



## Project Summary

# Alternative Oxidant and Disinfectant Treatment Strategies for Controlling Trihalomethane Formation

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To comply with the maximum contaminant level (MCL) for total trihalomethanes (TTHM), many utilities have modified their pre-oxidation and disinfection practices by switching to alternative oxidants and disinfectants in place of free chlorine. To evaluate the impact of these changes, a research project was initiated to study several water treatment plants that had recently adopted the use of chlorine dioxide, ozone, potassium permanganate, or chloramines to partially or fully offset the use of free chlorine.

The results of the study showed that total organic halide (TOX) formation paralleled THM formation at all eight of the utilities investigated. The alternative pre-treatment oxidants and disinfectants were depleted rapidly as a consequence of the high TOC concentrations in the waters examined. This implies that residual oxidants and disinfectants will not be carried very far into the process train, causing disinfection and oxidation effectiveness to be reduced. The case study results presented suggest that many utilities, particularly those with high TOC concentrations, will be unable to comply with a significantly reduced MCL for TTHM's using only alternative oxidants and disinfectants without sacrificing finished water quality. Further research is recommended before alternative oxidants and disinfectants can be promoted for extensive use.

*This Project Summary was developed by EPA's Water Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

The final rule establishing an MCL for total trihalomethanes (TTHM) in November 1979 was followed in March 1982 by a guidance document for utilities in which the U.S. Environmental Protection Agency (U.S. EPA) proposed treatment technologies that could be used to control trihalomethane (THM) levels. Three of the five "generally available" treatment methods included the use of chloramines ( $\text{NH}_2\text{Cl}$ ) or chlorine dioxide ( $\text{ClO}_2$ ) as alternative or supplemental disinfectants or oxidants, and the substitution of chloramines, chlorine dioxide, and potassium permanganate ( $\text{KMnO}_4$ ) as pre-oxidants in place of chlorine. The proposal also included, as an additional treatment method for consideration but which was not identified as "generally available," the use of ozone ( $\text{O}_3$ ) as an alternative or supplemental disinfectant or oxidant. These proposals were subsequently adopted by the U.S. EPA in February 1983.

Many water treatment plants have modified their method of disinfection to include the use of chlorine dioxide,

ozone, or permanganate as pre-oxidants with free chlorine as the final disinfectant, and free chlorine as pre-oxidant and primary disinfectant with combined chlorine as the final disinfectant.

When this project began in September 1983, numerous utilities were considering a modification in their oxidant and disinfectant treatment strategies to comply with the THM regulation and still provide an aesthetically acceptable and biologically safe (pathogen-free) supply of water to their customers. However, before such modifications could be encouraged on a widespread basis, an evaluation was needed of the extent to which utilities could comply with the THM regulation by using alternative oxidants and disinfectants, the costs associated with these changes, and the impact of these changes on other treatment objectives and overall finished water quality.

Accordingly, the objectives of this research project were to determine the following:

- (A) the extent to which water treatment plants that had recently adopted the use of chlorine dioxide, ozone, potassium permanganate, or chloramines to partially or fully offset the use of free chlorine had been able to comply with the THM regulation;
- (B) the impact of these modifications on other water quality parameters and other treatment objectives, such as disinfection, iron and manganese removal, total organic carbon (TOC), color and turbidity removal, total organic halide (TOX) formation, and control of taste, odor, and algae; and
- (C) the costs of these modifications and their impact on overall treatment costs and on the average consumer's water bill.

In order to address these objectives, this research project consisted of a series of case study evaluations of utilities adopting alternative oxidant and disinfectant strategies for controlling THM formation.

Of particular interest in connection with Objective B was the impact of these changes on TOX formation. TOX is a collective parameter representing the concentration of all organic halides that has found increased use as a surrogate parameter for other halogenated disinfection by-products which might prove harmful to man.

## Procedure

When this project began in September 1983, large water utilities supplying more than 75,000 consumers had been required to be in compliance with the 0.10 mg/L MCL for TTHM by November 1981. The utilities of intermediate size serving between 10,000 and 75,000 consumers had been required to initiate monitoring of their finished water in the distribution system in November 1982 and to be in compliance with the 0.10 mg/L MCL by November 1983. Because the start of this research project coincided with the THM compliance schedule for these utilities of intermediate size, and because it was believed that these smaller utilities might experience more difficulty in successfully implementing these alternative oxidant and disinfectant programs, this project focused on utilities serving between 10,000 and 75,000 consumers.

At the start of the project, letters were sent to directors of water supply programs in each of the 50 states as well as to each of the U.S. EPA regional offices informing them of the nature of this research project and requesting their recommendations of water utilities within their jurisdiction that might be case study candidates for this project. All of the EPA regional offices and 36 states responded with various recommendations. Telephone calls to many of these utilities and follow-up correspondence describing the nature of the investigation were initiated. Utilities with THM problems that were contemplating the use of alternative oxidant and disinfectant strategies or that had only recently changed their oxidant/disinfection scheme were identified.

Preliminary field visits were made to several of these candidate utilities to review the nature, quality, and variability of the source water, the type of treatment provided and the record of chemical usage, and the quality and variability of the finished water. Based upon these preliminary visits, an analysis of the available data, and, in some cases, preliminary chemical analysis of the THM concentration and THM formation potential of the water, selection of the utilities for detailed case study evaluation was made.

In selecting utilities for evaluation, an attempt was made to choose at least two utilities using or proposing to use each of the four alternatives (KMnO<sub>4</sub>, ClO<sub>2</sub>, O<sub>3</sub>, and NH<sub>2</sub>Cl). Consideration of chloramines was not emphasized at the expense of the other options even though it was, by far, the principal

alternative disinfection strategy being contemplated by the utilities recommended. Consideration was also given to utilities from different geographical regions and to utilities drawing water from different types of sources (i.e., rivers, lakes, groundwater). Utilities in the midst of implementing an alternative oxidant/disinfectant modification were considered ideal candidates for this study since they could provide the most suitable data base for making a meaningful "before and after" evaluation of the impact of the change. Finally, travel and scheduling logistics played a major role in the final selection, and the majority of the utilities selected for this detailed case study evaluation were from the southeastern United States.

The eight utilities examined in detail in this research project, along with selected characteristics of the operations, are shown in Table 1. The eight utilities are distributed among five states (Florida, Indiana, Virginia, North Carolina, and South Carolina), and all but Chesapeake served between 10,000 and 75,000 consumers. One utility uses groundwater as a source of water supply; the others used river or impounded water. Two utilities attempted to solve their THM problems using chloramination, three changed to chlorine dioxide as a pre-oxidant, two use permanganate as a pre-oxidant, and one used ozone for pre-treatment.

Samples were collected by the research team from the various treatment plants from December 1983 through December 1985 on approximately a quarterly basis in order to include operations over all four seasons of the year. TOC and UV samples were taken for raw, settled, and filtered water in order to measure organic carbon removal through the conventional treatment train. Terminal TTHM and TOX samples were collected primarily for raw and settled water in order to measure the extent of precursor removal by coagulation and settling. Instantaneous TTHM and TOX measurements were made on raw, settled, filtered, finished (tap), and representative distribution system samples in order to monitor the progression of trihalomethane and overall organic halide formation.

In addition, the monthly operating reports for the utilities were analyzed for the periods immediately preceding and following the modifications to assess the impact of the alternative oxidant/disinfectant treatment program. The cost of implementing the modifications were calculated from chemical dosages and

**Table 1** Utilities Selected for Detailed Evaluation

Utility	Service Population	Average Flow (in million gal/day)	Source of Water	Alternative Oxidant/Disinfectant Strategy
Chester Metropolitan Water District; Chester, SC	18,000	3.0	River	Moved point of Cl <sub>2</sub> addition to post-sedimentation; ClO <sub>2</sub> applied to raw water.
Bloomington Water Dept.; Bloomington, IN	53,000	12.4	Lake	Added ammonia after sedimentation to convert free chlorine to combined chlorine residual.
Lancaster County Water and Sewer Authority; Lancaster, SC	28,000	1.8	Impoundment	Moved point of Cl <sub>2</sub> addition to post-filtration; ClO <sub>2</sub> , KMnO <sub>4</sub> applied to raw water.
Monroe Water Dept.; Monroe, NC	15,000	7.0	Lake	Moved point of Cl <sub>2</sub> addition to post-sedimentation; relied on KMnO <sub>4</sub> application to raw water.
Palm Beach County Water Utilities Dept.; West Palm Beach, FL	60,000	6.6	Wells	Split part of Cl <sub>2</sub> addition between raw water and post-sedimentation; added ammonia post-sedimentation to produce combined chlorine residual.
Wilmington Public Works Dept.; Wilmington, NC	55,000	8.0	River	Moved point of Cl <sub>2</sub> addition to post-sedimentation; added KMnO <sub>4</sub> to raw water.
City of Belle Glade; Belle Glade, FL	20,000	4.5	Lake	Moved point of Cl <sub>2</sub> addition to post-filtration; installed two-stage ozonation for raw water and pre-filtration application.
Chesapeake Dept. of Public Utilities; Chesapeake, VA	77,000	8.4	River	Conjunctive use of Cl <sub>2</sub> and ClO <sub>2</sub> pre- and post-filtration; installed air-stripping towers prior to distribution.

operating costs provided by utility personnel.

The full report describes the treatment facilities for these eight utilities, presents the historical record of THM compliance monitoring, and presents and discusses the results of the research team's field sampling visits. The impact of the alternative oxidant/disinfectant treatment modifications on finished water quality, treatment plant operations and performance, and cost are evaluated. In addition, the complete data set for samples collected and analyzed by the research team as part of this research project is presented, and correlations between trihalomethane and total organic halide concentrations are explored.

## Results and Discussion

Of the eight utilities examined, two successfully reduced the extent of THM formation to unequivocally demonstrate compliance with the MCL for total trihalomethanes. The other six reduced THM formation significantly but either were unable to clearly demonstrate that they consistently met the requirements of the THM regulation as a result of the modifications, or encountered other difficulties in treatment plant operations or in producing an acceptable finished water. The two successful utilities were Bloomington, IN, and Palm Beach County, FL, both of which adopted chloramination to halt THM formation. While Bloomington experienced no

adverse impacts as a result of the modification, Palm Beach County did encounter some deterioration in finished water quality, notably an increase in color of the finished water causing the utility to periodically exceed the MCL of 15 color units, which is a primary standard in the State of Florida. The cost of implementing the modifications at both utilities was negligible; in fact, Palm Beach County experienced a decrease in chemical costs.

Of the other six utilities, Chester, SC, and Wilmington, NC, both appeared to comply with the TTHM standard as a result of the modifications, but only barely so. Both utilities moved the point of chlorine addition to post-sedimentation; Chester applied chlorine dioxide to the raw water at the flash mix basin while Wilmington applied potassium permanganate at the raw water pump station, 26 miles from the treatment plant. Neither utility experienced any serious adverse impacts on finished water quality or on treatment plant operations as a result of the modifications in oxidation/disinfection practice. At Chester, the turbidity of the finished water deteriorated somewhat after the utility switched to chlorine dioxide. The cost of changing from pre-chlorination to chlorine dioxide pre-treatment had a negligible impact at Chester; the chemical costs increased by \$0.035/1,000 gal, which amounted to 1.27% of the total water cost or an increase of \$1.76 per residence per

year. At Wilmington, the cost of permanganate pre-treatment increased the monthly-average chemical costs by only \$0.011/1,000 gal.

Monroe, NC, relied on potassium permanganate for pre-treatment and moved the point of chlorine addition to post-sedimentation, but did not achieve compliance with the MCL as a result of these modifications. Belle Glade, FL, implemented two-stage ozonation in place of pre-chlorination and reduced THM formation significantly from concentrations approaching 1,000 µg/L to concentrations below 200 µg/L, but the utility was still not in compliance with the MCL for total trihalomethanes. The color of the finished water improved and TOC removal increased by about 5%, but periodic growths of algae were observed in the recarbonation basins after making the pre-treatment modifications. A noteworthy observation is that, as a result of the switch from pre-chlorination to pre-ozonation, the distribution among THM species shifted. Before the change, chloroform constituted an average of 87% of the TTHM's, while after the change, chloroform constituted an average of only 40% of the TTHM's. The remaining 60% were distributed among the various brominated THM species. From a cost standpoint, it was difficult to discern any differences in operating costs after Belle Glade converted to two-stage ozonation. The principal increase in cost appeared to be the capital costs of the installation, which

amounted to an amortized annual cost of \$0.03/1,000 gal.

The last two utilities, Lancaster, SC, and Chesapeake, VA, experienced mixed results after adopting an alternative oxidant/disinfectant program involving chlorine dioxide. Both lowered THM production significantly and, at times, achieved running annual averages of less than 100 µg/L for total trihalomethanes, but neither utility operated consistently for a long enough time to judge the effectiveness of the modified program. Both raw waters had excessive oxidant demands, and both utilities used up to 6 mg/L of chlorine dioxide for pre-treatment. This resulted in high levels of chlorite in the finished water, approaching 3 mg/L at times for both utilities. Additionally, Lancaster County was plagued with manganese problems in their finished water after modifying their treatment program, and Chesapeake had difficulty carrying a residual disinfectant in their distribution system without resorting to high levels of post-chlorination, resulting in excessive THM formation. Chesapeake installed air-stripping towers prior to the high-service pumps feeding the distribution system but, while these seemed to expel effectively the volatile THM's, they did not help the utility achieve compliance with the MCL because of continued formation of THM's in the distribution system. Additionally, the air-stripping towers had no effect on the concentration of the non-volatile halogenated disinfection by-products that comprised about 70% of the TOX concentration.

Results from this research project demonstrate that TOX formation closely parallels THM formation for all of the utilities investigated. The instantaneous TTHM concentration in the finished water, including the distribution system, was strongly correlated with the instantaneous TOX concentration in the finished water. For 166 pieces of data, the correlation coefficient was 0.885. The TOX/TTHM ratio in the treated water was about 3.4:1 for surface waters treated by conventional coagulation, settling, and filtration at near-neutral pH values. On a chlorine-equivalent basis, the THM's comprised approximately 26% of the total organic halide concentration. The concentration of non-volatile organic halides, such as di- and tri-chloro-acetic acid, was collectively approximately three times the concentration of TTHM on a chlorine-equivalent basis.

In waters subjected to precipitative softening at alkaline pH values, the TTHM's comprised about 39% of the

total organic halide concentration in the finished water, on a chlorine-equivalent basis. A reduction in the extent of THM formation as a consequence of modifying the oxidant/disinfectant program resulted in essentially a parallel reduction in the extent of TOX formation.

## Conclusions and Implications

Alternative pre-treatment oxidants and disinfectants were depleted relatively rapidly, particularly in waters having TOC concentrations greater than 5 mg/L. The implications of this rapid rate of depletion are:

- that it will be difficult to carry residual oxidants through the pre-treatment process train;
- that disinfection effectiveness will be reduced as a result of the decrease in "Cxt" for disinfection, i.e., concentration of disinfectant (C) times contact time (t). This rapid rate of depletion will also impact the effectiveness of the oxidant for oxidizing taste and odor compounds, organic color, and iron and manganese.

Accordingly, based upon the results of the case studies, it can be concluded that many utilities will not be able to comply with a significantly reduced MCL for TTHM's using only alternative oxidants/disinfectants and conventional treatment without sacrificing overall finished water quality.

## Recommendations

Before endorsing the widespread application of alternative oxidants and disinfectants for controlling trihalomethane formation in drinking water, additional work needs to be done to better characterize and understand the behavior of these chemicals. The limitations of their use as well as their beneficial properties need to be determined, particularly for ozone and chlorine dioxide, which, until recently, have not been extensively used for drinking water treatment in the United States. As more utilities adopt the use of ozone and chlorine dioxide, detailed evaluations such as those reported in this investigation should be conducted and published so that others can learn from the successes and failures and, thereby, minimize additional failures in the future.

Of specific interest regarding chlorine dioxide and ozone are the kinetics of their reaction with impurities in water, especially humic material, which comprises most of the total organic carbon content of most natural waters. Such reactions are responsible for the

rapid rate of depletion of these strong oxidants, which in turn limits the disinfecting potential. These reactions can produce a variety of disinfection by-products that, for the most part, have not been identified nor have any associated adverse health effects been determined. Disinfection kinetics and by-product identification are areas of critical interest and intense research in the water supply field at this time.

With many utilities beginning to employ a variety of different oxidants and disinfectants during the course of treatment, e.g., permanganate treatment of raw water, chlorine dioxide treatment of settled water, and free or combined chlorine treatment of filtered water, a critical need exists for accurate and precise measurement of the individual oxidant and disinfectant residuals. With current analytical technology, particularly for routine water treatment laboratory use, it is difficult to distinguish among the various residual species.

Specific research questions generated by this research project are:

- What happens to the residual chlorite when water pre-treated with chlorine dioxide is post-treated with chlorine? Is chlorate the principal product of this reaction, or is additional chlorine dioxide produced to act as an oxidant and disinfectant a second time?
- What is the mechanism responsible for the shift in speciation toward brominated THM species when pre-chlorination is replaced by pre-ozonation? How is the extent of this redistribution influenced by the TOC/Br<sup>-</sup> formation in waters with appreciable bromide concentrations?
- What is the most effective means of ensuring the oxidation and retention of manganese in waters containing high concentrations of TOC when pre-chlorination is replaced by alternative oxidants and disinfectants for THM control? What factors are responsible for the retention and release of manganese from filter beds?
- How do water treatment plant operators establish an optimal pre-oxidant dosage to provide for the effective control of iron and manganese, taste and odor, and color, as well as for disinfection, and how do they control this dosage operationally? In the case of pre-chlorination, free chlorine residuals were used to establish the appropriate pre-chlorine dose. In the case of the rapidly depleted

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pre-oxidants chlorine dioxide, ozone, and permanganate, it is difficult to provide a sufficient pre-treatment dose to carry a residual oxidant very far into the treatment train.

It is recommended that these specific questions be addressed and answered before the widespread use of alternative oxidants and disinfectants is promoted.

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*The complete report, entitled "Alternative Oxidant and Disinfectant Treatment Strategies for Controlling Trihalomethane Formation," (Order No. PB 88-238 928/AS; Cost: \$32.95, subject to change) will be available only from:*

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