Pergamon

Wat. Sci. Tech. Vol. 40, No. 6, pp. 115–122, 1999
© 1999 IAWQ
Published by Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0273–1223/99 $20.00 + 0.00

PII: S0273-1223(99)00546-6

FACTOR SCREENING FOR OZONATING THE TASTE- AND ODOR-CAUSING COMPOUNDS IN SOURCE WATER AT DETROIT, USA

Khalil Z. Atasi*, Theping Chen*, Judith I. Huddleston**,
Connie C. Young*** and I. H. (Mel) Suffet***

* *McNamee, Porter & Seeley, Inc. 220 Bagley Ave., Suite 710, Detroit, Michigan 48226, USA*
** *Water Quality Division, Detroit Water and Sewerage Department, 6425 Huber, Detroit, Michigan 48211, USA*
*** *Environmental Health Science Dept., UCLA School of Public Health, 10833 Le Conte Ave., Los Angeles, California, USA*

ABSTRACT

Three odorants, geosmin (earthy), MIB (2-methylisoborneol) (musty), and IPMP (2-isopropyl-3-methoxy-pyrazine) (decaying vegetation/musty) were spiked into raw water taken from the Detroit River and subjected to bench-scale ozonation (with and without hydrogen peroxide). Statistical experiment design was employed to investigate operating variables such as ozone dose, ozone addition point, temperature, odorant spike level, and presence of hydrogen peroxide. Two additional odorants, *cis*-3-hexenyl acetate (grassy) and *trans,trans*-2,4-heptadienal (fishy) were also tested. Results showed that ozonation was capable of mitigating the spiked odorants in the Detroit source water. Ozone dose was the single most important factor in removing the odorants. Presence of hydrogen peroxide (without dose optimization) had a limited effect on odorant removal at tested pH and alkalinity conditions. Ozone application point and water temperature had significant impacts on ozone residual, but not on odorant removal. MIB was most difficult to remove by ozonation among the five spiked odorants. © 1999 IAWQ Published by Elsevier Science Ltd. All rights reserved

KEYWORDS

Drinking water; geosmin; IPMP; MIB; ozone; tastes and odors.

INTRODUCTION

The Detroit Water and Sewerage Department (DWSD) experiences periodic taste and odor (T&O) events in the raw water supplies. During these episodes, DWSD receives complaints from customers throughout the system. The objective of this treatability study was to evaluate ozonation technology in mitigating the T&Os. A broader scope of this comprehensive project has been described elsewhere (Chen *et al.*, 1996).

METHODS

Five odorants, which have been previously identified in DWSD raw water or U.S. drinking waters, were spiked into raw water taken from the Detroit River. They were geosmin (earthy), 2-methyl-isoborneol

(MIB; musty), 2-isopropyl-3-methoxy-pyrazine (IPMP; decaying vegetation/musty), *cis*-3-hexenyl acetate (grassy), and 1-pentene-3-one or *trans,trans*-2,4-heptadienal (fishy). Raw water pretreatment was described elsewhere (Chen *et al.*, 1996).

The custom-made 8 l glass ozonation reactor has ports for ozone feed and off-gas, thermometer, pressure gauge, hydrogen peroxide input, and liquid sampling. A fritted glass diffuser was used for delivering ozone to the reaction solution. A magnetic stirring bar provided additional mixing. Off-gas was sent either to a thermal ozone - off-gas destructor or to a two-stage potassium iodide (KI) trap. An ozone-in-air monitor with UV detector was used for monitoring gaseous ozone concentrations in the ozone feed and off-gas.

The ozone production rate was calculated from the ozone gas feed concentration and the ozone gas flow rate, and was confirmed by sending feed-gas to the KI trap for 10 minutes and subsequently titrating the KI solution with sodium thiosulfate. The ozone in the off-gas was captured by the KI traps. The transferred ozone mass and concentration were calculated from the applied ozone dose and off-gas ozone mass. The ozone dose control was achieved by conducting pre-testing prior to each actual test to obtain the relationship between the ozonation time and the transferred ozone dose. When maintaining a relatively constant ozone gas concentration and flow rate, the applied ozone dose and the transferred ozone are controlled by the reaction time. The use of transferred ozone dose allows the results of this bench testing to be transferable to the full-scale design.

Five operation variables were investigated. These were ozone dose, ozone addition point, temperature, odorant spike level, and presence of hydrogen peroxide. Other factors, such as pH and alkalinity, generally being quite consistent in the source water, were found to have limited impacts on geosmin removal in Great Lakes water because of the unfavorable conditions for $OH^{\bullet}$ radical oxidation (Huck *et al.*, 1996). A study by American Water Works Association (AWWA, 1991), however, found ozone with hydrogen peroxide to be much more efficient than ozone alone in removing MIB and geosmin in a different source water. Typical range of the raw water TOC level (1.5 to 3.0 mg/l) and settled water were tested. Raw water TOC level may be a potentially significant factor (Huck *et al.*, 1996). Contact time was not studied independent of ozone dose because the reaction rate between ozone and taste- and odor-causing compounds is believed to be fast (AWWA, 1991; Huck, 1996). In addition, the inactivation of *Cryptosporidium* is likely to determine the contact time design criteria for Great Lakes water (Crozes *et al.*, 1997).

Factorial statistical experiment design was employed to evaluate the potential interactions between factors that could not be known otherwise. It also identifies and compares each factor independently. In addition, it is the most effective screening method that requires fewer tests, thus fewer costly T&O analysis. The design of experiment approach also minimizes the impacts from the testing errors (Box *et al.*, 1978). Two 1/2-fractional 4-factor factorial designs (Tests A and B) were used with three odorants (MIB, geosmin, and IPMP). Test A was spiked with a high concentration of odorants. Test B was targeted at about 25% of the Test A level. Test C included aeration with oxygen and ozonation of all five odorants. Table 1 summarizes the raw water quality and the spike concentrations for all tests, and Table 2 shows the experiment conditions.

Table 1. Summary of Raw Water Quality

	pH	Turbidity (NTU)	TOC (mg/l)	Alkalinity (mg/l as $CaCO_3$)	UV_{254} (cm^{-1})	MIB[1] (ng/l)	Geosmin[1] (ng/l)	IPMP[1] (ng/l)	Grassy[1,2] (ng/l)	Fishy[1,2] (ng/l)
Test A	8.1	24.5[3]	2.9	90	0.094	26	40	51	--	--
Test B	7.9	6.8[3]	1.7	86	0.028	5	8.6	12	--	--
Test C	7.9	6.8[3]	1.7	86	0.028	26	35	34	45	203

Note: 1 measured value using absolute recovery without surrogate recovery adjustment;
2 compounds were unstable during storage; measured value of control sample;
3 settled water (after alum coagulation) was also used for these tests, which had turbidity value of 0.4 NTU.

Table 2. Summary of experimental design of ozonation factor screening test

Factor	Unit	Test A		Test B		Test C
		Low (-1)	High (+1)	Low (-1)	High (+1)	
Temperature	°C	10	22	7	20	10
Ozone dose, consumed	mg/l	0.5	1.85	0.6	2.0	2.1
Presence of peroxide[1]	--	none	yes	none	yes	yes
Point of application	--	settled	raw	settled	raw	raw

[1] the H_2O_2 dose was about 0.5 H_2O_2/O_3 mass ratio for Test A and 1.0 for Test B

Flavor profile analysis (FPA), closed-loop stripping analysis (CLSA) with gas chromatography and mass spectrometry (GC/MS), simultaneous distillation extraction (SDE) with GC/MS, and sensory-GC analysis were utilized for odorant analysis. Dissolved ozone, UV_{254}, TOC and other analysis were all conducted following Standard Methods (APHA, 1995). More details on the FPA, CLSA, SDE and GC/MS can be found elsewhere (Bruchet *et al.*, 1995).

RESULTS AND DISCUSSION

Analysis of variances (ANOVA) was employed to analyze the experimental data, using Design-Expert® 5.0 software (Stat-Ease, Inc.). Table 3 shows the statistical summary of the testing results. Standardized main effect is the difference between the average removals of two factor levels (shown in Table 2). Main effect is caused by single factor; two-factor interaction effect is caused by both interacting factors. The larger the effect, the more significant impact the factor has. The statistically significant effect is shown in bold font and included in the regression model, as shown in Table 3. Further details regarding experimental design and analysis can be found elsewhere (Box *et al.*, 1978).

Table 3. ANOVA Results of Ozonation of Spiked Raw Water (Test A&B)

	Best-fit Regression Model[1]	Standardized Effect[2]				Model F value[3]	Model p value[4]	r^2
		Temp	O_3 dose	H_2O_2	Point			
UV_{254}, cm^{-1}	UV = 0.039 - 0.0052(dose) + 0.025(point)	0.0005	**-0.010**	0.001	**0.050**	143	<0.0001	0.98
TOC, mg/L	TOC = 2.72 + 0.51(point)	0.14	0.038	0.013	**1.0**	207	<0.0001	0.97
SUVA, L/mg/M	SUVA = 1.3 - 0.19(dose) + 0.67(point)	-0.07	**-0.37**	0.05	**1.3**	127	<0.0001	0.98
Combined, %	rem.% = 157 + 79(dose) + 12(H_2O_2) - 11(point)	-11	**157**	**24**	**-23**	116	0.0002	0.99
MIB, %	rem.% = 48.6 + 23.6(dose)	-3.3	**47**	6.8	-4.8	56	0.0003	0.90
Geosmin, %	rem.% = 55 + 32(dose) + 6.5(H_2O_2)	-7.3	**64**	**13**	-6.3	78	0.0002	0.97
IPMP, %	rem.% = 53.1 + 22.9(dose) - 5.9(point)	0.25	**46**	3.8	**-12**	83	0.0001	0.97
UV_{254}, cm^{-1}	UV = 0.013 + 0.007(point)	0.0025	-0.001	0.0005	**0.013**	43	0.0006	0.88
TOC, mg/L	TOC = 2.0 - 0.081(temp) + 0.32(point)	**-0.16**	-0.04	0.013	**0.64**	68	0.0002	0.96
SUVA, L/mg/M	SUVA = 0.58 + 0.1(temp) + 0.24(point)	**0.19**	-0.01	0.08	**0.48**	13	0.01	0.83
Combined, %	rem.% = 170 +76.8(dose)+ 10.8(H_2O_2) - 7.5(point)	10	**154**	**22**	**-15**	173	0.0001	0.99
MIB, %	rem.% = 47.5 + 32.5(dose)	5.0	**65**	5.0	-5.0	121	<0.0001	0.95
Geosmin, %	rem.% = 68.4 + 26.1(dose) + 5.1(H_2O_2)	-1.5	**52**	**10**	-4.0	86	0.0001	0.97
IPMP, %	rem.% = 54.9 + 18.4(dose)	6.3	**37**	6.3	-6.3	58	0.0003	0.90
O_3 residual, mg/L	O_3 (mg/L) = 0.33 - 0.09(temp) + 0.15(dose) - 0.05(H_2O_2) - 0.11(point)	**-0.18**	**0.31**	**-0.10**	**-0.22**	19	0.02	0.96

Note:

[1] all factors are in coded scale from (-1, low level) to (+1, high level). Models can also be converted to actual factor

[2] all two-factor interaction effects were statistically insignificant and were

[3] The F-distribution is a probability distribution used to compare variances by examing the ratio. If they are equal, F-value would be 1. The F-value generated by ANOVA analysis is the ratio of model mean square to the error square. The larger the F-value and the more likely the variance contributed by the model is significantly larger random error, and the lower probability of "> F value" will

[4] probability value. For example, p = 0.05 means that the probability of "> F value" for this model is less than 5%, the model has a confidence level of greater than 95%.

[5] **BOLD** fonts represent "significant" effects based on the t-test and model p value.

For example, Table 3 shows the main effects of the combined (in sum) removal of all three odorants in both Tests A and B. Figure 1 plotted these main effects and two-factor interacting effects. The 157% effect of factor "ozone dose" in Test A means that the average combined odorant removal was 157% higher at high ozone level (1.85 mg/l) than at low level (0.5 mg/l). Adding hydrogen peroxide (a high level) increased the combined odorant removal by 24% on average. Ozonation of raw water (a high level) had 23% lower combined odorant removal than ozonation of settled water. In this case, temperature and all two-factor interacting factors were insignificant and thus were not included in the regression model. The best-fit regression model for combined odorant removal in Test A can thus be derived as the following:

Combined odorant removal, % = 157 + 78.5(dose) + 12(H_2O_2) - 11.25(point), if using normalized factor value (-1 to +1), as shown in Table 2.

Table 3 also shows that the regression model for overall combined odorant removal in Test A has a confidence level of 99.98% (1-0.0002=0.9998 of model significance probability; see footnotes in Table 3). The r^2 of 0.99 represents the correlation coefficient between the predicted and actual values, as plotted in Figure 2. Further details regarding the experimental design and analysis can be found elsewhere (Box *et al.*, 1978). It should be noted that the 2-level experimental design is designed for screening the factors (or operational variables). The models and plots presented below are based on linear-regression, which should be regarded as "trend" prediction only. Further optimization involving second-order regression analysis is beyond the scope of this paper.

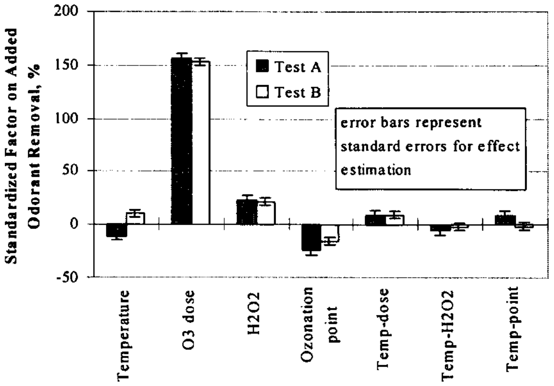

Figure 1. Standardized effect on combined odorant removal - Test A&B

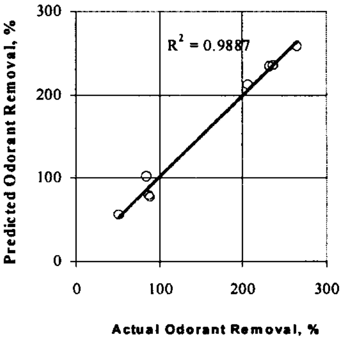

Figure 2. Predicted vs. actual added odorant removal - Test A

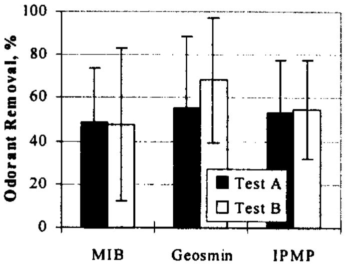

Figure 3. Actual odorant removal under various reaction conditions.

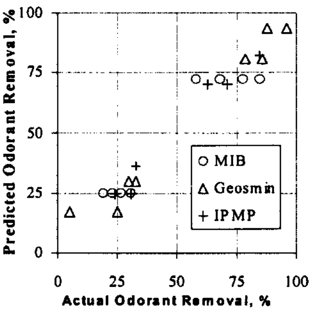

Figure 4. Predicted vs. actual odorant removal - Test A.

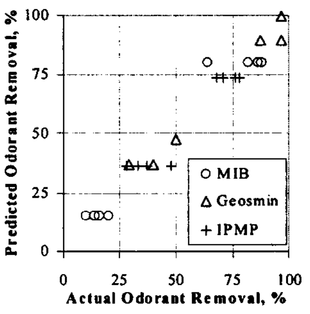

Figure 5. Predicted vs. actual odorant removal - Test B.

Figure 3 presents the average removals and standard deviations for all three odorants during Tests A and B. Although the spike levels of Test A were about four times the levels of Test B, the average percentage removals were very similar for MIB and IPMP between the two tests, except average geosmin removal in

Test B was about 10% higher than in Test A. It is also noted that the TOC levels in the raw water of Tests A and B were 2.9 and 1.7 mg/l, respectively. It is unknown if TOC have had an impact on this finding. Among three spiked odorants, average geosmin removal was the highest, and average IPMP removal was higher than average MIB removal. Figures 4 and 5 compare the predicted removals (by regression model) with the actual removals for all three odorants in Tests A and B, respectively. Figures 4 and 5 also show that 95% of geosmin, 80% IPMP and MIB can be removed in actual runs under the favorable conditions.

Figures 6 through 13 graphically illustrate the impacts of the key factors on odorant removals and other parameters, as shown in Table 3.

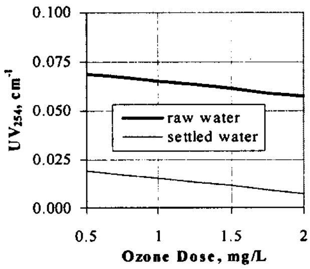

Figure 6. Impacts of ozone dose and application point on UV_{254} - Test A.

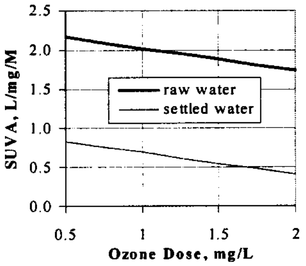

Figure 7. Impacts of ozone dose and application point on SUVA - Test A.

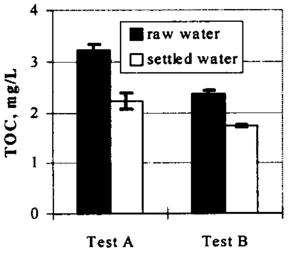

Figure 8. Impact of coagulation on TOC.

Settled water is different from the raw water mainly in UV_{254} and TOC (plus a slight decrease of pH and alkalinity). UV_{254} and TOC represent the bulk of the primary organic constituents in water that competes with odorants for ozone. Figure 6 shows that ozonation point and ozone dose are the major factors affecting the UV_{254} absorbance of the water. Alum coagulation and settling was the most important factor in reducing UV_{254}, which alone reduced UV_{254} from about 0.07 to 0.02 cm^{-1} (or up to 70%). Higher ozone dose (2 mg/l) also decreased the UV_{254} by about 0.015 cm^{-1}, compared to lower ozone dose (0.5 mg/l). Figure 7 shows these factors' impact on specific UV_{254} absorbance (SUVA), which is defined as UV_{254} absorbance (in m^{-1}) normalized per mg/l of DOC, a measure of the high molecular weight fraction of organic carbons (e.g., humic substances) in water. Ozonation point and ozone dose again had similar impacts to SUVA as to UV_{254}. Coagulation alone lowered SUVA from 2.2 to 0.8 L/mg/m (about 60% reduction). Ozonation can also lower the SUVA as indicated by the effect of ozone dose. As shown in the Figure 7, increasing ozone dose from 0.5 mg/l to 2 mg/l lowered SUVA to a limited extent, about 0.4 L/mg/m. Figure 8 shows that TOC reduction (up to 30%) was only achievable by alum flocculation, using the actual TOC data of the sixteen experimental runs. These findings indicate that settled water had up to 70% less high molecular organic carbon and up to 30% lower TOC content than raw water, as indicated by UV_{254}, SUVA and TOC values. Ozonation only achieved limited reduction of UV_{254} and SUVA, but not TOC.

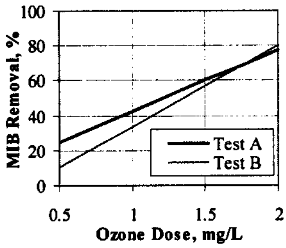

Figure 9. Impacts of O_3 dose and spike level on MIB removal.

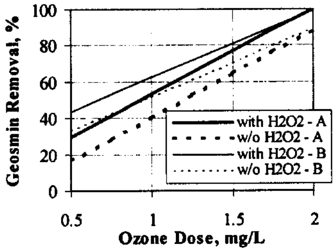

Figure 10. Impacts of O_3 dose, H_2O_2, and spike level on Geosmin removal.

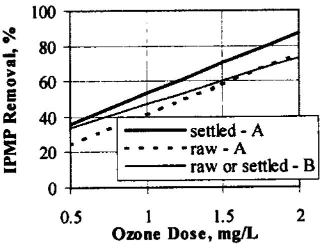

Figure 11. Impacts of O_3 dose, dosing point, and spike level on IPMP removal.

The main effects in Table 3 show that only ozone dose was statistically responsible for MIB removal. Figure 9 illustrates that at 0.5 mg/l ozone dose, only 10% and 25% MIB were removed in Tests B and A, respectively. However, MIB removal increased to 80% in both tests at 2 mg/l ozone dose, a 60% increase. None of the water temperature, H_2O_2, ozone application point, or spike level had significant impacts on MIB removal. It is noted that the odorant removal was almost unaffected by up to 30% TOC and up to 70% UV_{254} reduction in the settled water after coagulation, nor up to 15% UV_{254} reduction (with no TOC reduction) by ozonation. This may indicate that the competing TOC and UV_{254} are so dominant, even in the moderate TOC water such as Detroit River water, that the ozone application point (on raw or settled water, and pre- or intermediate ozonation) may not have effect on odorant removal. For an unknown reason, this is dramatically different from the ozone decay rate that is much faster in the raw than the settled water (data not shown).

Figure 10 plots the impacts from ozone dose, H_2O_2, and spike level on geosmin removal. Ozone dose was the most important factor, which increased geosmin removal from an average of 30% at 0.5 mg/l ozone to 95% at 2 mg/l ozone. Presence of H_2O_2 increased the geosmin removal by about 10% in both Tests A and B. The lower spike level in Test B had about 10% better geosmin removal than lower spike level in Test A, at low ozone dose condition, but both had similar removals at 2 mg/l ozone dose.

Figure 11 shows that ozone dose was also the controlling factor in removing IPMP. Increasing the ozone dose from 0.5 mg/l to 2 mg/l increased the IPMP removal from about 30% to 80% in Test A, and from 35 to 75% in Test B. Ozonation of settled water also had a 10% higher IPMP removal than in the raw water in Test A, but showed no significant increase for Test B. Again, IPMP removals in both tests under different spike levels were similar.

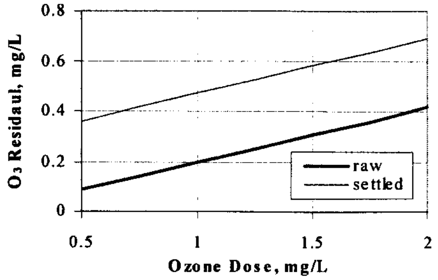

Figure 12. Impacts of O_3 dose, application point on O_3 residual - Test B.

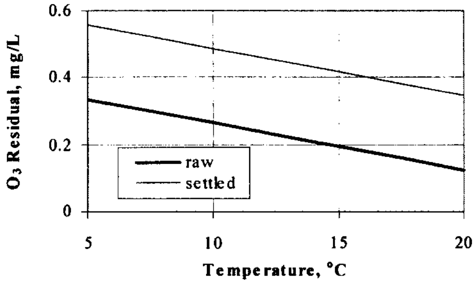

Figure 13. Impacts of temperature, ozonation Point on O_3 residual - Test B.

Figures 12 and 13 show the initial ozone residual (at the end of the ozonation) as a function of the operation conditions in Test B. Figure 12 shows that increasing ozone dose from 0.5 mg/l to 2 mg/l raised the ozone residual from 0.1 to 0.4 mg/l in raw water, and from 0.37 to 0.7 mg/l in settled water. Ozonation of settled water yielded higher ozone residual (over 0.25 mg/l) than to the raw water when other conditions were the same. Lowering the water temperature from 20°C to 5°C also increased the ozone residual by 0.2 mg/l. Therefore, the point of ozonation and the water temperature were not critical in direct odorants removal, but had a significant impact on ozone residual level (in addition to ozone dose.) Ozonated settled water had a higher ozone residual than ozonated raw water, and colder water maintained higher ozone residual. Ozone residual is one of the key design criteria for design of ozonation process to satisfy disinfection needs. Therefore, impacts on water temperature and application point should be evaluated for disinfection when applying ozonation for T&O control. Detailed ozone decay studies and disinfection design criteria evaluations are not covered in this paper.

Test C results plotted in Figure 14 show that ozone with hydrogen peroxide removed grassy and fishy odorants to below detection. It also reduced geosmin, MIB and IPMP levels as demonstrated in Tests A and B. Test C also showed that aeration by oxygen did not impact on the removal of these odorants.

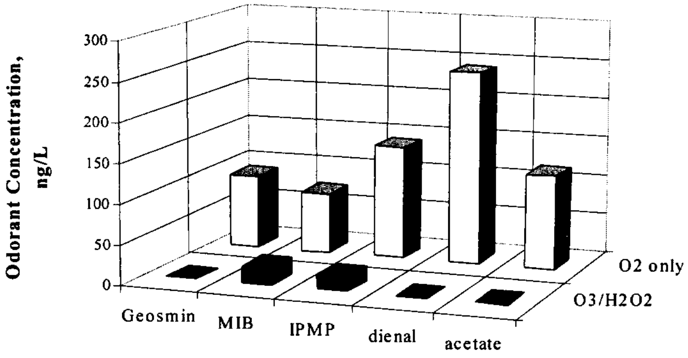

Figure 14. Ozonation removal of five odorants - Test C.

CONCLUSIONS

As expected, ozone dose is one of the most important factors in T&O removal. However, it is a significant finding that ozone dose is far more important than temperature, application point (reflecting TOC, UV_{254}, pH and alkalinity difference), presence of hydrogen peroxide, etc. for odorant removal. For example, the relative insignificance of ozone application point (to raw or settled water) is a finding not considered or reported upon before. It is well known that the ozone decay and consumption is much faster in the raw water than in settled water, or in high TOC water than in low TOC water. The site-specific insignificant $OH^{\bullet}$ radical oxidation mechanism is not widely expected either, even at the tested pH and alkalinity conditions. For example, one pilot study (AWWA, 1991) showed that ozone with hydrogen peroxide achieved higher T&O removals than ozone alone on two raw water sources (which had alkalinity of 75 and 130 mg/l as $CaCO_3$, pH of 8 and 8.3, TOC of 3 mg/l and higher, respectively.)

The conclusions of this ozonation study were:

- Ozonation is effective in mitigating the odors in both the spiked raw water and the source water during actual T&O events. Over 95% geosmin and 80% of MIB and IPMP removal are achievable for Detroit source raw water with an ozone dose of up to 2 mg/l.
- Ozonation removal of odorants, under the tested conditions, was almost exclusively dependent upon the ozone dose. On average, 20% to 30% odorant removals was achieved with 0.5 mg/l ozone, compared to 80% to 95% removal with 2 mg/l ozone.
- Hydrogen peroxide as a catalyst enhanced the odorants removal to a limited extent around pH of 8, and was deemed unnecessary for T&O control in the Detroit River source water.
- Applying ozone to settled water (which had lower turbidity, UV_{254}, and TOC) had slightly higher odorant removal than to the raw water, but achieved much higher ozone residual and usually a lower decay rate, which is critical for design of a disinfection facility.
- Water temperature had almost no effect on odorant removal, but ozone residual was much higher in cold water and had a slower decay rate.
- The levels of odorant as tested had no significant impact on the percentage removal of the odorants.
- Geosmin was found more easily removed by ozone than IPMP or MIB, and fishy and grassy odors were easily removed by ozonation.

ACKNOWLEDGMENT

The authors would like to thank Andrew Ross, Les Opachak, Chitralekha Joshi, Pamela Turner, and Mary Lynn Semegen, all with DWSD, for their contribution to the project.

REFERENCES

AWWA Research Foundation (1991). *Pilot-Scale Evaluation of Ozone and PEROXONE.* Prepared by Metropolitan Water District of Southern California and James M. Montgomery, Consulting Engineers, Inc. ISBN 0-89867-577-4.

APHA, AWWA, WEF (1995). *Standard Methods for Examination of Water and Wastewater*, 19th ed. ISBN 0-87533-223-3.

Box, G.E.P, Hunter W.G. and Hunter J.S. (1978). *Statistics for Experimenters: An Introduction to Design, Data Analysis, and Model Building.* Wiley-Interscience, New York.

Bruchet, A., Khiari D. and Suffet I.H. (1995). Monitoring and analysis. In: *Advance in Taste-and-Odor Treatment and Control*, Suffet, I.H., Mallevialle, J. and Kawczynki, E. (ed). AWWAREF Report. ISBN 0-89867-744-0.

Chen, Theping, Atasi K.Z., Huddleston J.I., Garber J.B., Young C.C. and Suffet I.H. (1996). Comprehensive Investigation of Drinking Water Tastes and Odors in Detroit, Michigan. *Proc. Of AWWA Water Quality Tech. Conf.*, Boston, Massachusetts, USA. Nov. 1996.

Croze, G., Hagstrom J., and White P. (1997) Approach to Design of Ozone Facilities for *Cryptosporadium* Inactivation on Lake Michigan. *Proc. Of AWWA Water Quality Tech. Conf.*, Denver, Colorado, USA. Nov. 1997.

Huck, P.M., Anderson W.A., Andrews S.A., Pereira G., and Lang C.L. (1996) Evaluating the Feasibility of Advanced Oxidation Processes for Removal of Geosmin. *Proc. of AWWA Water Quality Tech. Conf.*, Boston, Massachusetts, USA. Nov. 1996.