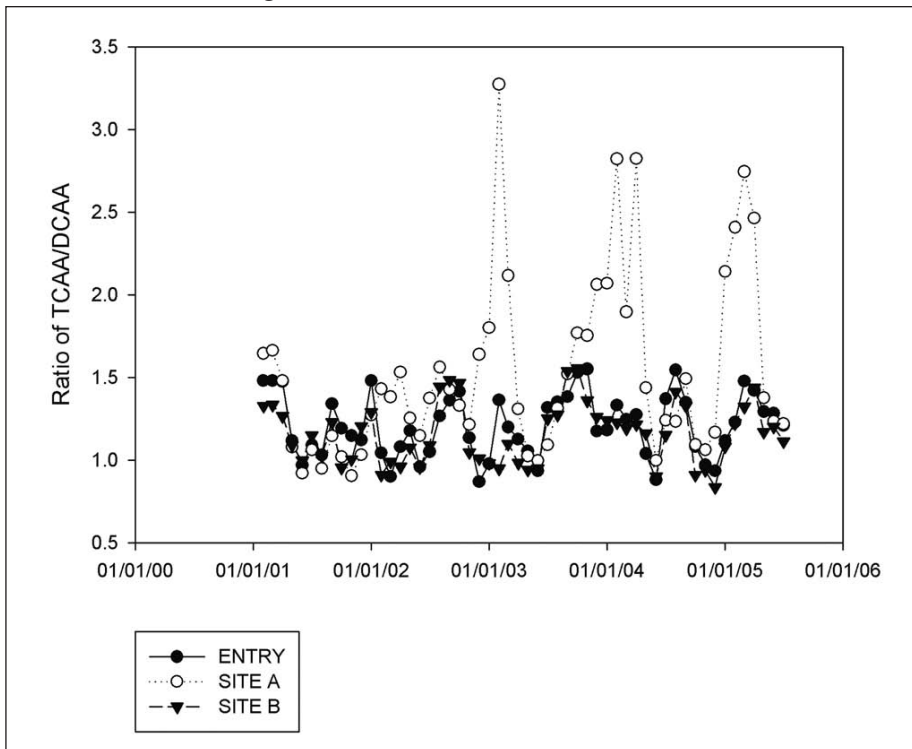


Figure 5. Ratio of TCAA over DCAA



is clear evidence of degradation of the DCAA over TCAA at Site A during the winter months, when the ratio of TCAA/DCAA reaches over 3.0. The HAA5 level at site A can be described by:

$$\text{HAA5(ppb)} = 3.29 + 5.62 \times \text{Dose} - 84.79 \times \text{NO23} + 545.84 \times \text{UV-254} + 0.67 \times \text{Temp} \quad (2)$$

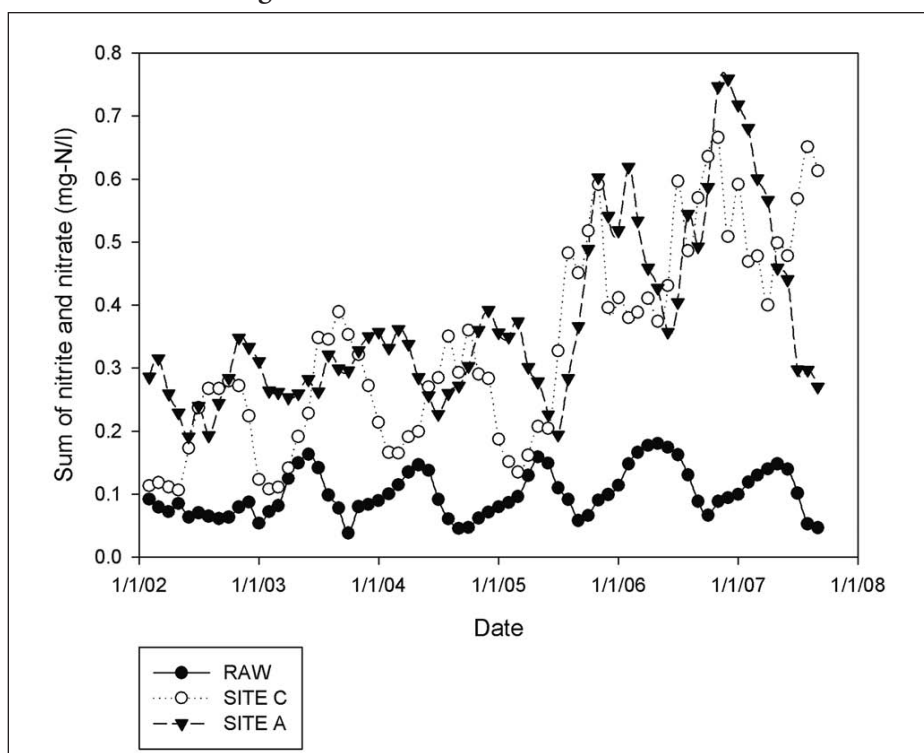
Equation (2) has an r^2 of 0.80 and the standard error is 5.7 ppb. In this equation, Dose is the chlorine dose at the Reservoir in mg/L as chlorine, NO23 is the sum of nitrite and nitrate in mg of N/L, UV-254 is the raw water absorbance in Abs/cm and Temp is the location water temperature in degrees Centigrade. Figure 6 shows the variation of nitrite and nitrate in the raw water, Site A and another site in Lynnfield (Site C). There are regular variations and the peak nitrite and nitrate level occurs in different months for Site A and C. The peak nitrite and nitrate at Site A occurs during the winter months. This is surprising, heterotrophic bacteria (HPC) monitoring does show that there

is a low level throughout the year at this site. There is also degradation of total organic carbon (TOC) at this site in winter months. The evidence is suggestive that microbial degradation can occur even at low temperatures (lowest temperature was about 4°C). Nitrification has not been a problem for MWRA since 1995

Small amounts of monochloroacetic acid are formed with ozone/chloramination and they persist into the system. The major component of HAA with ozone/chloramination is DCAA, and this is degraded in the distribution system.

The use of ozone is known to promote the formation of aldehydes.^{7,8} During a pilot period of testing with ozone from November 2002 to November 2003, the amount of aldehydes formed ranged from 24 to 69 ppb, with an average of 42 ppb; the amount of keto-acids formed ranged from 87 to 205 ppb, with an average of 129 ppb.⁹ Figure 7 shows the change in DBP components

Figure 6. Variation of nitrite and nitrate



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entering the system as ozone was added instead of chlorine. Figure 8 shows the aldehydes detected during a sampling episode in August 2005, with a range from 3 to 46 ppb and an average of 28 ppb. The most commonly detected aldehydes include acetaldehyde, formaldehyde, glyoxal and methyl glyoxal. Of these, formaldehyde and methyl glyoxal show clear patterns of degradation in the distribution system. Figure 9 show that the total aldehyde level is also correlated with the level of nitrite plus nitrate, similar results are obtained when formaldehyde is plotted against the sum of nitrite and nitrate. These observations have been repeated for many more sampling episodes since 2005.

The amount of TOX ranged from 81 to 163 ppb (as chlorine), with an average of 128 ppb during pilot testing. Sampling in October 2005 showed a TOX level of about 55 ppb as Cl at the JJCWTP, of which 15% can be accounted for by the amount of HAA and THM4 detected.

This decreased to 14 ppb at a site with extreme biological activity (75% dehalogenation).

Before JJCWTP went on line, about 10 ppb of bromide reacted with chlorination and 50% of this could be explained by the sum of bromochloroacetic acid and bromodichloromethane. With ozone there is little bromide loss between raw water and entry into the system. Monthly samples for bromate were mostly below detection limit of 2.5 ppb. It was detected twice at a level slightly less than 5 ppb in November and December 2005 and might be due to bromate from the hypochlorite rather than formation from ozone. MWRA also sampled for NDMA in 2005 and 2006, and the highest level detected was less than 5 ng/L at Site A.

Conclusion

Currently MWRA meets all regulated DBP levels for bromate (regulated when ozone is used), HAA5 and THM4. HAA5 and THM4

Figure 7. DBP components at entry to system

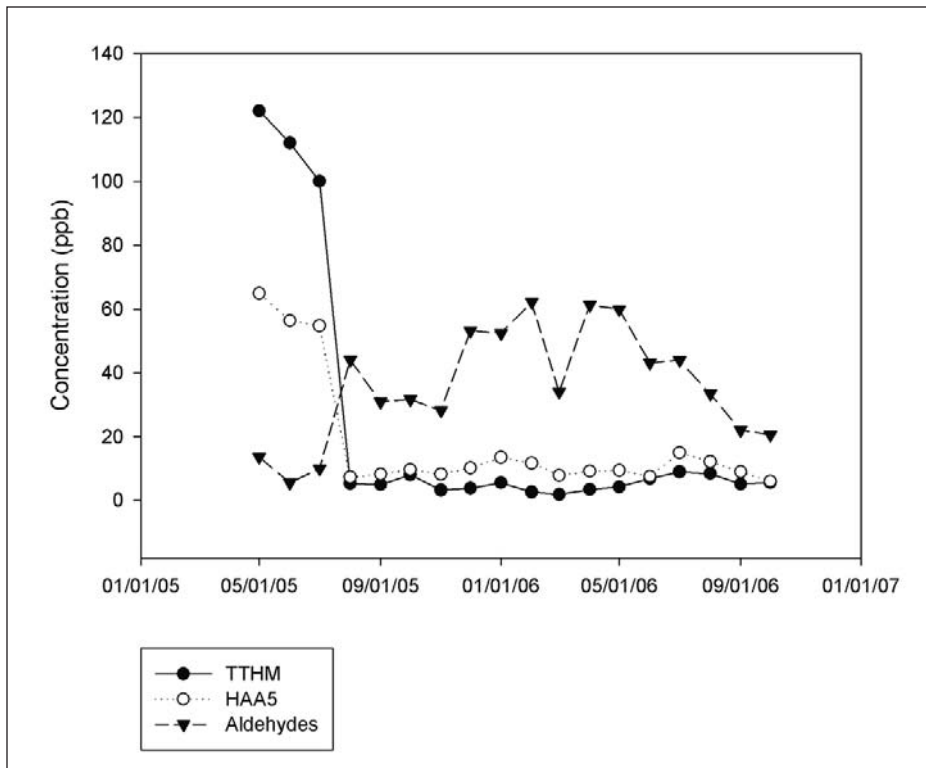


Figure 8. Spatial behavior of aldehydes (August 2005 sampling)

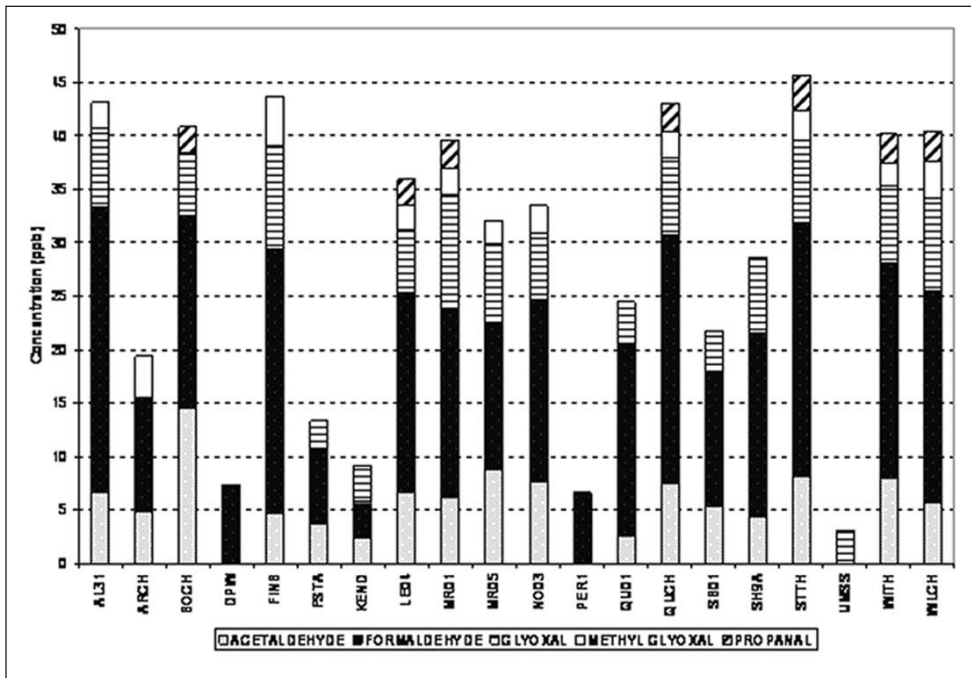
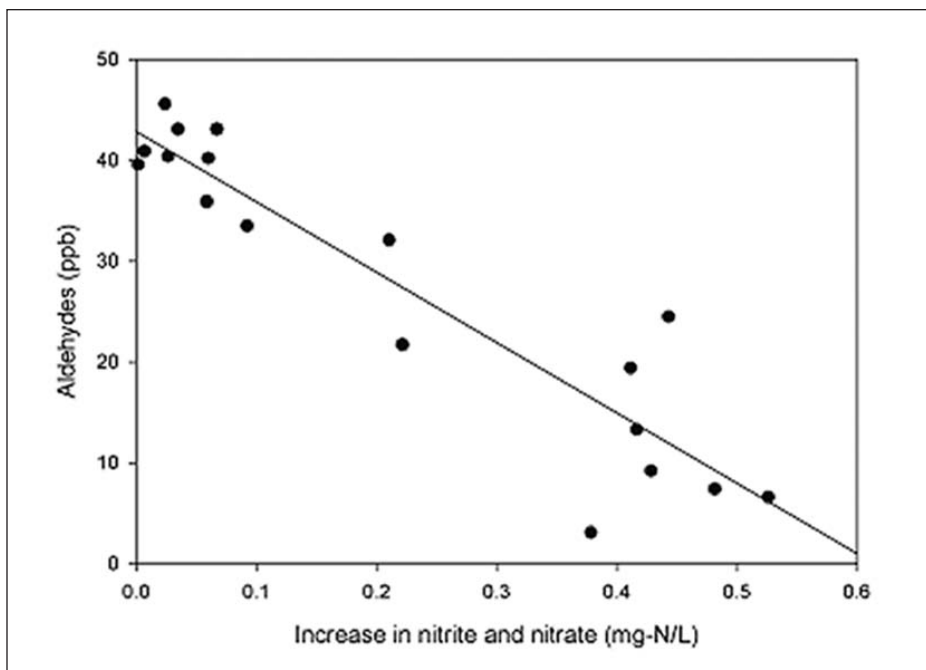


Figure 9. Relationship between aldehyde levels and nitrification



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are regulated as running annual averages (RAA) based on quarterly sampling and the limits are 60 and 80 ppb, respectively. The RAA of HAA5 went from 34 ppb in 1998 to a high of 41 ppb by the second quarter of 2005 and is now < 8 ppb. The RAA of THM4 went from a low of <10 ppb prior to 1990 to a high of 77 ppb by the second quarter of 2005 and is now < 6 ppb. In this sense the use of ozone was very beneficial in lowering the amounts of regulated DBP, as well as providing better protection against pathogens.

The production of regulated DBP under chlorination can be described by relatively simple equations. There is little additional formation of THM4 with the use of chloramination, and there is no need for large number of sampling locations for compliance purposes. This is not true for HAA because it undergoes degradation in the distribution system.

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References

1. Sung, W. Balancing the Lead and DBP rule for MWRA from September 2003 to December 2004. *J. New Eng. Water Works Assoc.* **2005**, *75*, 87-91.
2. Sung, W. Fine-tuning the Corrosion Control Targets of Alkalinity and pH for MWRA. *J. Wat. Sup. Res. Technol. – AQUA.* **2003**, *52*, 383-394.
3. Sung, W.; Reilley-Matthews, B.; O'Day, D. K.; Horrigan, K. Modeling DBP Formation, *J. Am. Water Works Assoc.* **2000**, *92*, 53-63.
4. Williams, S. L.; Williams, R. L.; Gordon, A. S. Degradation of Haloacetic Acids at Maximum Residence Time Locations. *Proc.-Water Quality Technol. Conf.*, **1995**, 1375-1366.
5. Zhou, H. J.; Xie, Y. F. Using BAC for HAA Removal Part 1: Batch Study. *J. Am. Water Works Assoc.* **2002**, *94*, 194-200.
6. Tung, H. H.; Unz, R. F.; Xie, Y. F. HAA Removal by GAC adsorption. *J. Am. Water Works Assoc.* **2006**, *98*, 107-112.
7. Weinberg, H. W.; Glaze, W. H.; Krasner, S. W.; Scimmenti, M. J. Formation and Removal of Aldehydes in Plants that Use Ozonation. *J. Am. Water Works Assoc.* **1995**, *85*, 72-85.
8. Gagnon, G. A.; Booth, S. D. J.; Peldszus, S.; Mutti, D.; Smith, F.; Huck, P. M. Carboxylic Acids: Formation and Removal in Full-Scale Plants. *J. Am. Water Works Assoc.* **1997**, *89*, 88-97.
9. Hulse, R. A.; Capuzzi, A. J.; Spencer, C. M.; Malley, J. P.; Farabaugh, S. *Evaluation of ozone and ultraviolet light.* AWWARF report 91046F. **2005**, Denver, CO.