Comparison of disinfection byproduct (DBP) formation from different UV technologies at bench scale

W. Liu*, S.A. Andrews*, J.R. Bolton***, K.G. Linden**, C. Sharpless** and M. Stefan***

* Dept. of Civil Engineering, University of Waterloo, Waterloo, ON, Canada N2L 3G1
(E-mail: *saandrews@uwaterloo.ca*)

** Dept. of Civil and Environmental Engineering, Duke University, Durham, NC, 27708, USA

*** Bolton Photosciences Inc., 92 Main St. Ayr, ON, Canada N0B 1E0

Abstract The impact of UV irradiation on disinfection byproduct (DBP) formation was investigated for low pressure, medium pressure and pulsed UV technologies using a broad range of UV doses. Four classes of DBPs (THMs, HAAs, aldehydes and carboxylic acids) were examined. This enabled the determination of effects resulting from the direct action of UV irradiation on natural organic matter (aldehydes, carboxylic acids) as well as effects on the ultimate formation of chlorinated DBPs (THMs and HAAs) from secondary chlorination. For doses of less than 1,000 mJ/cm^2, UV irradiation did not affect THM and HAA formation in subsequent chlorination processes, however higher UV doses resulted in lower ultimate concentrations of THMs and HAAs. UV irradiation also resulted in the formation of aldehydes and carboxylic acids at UV doses above 500 mJ/cm^2, compounds that are known to adversely effect drinking water biostability.
Keywords Aldehydes; carboxylic acids; DBPs; HAAs; THMs; UV

Introduction

UV technologies have become attractive options for both disinfection processes and advanced oxidation processes (AOPs) to address increasing concerns regarding the inactivation of *Cryptosporidium parvum* and *Giardia lamblia* and the decomposition of micro-contaminants (Clancy *et al*., 2000; Craik *et al*., 2001; Malley *et al*., 1995; Andrews *et al*., 1995). UV irradiation has been demonstrated to be an effective treatment for the inactivation of *Cryptosporidium parvum* and *Giardia lamblia* for which conventional chlorination is generally less effective. UV irradiation also plays a key role as a cost-effective manner to decompose micro-pollutants in source waters, such as NDMA (Jobb *et al*., 1994), toluene (Andrews *et al*., 1999), atrazine (Beltran *et al*., 1996), metolachlor (Wilson and Mabury, 2000), diazinon (Doong and Chang, 1998), and carbaryl (Patterson *et al*., 1998). Accordingly, concerns have emerged about whether UV irradiation directly produces byproducts, and whether UV irradiation ultimately impacts the concentrations of chlorinated DBPs formed in subsequent chlorination processes that are needed to maintain disinfection residuals throughout distribution systems.

Of the DBPs directly formed in UV irradiation processes, aldehydes and carboxylic acids are two classes of organic oxidation byproducts that have been observed in several studies pertaining to drinking water treatment. They have been linked either to potential toxicity effects (e.g. aldehydes) (Bull and Kopfler, 1991) or to the ultimate biostability of the finished water (aldehydes and carboxylic acids) (Huck *et al*., 1998; Camper and Jones, 2000). Individual aldehydes of interest include formaldehyde, acetaldehyde, glyoxal, and methyl-glyoxal. Carboxylic acids of interest include formic acid (as formate), acetic acid (as acetate) and oxalate acid (as oxalate). These compounds have typically been observed in the highest concentrations relative to other aldehyde and carboxylic acid byproducts.

Previous studies into DBP formation potentials in drinking water using low pressure UV lamps have indicated no appreciable formation of DBPs (Malley *et al*., 1995; Stewart *et al*.,

1993). It has been hypothesized that the photochemical energy at UV doses required for disinfection is so low that no measurable changes in molecular structure and functional groups of humic matter in the water are observed. However, approximately 10 to 100 µg/L formaldehyde and acetaldehyde was observed in a bench-scale experiment using a 1 kW MP UV lamp applied to two drinking water sources (Andrews *et al.*, 1995), and some production of formaldehyde and assimilable organic carbon (AOC) was detected in experiments involving pulsed UV irradiation (Mofidi *et al.*, 1998).

The research reported herein evaluated the impacts of different UV technologies, i.e. low-pressure UV (LP UV), medium-pressure UV (MP UV) and pulsed-UV (P-UV), on DBP formation including both from direct irradiation and from subsequent chlorination. UV doses included both low doses (below 100 mJ/cm^2), typically employed for disinfection, and high doses (up to 6,360 mJ/ cm^2) typically encountered in oxidation applications.

Materials and methods

All tests were performed with freshly prepared synthetic water whose constituents are shown in Table 1. The synthetic water was intended to simulate typical drinking water quality with a total organic carbon (TOC) level of approximately 3 mg/L by combining these constituents into Millipore-UV® water. All of the inorganic chemicals used in the preparation of the synthetic water were analytical or USP grade. Humic acid was IHSS Suwannee River Natural Organic Matter (NOM), and alginic acid was purchased from Aldrich Chemical Company Inc. The pH of the synthetic water was approximately 8.3, with TOC at the range of 2.54 to 3.28 mg/L.

Samples of synthetic water (350 mL) were prepared in the Duke University (Duke), Bolton Photosciences Inc. (BPI) and Metropolitan Water District (MWD) laboratories according to the Table 1. Samples were placed in a 125×65 mm crystallization dish (sample depth approximately 3 cm) and irradiated with either MP UV, LP UV or P-UV. The MP UV experiments were performed using similar MP UV lamps at two different laboratories, designated as laboratories A and B, providing a measure of the comparability of the results obtained from the different laboratories. The P-UV experiments were also performed in two different laboratories, designated as laboratories A and C, but utilized different P-UV lamps. The LP UV experiment was performed in laboratory A only.

The UV irradiation tests were performed at doses of approximately 0, 40, 140, 500, 1,000, and 6,360 mJ/cm^2. LP UV irradiations were first performed in triplicate except for the 140 and 5,000 mJ/cm^2 doses, for which 5 replicates were obtained. After good reproducibility was observed in the tests, MP UV and P-UV irradiations were then performed in duplicate except for the 140 and 1,000 mJ/cm^2 doses, which were performed in triplicate. The lower doses represented those that may be encountered during disinfection, while the higher doses represented those used in oxidative applications. Samples were refrigerated and then shipped on ice in coolers, within a day following the irradiations, to the University of Waterloo for UFC testing and DBP analyses. Samples shipped to the laboratory at University of Waterloo for DBP analysis included 20 mL samples for carboxylic acids analysis, 40 mL of sample for aldehydes analysis, and 250 mL of sample for the UFC tests and subsequent analysis of THMs and HAAs.

DBP analyses and Uniform Formation Condition (UFC) tests were initiated upon receipt of the samples at the UW laboratory. Aldehyde concentrations were determined by

Table 1 Synthetic water constituents

	Ca^{2+}	Mg^{2+}	Na$^+$	(CO$_3$)$_{TOT}$	NO$_3^-$	Cl$^-$	SO$_4^{2-}$	Humic acid	Alginic acid
mg/L	29.1	9.99	36.2	90	3.00	40.0	55.0	2.56	5.32

GC-ECD analysis of extracted PFBHA derivatives (APHA-AWWA-WEF, 1995). Carboxylic acid concentrations were determined by ion chromatographic analysis of chloroform-preserved samples (Peldszus *et al*., 1996). UFC tests were performed according to the procedure reported by Summers and co-workers (Summers *et al*., 1996). Residual chlorine was quenched with sodium thiosulfate immediately at the conclusion of the 24-hour reaction period, following which THM and HAA analyses were performed according to Standard Methods (APHA-AWWA-WEF, 1995) with minor modifications.

Travel standards and travel blanks for each class of DBP were included with each batch of samples. Laboratory standards and blanks were also prepared at the time of analysis of each set of samples.

Results and discussion

In general, neither LP UV, MP UV nor P-UV had a significant effect on the formation of DBPs at doses of 500 mJ/cm^2 or less (UV disinfection doses). At or above doses of 1000 mJ/cm^2, however, LP UV, MP UV and P-UV caused changes in the NOM of the synthetic water such that DBP concentrations were affected to similar degrees.

The following sections contain summaries of the results obtained in these experiments. Figures 1–4 provide averages of DBP concentrations obtained at the different UV doses employed and their standard deviations (shown as error bars). These figures have been plotted on a log scale only to facilitate visualization of the data and comparison of trends. Data obtained without UV irradiation (i.e. at 0 mJ/cm^2 UV dose) have been plotted as 1 mJ/cm^2 UV dose to enable inclusion of this data in this style of plot.

Trihalomethanes

The differences in THM yields obtained from synthetic water irradiation with the different UV technologies were small, particularly in the UV dose range typical for disinfection. UV irradiation followed by UFC testing at low doses (<500 mJ/cm^2) did not have an effect on the THM concentrations observed following UFC testing (Figure 1). This was true for each of the lamp technologies tested, and for each of the laboratories. The results are in general agreement with those reported by other researchers (Malley *et al*., 1995; Zheng *et al*., 1999a, 1999b). The UFC test was reasonably reproducible, with standard deviations of replicate samples of generally less than 5 µg/L being obtained for THM concentrations of 51 to 137 µg/L. The THMs were composed almost exclusively of chloroform in these samples. This was not unexpected given that the synthetic water did not contain appreciable concentrations of bromide.

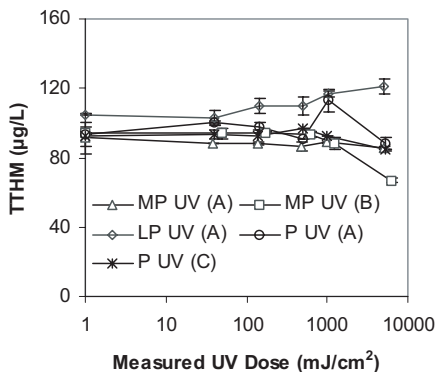Higher UV doses (>1,000 mJ/cm^2) did not affect the resulting THM concentrations from

W. Liu *et al.*

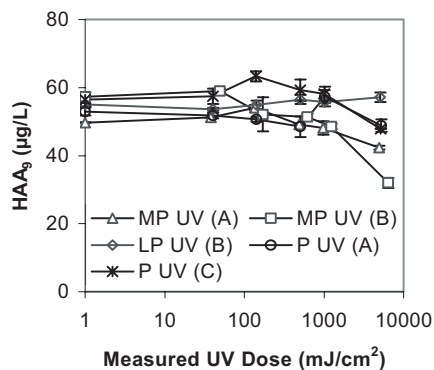**Figure 1** TTHM concentrations from UV irradiation followed by UFC testing

Figure 2 HAA$_9$ concentrations from UV irradiation followed by UFC testing

517

subsequent UFC tests that followed the MP UV and P-UV irradiations performed in Laboratory A and P-UV irradiations performed in Laboratory C. Only minor decreases of THMs (less than 9%) were observed at the nominal dose of 5,000 mJ/cm^2 in these experiments. However, a 15% increase in THM concentrations was observed in LP UV testing performed in Laboratory A upon increasing the UV dose to a nominal 5,000 mJ/cm^2, and a 29% decrease in THM concentrations was observed in the MP UV experiments performed in Laboratory B.

The decrease in THMs observed in the MP UV experiments performed in Laboratory B was determined to be due to the presence of approximately 2 mg/L hydrogen peroxide during UV irradiation, resulting in advanced oxidation conditions. These results are comparable to those obtained from formal testing of the advanced oxidation process, described in another paper (Liu *et al.*, 2002).

Haloacetic acids

LP UV irradiation followed by UFC testing did not have an effect on the HAA concentrations observed regardless of the UV dose employed (Figure 2). The P-UV technologies did not have appreciable effects on the HAA concentration generated in either Laboratory A or Laboratory C, although slight decreases of 8% and 15% were observed at high UV doses of 5,244 mJ/cm^2 and 5,153 mJ/cm^2, respectively. The MP UV technologies resulted in larger decreases of HAAs compared to other UV technologies. The greatest decreases in HAA concentration (at the highest UV doses) were observed to be 15% and 44% under MP UV irradiation, respectively. The UFC test was reasonably reproducible, with standard deviations of replicate samples of generally less than 3 µg/L being obtained for HAA data of concentrations of 32 to 70 µg/L.

It is reasonable that at high UV doses, HAA precursors were probably partly destroyed, contributing to the lower HAA concentrations observed in the following UFC tests. Destruction of the HAA precursors was not observed in terms of TOC concentrations, however (data not shown).

The HAAs were composed almost exclusively of dichloroacetic acid and trichloracetic acid in these samples. This was not unexpected given that the synthetic water did not contain appreciable concentrations of bromide.

In regards to differences observed for samples from different laboratories, UFC testing of synthetic water prepared in each of Laboratories A, B and C (i.e. at a UV dose of 0 mJ/cm^2) showed only minor differences in the THM concentrations and HAA concentrations observed (91.4 to 105 µg/L for THMs and 49 to 56 µg/L for HAAs obtained before UV irradiation, respectively). This indicated that both the preparation of the synthetic water and UFC testing procedure were consistently performed with respect to the ultimate formation of THMs and HAAs. Similarly, photolysis procedures were performed comparably well in Laboratories A, B and C, as indicated by the similarity in THM and HAA results obtained by all laboratories in parallel experiments involving MP UV and P-UV.

Aldehydes

Aldehydes were produced from each of LP UV, MP UV and P-UV irradiation, although significant increases in concentrations above background levels were not observed below applied doses of approximately 500 mJ/cm^2 for either UV technology (Figure 3). Above 500 mJ/cm^2, a direct relationship between UV dose and aldehyde concentration was observed under irradiation of MP UV and P-UV, although increases in aldehyde concentrations with increases in LP UV dose were only approximately half those observed for MP UV irradiation of synthetic water. For P-UV irradiation, noticeable increases in aldehydes were only observed with doses above 1,000 mJ/cm^2. Maximum increases in aldehyde
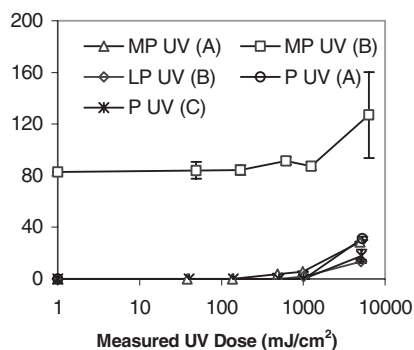
Figure 3 Aldehyde concentrations from UV irradiation of synthetic water
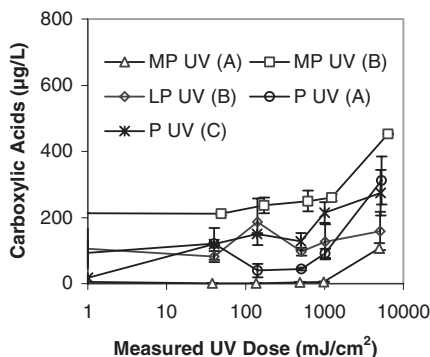

Figure 4 Carboxylic acid concentrations from UV irradiation of synthetic water

concentrations observed at the highest UV doses applied were approximately 13 µg/L for LP UV irradiation, 29 to 45 µg/L for MP UV irradiation, and 18 to 31 µg/L for P-UV irradiation. The reproducibility of the irradiation and analytical procedures was good, resulting in relative standard deviations in replicate tests of less than 5%. Although a relatively high level of aldehydes (83 µg/L) was observed in the synthetic water of Laboratory B, this did not appear to affect the formation of additional aldehydes upon UV irradiation. Formaldehyde and acetaldehyde were the main species detected in these tests.

Carboxylic acids

Carboxylic acids appeared to be produced from each of LP UV, MP UV and P-UV irradiation, although significant increases in concentrations above background levels were not observed below applied doses of approximately 1,000 mJ/cm^2 for either MP UV or LP UV technology (Figure 4). However, a significant increase in carboxylic acid concentrations was observed with P-UV doses above 40 mJ/cm^2 as performed in Laboratory C. Also, in the case of the LP UV and P-UV experiments performed in Laboratory A, the scatter in the data was such that changes in carboxylic acid concentration may not have been statistically significant for that UV technology. Maximum increases in carboxylic acid concentrations observed at the highest UV doses applied were approximately 100 µg/L for MP UV experiments performed at Laboratory A, 240 µg/L for MP UV experiments performed at Laboratory B and 256 µg/L for P-UV experiments performed in Laboratory C. Although a relatively high level of carboxylic acids (213 µg/L) was observed in the synthetic water of Laboratory B, this did not appear to affect the formation of additional carboxylic acids upon UV irradiation. In all samples, formate, acetate and oxalate were the main species of carboxylic acids.

The carboxylic acid analytical procedure carries with it the lowest precision of the four classes of DBPs included in this research (RSD of 2.9% to 47%). The higher RSDs were typically associated with earlier experiments in this project, with RSDs values of approximately 10% to 20% being obtained for more recent experiments. Despite this and the relatively high background levels of carboxylic acids present in the synthetic water matrix, the effects of UV irradiation on carboxylic acid formation may still be observed. For example, the relatively high level of carboxylic acids (213 µg/L) observed in the synthetic water of Laboratory B did not appear to affect the observation of the formation of additional carboxylic acids upon MP UV irradiation.

519

Conclusions

This research investigated the impacts of low pressure, medium pressure and pulsed UV irradiation on DBP formation. A wide range of UV doses was employed in these experiments; doses that were either typical of disinfection (less than 500 mJ/cm^2) or advanced oxidation processes (up to 6,300 mJ/cm^2). Four classes of DBPs were investigated, of which aldehydes and carboxylic acids were generated directly from UV irradiation and THMs and HAAs were generated during UFC test following UV irradiation. The reproducibility of the experiments within each laboratory and among the different laboratories was also assessed and found to be acceptable. Generally, UV irradiation under low UV doses (less than 500 mJ/cm^2) typically for disinfection did not affect the formation of any of the above DBPs. However, at doses of up to 1,000 mJ/cm^2 or higher, UV irradiation resulted in variations in the observed DBP concentrations in different ways.

For chlorinated DBPs that formed in the UFC tests following UV irradiation (THMs and HAAs), no significant variations were observed even at high UV doses. This was especially true for THMs. However, minor decreases of THMs (less than 9%) were observed at the nominal dose of 5,000 mJ/cm^2 in all UV irradiations except in the LP UV experiment (THMs increased by 15%). This abnormal trend requires further investigation. Below the doses of 1,000 mJ/cm^2, increases in UV dose resulted in increases for HAA concentrations, except that very high UV doses (nominally 5,000 mJ/cm^2) resulted in fewer HAAs being formed in the subsequent UFC tests. At these very high doses, a maximum decrease in HAA concentration of 44% was obtained using MP UV irradiation.

For two classes of DBPs formed directly from UV irradiation (aldehydes and carboxylic acids), increases in DBP concentrations were observed at high UV doses (>1,000 mJ/cm^2), although no significant aldehydes and carboxylic acids were produced below applied doses of approximately 1,000 mJ/cm^2. Above 500 mJ/cm^2, a direct relationship between UV dose and aldehyde concentration was observed under irradiation of MP UV and P-UV.

In summary, UV doses of less than 1,000 mJ/cm^2 (including doses that are typical for the inactivation of *Cryptosporidium* and *Giardia*) did not affect chlorinated DBP formation during subsequent chlorination, and fewer THMs and HAAs were formed after UV irradiation at high UV doses and subsequent chlorination. UV irradiation resulted in the direct formation of aldehydes and carboxylic acids at doses above 500 mJ/cm^2, compounds which are known to have an adverse effect on drinking water biostability.

Acknowledgements

References

Andrews, S.A., Huck, P.M., Chute, A.J., Bolton, J.R. and Anderson, W.A. (1995). UV oxidation for drinking water-feasibility studies for addressing specific water quality issues. *Proc. AWWA WQTC, New Orleans, LA*, 1881–1898.

Andrews, S.A, Peldszus, S., Moralejo, C., Anderson, W.A. and Huck, P.M. (1999). Stable by-products of the photo-oxidative advanced oxidation of BTEX compounds in groundwater. *Proc. AWWA WQTC, Tampa, FL*.

APHA-AWWA-WEF (1995). *Standard Methods for the Examination of Water and Wastewater*. 19th Ed., Washington D.C.

Beltran, F.J., Gonzalez, M., Rivas, J.F. and Alvarez, P. (1996). Aqueous UV radiation and UV/H2O2 oxidation of atrazine first degradation products: deethylatrazine and deisopropylatrazine. *Environmental Toxicology and Chemistry*. **15**(6), 868–872.

Bull, R.J. and Kopfler, F.C. (1991). *Health effects of disinfectants and disinfection by-products*. AWWARF and AWWA, Denver, CO.

Camper, A.K. and Jones, W.L. (2000). *Factors affecting microbial growth in model distribution systems*. AWWARF and AWWA, Denver, CO.

Clancy, L.J., Bukhari, Z., Hargy, M.T., Bolton, R.J., Dussert, B.W. and Marshall, M.M. (2000). Using UV to inactivate Cryptosporidium. *J. AWWA*, **97**(9), 97–104.

Craik, S.A., Weldon, D., Finch, G.R., Bolton, J.R. and Belosevic, M. (2001). Inactivation of Cryptosporidium parvum oocyst using medium- and low-pressure ultraviolet radiation. *Water Research*, **35**(6), 1387–1398.

Doong, R. and Chang, W. (1998). Photoassisted iron compound catalytic degradation of organophosphorous pesticides with hydrogen peroxide. *Chemosphere*, **37**(13), 2563–2572.

Huck, P.M., Finch, G.R., Hrudey, S.E., Peppler, M.S., Amirtharajah, A., Bouwer, E.J., Albritton, W.L. and Gammie, L. (1998). *Design of biological processes for organics control*. AWWARF and AWWA, Denver, CO.

Jobb, D.B., Hunsinger, R.B., Meresz, O. and Taguchi, V. (1994). Ultraviolet degradation of N-nitrosodimethylamine (NDMA) in the Ohsweken (Six Nations) water supply. *Proc-Annu. Conf. AWWA*, 211–218.

Liu, W., Andrews, S.A., Sharpless, C., Stephan, M., Linden, K.G. and Bolton, J.R. (2002). *The impact of UV/H_2O_2 advanced oxidation on DBP formation* (in preparation).

Malley, J.P., Shaw, J.P. and Ropp, J.R. (1995). *Evaluation of by-products produced by treatment of groundwaters with ultraviolet irradiation*. AWWARF and AWWA, Denver, CO.

Mofidi, A.A., Baribeau, H., Green, J.F., Leon, R.D. and Wolfe, R.L. (1998). Disinfection using high-intensity pulsed-ultraviolet irradiation. *Proceedings, AWWA WQTC, San Diego*, CA, 5A–3

Patterson, H.H., Bachman, J. and Kanan, S. (1998). Kinetics and the influences of dissolved organic matter on the photodecomposition of the carbonate pesticides carbofuran, carbaryl and aldicarb. *ACS National Meeting, Am. Chem. Soc., Div. Environ. Chem.*, **38**(2), 105–106.

Peldszus, S., Huck, P.M. and Andrews, S.A. (1996). Determination of short-chain aliphatic, oxo- and hydroxy-acids in drinking water at low microgram per liter concentrations. *J. Chromatography A*. **723**, 27–34.

Stewart, M.H., Hwang, C.J., Hacker, P.A., Yates, R.S. and Wolfe, R.L. (1993). Microbial and chemical implications of using ultraviolet irradiation for treatment of biological filter effluent. *AWWA WQTC, Miami FL*, 1313–1339.

Summers, R.S., Hooper, S.M., Solarik, G. and Owen, D. (1996). Assessing DBP Yield: Uniform Formation Conditions. *J.AWWA*, **81**(7), 80–93.

Wilson, R.I. and Mabury, S.A. (2000). Photodegradation of metolachor: isolation, identification and quantification of monochloroacetic acids. *Jour. Agricultural and Food Chemistry*, **48**(3), 944–950.

Zheng, M., Andrews, S.A. and Bolton, J.R. (1999a). Impacts of medium pressure UV and UV/H2O2 treatment on disinfection byproducts formation. *Proceedings, AWWA Annual Conference and Exhibition, Chicago, Illinois*.

Zheng, M., Andrews, S.A. and Bolton, J.R. (1999b). Impacts of medium pressure UV and UV/H2O2 on subsequent THM and HAA formation. *Proceedings, AWWA WQTC, Tampa, FL*.

521