REDUCTION OF ODORS ASSOCIATED WITH CHLORINE DIOXIDE APPLICATIONS TO DRINKING WATER

by

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(ABSTRACT)

Chlorine dioxide has been used in drinking water treatment for the reduction of trihalomethanes and tastes-and-odors. Recently, chlorine dioxide was implicated as the source of offensive "cat-urine-like" and "kerosene-like" odors in drinking water. The purpose of this project was to determine the cause of odors observed in customers homes at times when chlorine dioxide was being applied to drinking water. Data were obtained through a survey and field sampling at utilities experiencing odor events. Once the cause was determined, potential water-treatment procedures were evaluated in laboratory-scale studies.

Results from a survey sent to water utilities throughout the United States showed that customers who recently had installed new carpeting complained of odors more than those who had not. The use of chlorine dioxide caused responses to intensity of certain tastes-and-odors to increase, two of these odors were cat urine and kerosene.

Field sampling at two water companies during odor events resulted in the discovery of low-levels of residual chlorine

dioxide (0.2-0.7 mg/L) at the tap's of customers. Both the cat-urine- and kerosene-like odors were detected by the research team. To verify a proposed mechanism of odor generation, chlorine dioxide was volatilized in a room with new carpeting. Both odors were produced in amounts great enough to be easily detected by the entire panel.

The removal of residual chlorite from drinking water would block a mechanism by which chlorine dioxide may be reformed from reactions between residual chlorite and free chlorine added for distribution system residual maintenance. Chlorite was removed by powdered activated carbon (PAC) enmeshed in alum floc in laboratory-constituted water and Po River water. A high level of PAC (50 mg/L) was required to effect good removal. A simulated floc-blanket clarifier effectively removed high levels of chlorite (>5 mg/L) from drinking water for long periods (12 hours) when PAC in high concentration was enmeshed in the floc.

Chlorine dioxide reformed in the distribution system of two water companies. When customers opened water faucets, chlorine dioxide volatilized into the room and reacted with organic compounds present in the household air (e.g. from new carpeting) producing the offensive cat-urine-like and kerosene-like odors. The reformation of chlorine dioxide could be effectively eliminated if residual chlorite could be removed by contact with high levels of PAC enmeshed in an alum floc such as one could produce in a floc-blanket clarifier.

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TABLE OF CONTENTS

ABSTRACT. ii

ACKNOWLEDGEMENTS. iv

LIST OF TABLES. x

LIST OF FIGURES xiv

I. INTRODUCTION. 1

A. Background 1

B. Research Objectives. 3

C. Experimental Design. 4

II. LITERATURE REVIEW. 6

A. Introduction 6

B. Tastes-and-Odors 7

1. Importance. 7

2. Taste-and-Odor Control with Chlorine Dioxide 8

3. Taste-and-Odor Enhancement with Chlorine Dioxide 18

C. Chemistry of Chlorine Dioxide. 21

1. Physical and Chemical Properties. 21

2. Generation of Chlorine Dioxide. 21

3. Oxidative Capacity. 23

4. Oxidation of Manganese. 24

5. Oxidation of Iron 25

6. Reactions with Humic Substances 28

7. Fate of Chlorine Dioxide. 30

D. Health Effects 31

1. Chlorine. 31

2. Chlorine Dioxide. 33

3. Comparison of Chlorine and Chlorine Dioxide Mutagenicity. 34

4. Chlorite. 34

5. Chlorate. 36

6. Potential Amelioration Techniques 37

E. Interactions of Chlorine Species with Activated Carbon 38

1. Previous Adsorption Studies 38

2. Adsorption or Reduction 46

F. Pulsed-Bed, Solids Contact Clarifier 46

1. Process Description 46

2. Applications of the Superpulsator 47

III. METHODS AND MATERIALS 51

A. Survey 51

1. Summary of the Survey 51

2. Total Design Method 52

3. Interpretation of the Survey. 52

4. Design of the Database. 53

5. Statistical Methods 53

a. Descriptive Statistics 53

b. Statistical Tests. 54

B. General Analytical Techniques. 57

1. Glassware 57

2. Instrumentation 57
a. Field Instruments. 57
b. Laboratory Instruments 58
3. Chemicals 59
a. Inorganic Salts. 59
b. Chlorine Dioxide 60
c. Carbon 60
4. Characterization of River Waters. 62
C. Field Studies. 62
1. Sampling Strategy 63
2. Confirming Experiments. 64
D. Laboratory Studies 65
1. Fate of Chlorite at the Carbon Surface. .65
2. Kinetic Studies of PAC in Laboratory-Constituted Water 66
3. Kinetic Studies with PAC in Po River Water 67
4. Simulation of a Floc-Blanket Clarifier. .68
IV. RESULTS. 69
A. Survey. 69
1. Descriptive Statistics. 69
a. Overview 69
b. Source Description 70
c. Treatment Provided 70
d. Chlorine Dioxide Use 70
e. History of Taste-and-Odor Problems .79

2. Statistical Tests 83

a. Correlation. 85

b. Chi Square 85

c. Wilcoxon Paired-Sample Test. 85

d. Clustering 87

B. Field Studies. 94

1. Kentucky. 94

2. West Virginia 96

3. Confirming Experiments. 96

C. Laboratory Studies 96

1. Fate of Chlorite in the Presence of Activated Carbon. 96

2. Kinetic Studies with PAC in Laboratory-Constituted Water 106

3. Kinetic Studies with PAC in Po River Water 120

4. Simulation of a Floc-Blanket Clarifier. .125

V. DISCUSSION OF THE RESULTS 133

A. Survey 133

1. Descriptive Statistics. 133

2. Statistical Tests 135

B. Field Studies. 139

C. Laboratory Studies 140

1. Fate of Chlorite in PAC-Treated Water . .140

2. Kinetic Studies with PAC in Laboratory-Constituted Water 142

3. Kinetic Studies with PAC in Po River Water 142

4. Simulation of a Floc-Blanket Clarifier. .143
VI. SUMMARY AND CONCLUSIONS. 145
A. Summary of the Survey Results. 145
B. Summary of Field Results 147
C. Summary of Laboratory Results. 148
D. Conclusions. 149
E. Recommendations for Future Research. 150
VII. LITERATURE CITED. 152
APPENDIX A - Survey as Sent to Customers. 158
APPENDIX B - Letters Sent to Customers with Survey. . .171
APPENDIX C - Tabulated Survey 178
APPENDIX D - Survey Statistics. 198
APPENDIX E - Laboratory Data. 216
VITA. 231

LIST OF TABLES

Table Number		Page
1	Redox Potential of Oxidizing Species	11
2	Threshold Odor Numbers with and without Chlorine Dioxide Treatment at Valparaiso, Indiana	13
3	Company's Reporting Odors Directly Correlated with New Carpeting in Homes of Customers	20
4	Health Effects Related to Chlorination By-Products.	32
5	Effects of Disinfectants on Mutagenicity. TA 104 and TA 100 are Salmonella typhimurium tester strains for the Ames test. LGA is the Luminescent Genotoxic Assay.	35
6	Chloride Mass Balance for Chlorite GAC Reaction	42
7	Comparison of Conventional Clarification and the Superpulsator®	48
8	Effect of the Superpulsator® on the Removal of Turbidity at Fluctuating Influent Conditions.	49
9	Classes of Tastes-and-Odors as Determined by the Research Team. The Classes were Generated from the Thirty-Nine Original Taste-and-Odor Descriptions on the Survey Sent to Water Treatment Companies that Use Chlorine Dioxide	55
10	Annual Raw Water Quality Data as Reported by Water Utilities Responding to the Chlorine Dioxide Survey	73
11	Annual Finished Water Quality Data as Reported by Water Utilities Responding to the Chlorine Dioxide Survey	74

12 Example of a Contingency Table Used In Chi-Square Analyses to Evaluate Responses to Intensity of Kerosene Odors (if value=1 then the odor was never observed, if value=5 then the odor was frequently observed) when Chlorine versus Chloramine was Used as a Final Disinfectant. The Values Below the Intensity Numerals are the Total Number of Responses to Each Intensity Level by the Companies Participating in the Chlorine Dioxide Survey. 86

13 Odors that were Statistically Different in the Presence Compared to the Absence of Chlorine Dioxide as Determined by Responses from Companies Participating in the Chlorine Dioxide Survey. The Odors Listed Below were More Intense in the Presence of Chlorine Dioxide. There were no Differences Observed for Tastes. The Wilcoxon Paired-Sample Test was Used to Determine Differences. 88

14 Responses to Odor Descriptions Reported by Companies Participating in the Chlorine Dioxide Survey were Correlated to One Another by Using a Computerized Cluster Analysis. The Groups of Odors that Companies Responded Similarly to as Determined by the Correlation Matrix are Listed Numerically. Chlorine Dioxide was in Use 89

15 Responses to Taste Descriptions Reported by Companies Participating in the Chlorine Dioxide Survey were Correlated to One Another by Using a Computerized Cluster Analysis. The Groups of Odors that Companies Responded Similarly to as Determined by the Correlation Matrix are Listed Numerically. Chlorine Dioxide was in Use 91

16 Responses to Taste Descriptions Reported by Companies Participating in the Chlorine Dioxide Survey were Correlated to One Another by Using a Computerized Cluster Analysis. The Groups of Tastes that Companies Responded Similarly to as Determined by the Correlation Matrix are Listed Numerically. Chlorine Dioxide was Not in Use 93

17 Chlorine, Chlorite, and Chlorine Dioxide Concentrations (mg/L) Determined by the Amperometric Method in Lexington, Kentucky 95

18 Chlorine, Chlorite, Chlorate, and Chlorine Dioxide Concentrations (mg/L) Determined by the Flow Injection Analysis (FIA) and Amperometric (AMP) Methods in Charleston, West Virginia . .97

19 Odors Generated Upon Volatilizing Chlorine Dioxide in a Room with New Carpeting Located in Blacksburg, Virginia 98

20 Comparison of Ion Chromatography (IC), Amperometric Titration (AMP) and Flow Injection Analysis (FIA) for the Determination of Chlorite. Chlorite was Contacted with Different Concentrations of PAC for 15 minutes and 30 minutes in Milli-Q Water. 103

21 Comparison of Ion Chromatography (IC) and Flow Injection Analysis (FIA) for the Determination of Chlorate. Chlorite was Contacted with Different Concentrations of PAC for 15 minutes and 30 minutes in Milli-Q water. 104

22 Comparison of Ion Chromatography (IC), Amperometric Titration (AMP), and Flow Injection Analysis (FIA) for the Determination of Chlorite. Chlorite was Contacted with PAC (50 mg/L) in Milli-Q water for 48 hours in a Batch Reactor. 108

23 Comparison of Ion Chromatography (IC) and Flow Injection Analysis (FIA) for the Determination of Chlorate. Chlorite was Contacted with PAC (50 mg/L) in Milli-Q Water in a Batch Reactor for 48 Hours 109

24 Reaction Rates (k) for Each Treatment Applied to Laboratory-Constituted Water for the Reduction of Chlorite. . .119

25 Water Quality Characteristics of Po River Water. 121

26 Water Quality Characteristics of Mattaponi River Water. 130

27 Resemblance of Computer Generated Clusters to the Research Team's Imposed Classes for Odors. 138

LIST OF FIGURES

Figure Number		Page
1	Average Monthly Threshold Odor Numbers (TON) for 1947 when Chlorine Dioxide was not in Use and 1948 when Chlorine was in Use at Valparaiso, IN	15
2	Effect of Solution pH and Oxidant Dosage on the Oxidation of Soluble Manganese by Chlorine Dioxide.	26
3	Effect of Solution TOC and Oxidant Dosage on the Oxidation of Soluble Manganese by Chlorine Dioxide.	27
4	Schematic Diagram of the Chlorine Dioxide Generator.	61
5	Distribution of Raw Water Sources Used by Companies Surveyed.	71
6	Distribution of Populations Served by Companies Surveyed	72
7	Distribution of Coagulants by Companies Surveyed	75
8	Distribution of Filtration Methods Used by Companies Surveyed.	76
9	Distribution of Major and Secondary Reasons Given in the Chlorine Dioxide Survey for Applying the Oxidant. . . .	77
10	Monthly Chlorine Dioxide Use as Indicated by Companies Answering the Chlorine Dioxide Survey.	78
11	Distribution of Years of Generator Installation by Companies Surveyed . .	80
12	Test Schedule of Chlorine Dioxide Generator Efficiencies as Determined through the Survey	81
13	Location of Odors in Homes of Customers Represented by the Companies Surveyed.	82

14 Mean of Customer Complaints Attributed to New Carpeting or Recent Decoration by Companies Surveyed. 84

15 Odor Groupings as Determined by Computerized Clustering of Responses to Odor Descriptions Given by Companies Answering the Chlorine Dioxide Survey. Similar Responses are Grouped Together Through a Correlation Matrix. Clusters are Surrounded by Boxes; Ultimately, Seven Clusters were Produced for Odors .90

16 Taste Groupings as Determined by Computerized Clustering of Responses to Taste Descriptions Given by Companies Answering the Chlorine Dioxide Survey. Similar Responses are Grouped Together Through a Correlation Matrix. Clusters were Surrounded by Boxes; Ultimately, Five Clusters were Produced for Tastes 92

17 Chlorite Removal in Milli-Q Water Containing Several Concentrations of PAC (15-minute Contact Time) 99

18 Chlorite Removal in Milli-Q Water Containing Several Concentrations of PAC (30-minute Contact Time) 101

19 Chlorite (A) Removal, and Chloride (B) and Chlorate (C) Formation after 15 minute and 30 minute Reactions with Several PAC Concentrations in Milli-Q Water. 102

20 Chlorite, Chloride, and Chlorate Remaining in Distilled Water After Seven-Day's Contact with Varying Concentrations of PAC. 105

21 Removal of Chlorite by PAC (50 mg/L) in Milli-Q Water 107

22 Evaluation of Second Order Kinetics for the Reduction of Chlorite in Milli-Q Water Using PAC (A). The Log of the X-Axis was Taken to Highlight the Early Reaction Times (B) 110

23 The Reduction of Chlorite in Laboratory-Constituted Water. 112

24 Chlorite Removal in Laboratory-Constituted Water for the Control Run. The Mean Data are Based on Three Different Experiments and Error Bars are One Standard Deviation 113

25 Chlorite Removal in Laboratory-Constituted Water by Alum. The Mean Data are Based on Three Different Experiments and Error Bars are One Standard Deviation 114

26 Chlorite Removal in Laboratory-Constituted Water by PAC (10 mg/L). The Mean Data are Based on Three Different Experiments and Error Bars are One Standard Deviation 115

27 Chlorite Removal in Laboratory-Constituted Water by PAC (50 mg/L). The Mean Data are Based on Three Different Experiments and Error Bars are One Standard Deviation 116

28 Chlorite Removal in Laboratory-Constituted Water by the Combination of Alum and PAC (10 mg/L). The Mean Data are Based on Three Experiments and Error Bars are One Standard Deviation. 117

29 Chlorite Removal in Laboratory-Constituted Water by the Combination of Alum and PAC (50 mg/L). The Mean Data are Based on Three Experiments and Error Bars are One Standard Deviation. 118

30 Concentrations of Chlorine Dioxide and Chlorite During Preoxidation of Po River Water by Chlorine Dioxide. Initial Dose was Determined in Distilled Water. . . .122

31 The Reduction of Chlorite in Po River Water. 123

32 The Reduction of Chlorine Dioxide in Po River Water by One of Four Treatments. .124

33 The Reduction of Chlorine Dioxide and the Subsequent Formation of Chlorite in Po River Water During the Control Run. The Mean Data are Based on Three Experiments and Error Bars are One Standard Deviation 126

34 The Reduction of Chlorine Dioxide and the Subsequent Formation of Chlorite in Po River Water During Alum Treatment. The Mean Data are Based on Three Experiments and Error Bars are One Standard Deviation 127

35 The Reduction of Chlorine Dioxide Followed by Chlorite Reduction in Po River Water During PAC Treatment (50 mg/L). The Mean Data are Based on Three Experiments and Error Bars are One Standard Deviation 128

36 The Reduction of Chlorine Dioxide and Chlorite by Alum and PAC Treatment in Po River Water. The Mean Data are Based on Three Experiments and Error Bars are One Standard Deviation. 129

37 The Removal of Chlorite Through the Simulation of a Floc-Blanket Clarifier. The Feed Concentration of Chlorite was 9.58 mg/L. 132

CHAPTER 1

INTRODUCTION

BACKGROUND

Chlorine dioxide has been applied in drinking water treatment since the early 1940's for the removal of obnoxious tastes-and-odors (Synan, 1944). In 1974, chlorination of water was found to result in the formation of trihalomethanes (THM; Rook, 1974). Trihalomethanes are low-molecular-weight, organic compounds that cause an increased incidence of tumor formation in laboratory animals (National Cancer Institute, 1976). To decrease the level of THM's in drinking water, the U.S. Environmental Protection Agency (USEPA) suggested that chlorine dioxide be applied as a preoxidant, alternative, or as a supplemental oxidant to chlorine (USEPA, 1983).

Recently, the application of chlorine dioxide has been associated with offensive odors at random points throughout the distribution system of many water companies. Consumers have become both irritated and frightened by obnoxious cat-urine-like and kerosene-like odors they smell when they use their water. The level of fear can be better understood from the following quote taken from the November 9, 1986 Lexington Herald-Leader newspaper, Lexington, Kentucky.

"Could it be that new chemicals are being formed from the chlorine dioxide that are causing the smell? If this is the case, what effect will these new chemicals have on our population? I guess we, as guinea pigs, will just have to wait and see. I suggest we should watch the cancer statistics."

The American Water Works Association Research Foundation (AWWARF) was established in the early 1980's to promote and fund research into water treatment techniques that could be used to solve water problems. Early in 1988, AWWARF sought proposals that would identify the cause of odors associated with chlorine dioxide and investigate techniques to alleviate the odors. Researchers at Virginia Polytechnic Institute and State University (VPI&SU) were awarded the project based on a proposal entitled "Cause and Control of Taste-and-Odor Problems Associated with the Use of Chlorine Dioxide as a Primary Disinfectant and Oxidant." The goals of this project were as follows.

1. Collect historical data from utilities where chlorine dioxide was being applied in order to determine if a relationship existed between water-quality and the nature of complaints.

2. Identify the specific agent(s) responsible for the taste-and-odor episodes associated with chlorine dioxide by sampling both air and water at sites experiencing odor events.

3. Reproduce in the laboratory the odor(s) observed in the field to establish the conditions under which it is produced.

4. Propose methods for controlling the taste-and-odor problems associated with preoxidation of raw water with chlorine dioxide.

RESEARCH OBJECTIVES

This research was a subset of the AWWARF research proposal previously described. Specifically, the objectives of this research were:

1. Conduct a survey of water utilities to determine:
    a. if water quality parameters were associated with odor events.
    b. if the dose of chlorine dioxide was correlated with an increase in odor events.
    c. if odors were different when chlorine dioxide was in use compared to when it was not in use.
    d. if the final disinfectant caused odors.
2. Sample residual oxidants at sites experiencing odors.
3. Determine, through laboratory testing, methods to remove the odor-causing compound(s).

EXPERIMENTAL DESIGN

To meet the research objectives established, the survey and on-site sampling were conducted first to determine what type of laboratory study would be appropriate for odor removal.

The survey was sent to thirty-seven utilities that applied chlorine dioxide. To ensure a good response to the survey, the "total design method" was utilized (Dillman, 1978). The total design method consisted of an initial mailing of the survey, followed by a postcard reminder two weeks later, followed by a second copy of the survey five weeks later. Data collected from the survey were entered into a database on the mainframe computer. The data were then analyzed by application of the Statistical Analysis System (SAS), release 5.18, at the VPI&SU computing center.

Field studies focused on finding the cause of the odors and on monitoring of residual oxidants (chlorine dioxide, chlorite, chlorate, and chlorine) in two cities during odor events. Samples were taken from various points in the plant, at homes experiencing the odor problems, and at neighboring homes free of the problem. Oxidants were determined by both amperometric titration (Aieta et al., 1984) and flow injection analysis (Themelis et al., 1989).

From analyses of the survey and field sampling for residual oxidants, the conclusion was that chlorine dioxide

reforms in the distribution system from chlorite. The reformed chlorine dioxide volatilizes in the homes of customers and reacts with precursor organic compounds in the household air, many of which originate from new carpeting (Hoehn et al., 1990). The purpose of the laboratory phase of the project was to remove residual chlorite from drinking water so chlorine dioxide could not reform in the distribution system.

Four experiments were performed to investigate removal of residual chlorite. First, water containing chlorite was treated with powdered activated carbon (PAC) to determine if chlorite could be removed. A mass balance was conducted by monitoring chlorite, chlorate, and chloride. Second, laboratory-constituted water containing chlorite was treated with alum alone, carbon alone, and alum and carbon in combination. The kinetics of the removal of chlorite were evaluated. Third, river water was treated with chlorine dioxide for thirty minutes, then treated with alum alone, carbon alone, and alum and carbon in combination. Residual chlorite was measured at intervals. The rate of chlorite removal was determined for the reaction conditions. Fourth, water containing chlorite was contacted with a high level of PAC enmeshed in alum to simulate a pulsed-bed, solids-contact clarifier. Residual chlorite in the effluent was monitored.

CHAPTER 2

LITERATURE REVIEW

INTRODUCTION

The literature review consists of five main sections. The first section provides a chronological history of chlorine dioxide use for the removal of tastes-and-odors; the section is closed with very recent information concerning the enhancement of odors with the use of chlorine dioxide. As a review, the second section provides information concerning the fundamental chemistry of chlorine dioxide. Since the discovery of carcinogenic substances in drinking water in the early 1970's, the health effects of chemicals used in water treatment have become an area of active research. Some of these studies concerning chlorine dioxide and it's residual oxidants are summarized in section three. Activated carbon was used in this current research as a means to remove residual chlorite from drinking water, previous studies concerning oxidants and activated carbon are presented as section four. The final section reviews recent studies of water treatment with powdered activated carbon in a pulsed-bed, solid-contact clarifier. The clarifier was simulated in this current research, to determine it's potential for chlorite removal.

TASTES-AND-ODORS

IMPORTANCE

The purpose of water treatment is to remove unacceptable constituents from water to make it safe and palatable. Offensive tastes-and-odors may either discourage consumers from drinking treated water or cause them to think that the water quality is unacceptable. A fundamental goal in water treatment, therefore, is to remove offensive tastes-and-odors that encourage the consumer to seek an alternate source which may not meet the standards for potable water.

One such incidence occurred in Whiting, Indiana, before 1934 (Besozzi and Vaughn, 1949). Residents in Whiting, which is located along the south shore of Lake Michigan, found their water "virtually undrinkable" because of tastes-and-odors. The tastes-and-odors were attributed to severe pollution of the raw water source (Lake Michigan) by both industrial and domestic wastes. Threshold odor numbers (TON) ranging from 500 to 1,000 were observed on several occasions. The current secondary maximum contaminant level (MCL) for odor is 3 TON. The water was treated with alum for coagulation and chlorine for disinfection, but tastes-and-odors persisted. Because of the offensive tastes-and-odors in the water, bottled water companies were distributing most of the water used for drinking at costly prices to the consumer.

TASTE-AND-ODOR CONTROL WITH CHLORINE DIOXIDE

Tastes-and-odors are either synthetically fabricated or naturally occurring (Lin, 1976). Synthetically made tastes-and-odors are chemicals originating from industrial discharges and by-products of treatment whereas the naturally occurring ones are associated with the presence of decaying organic matter and biological growths. Currently, the two most-common treatment techniques for controlling tastes-and-odors in surface-water supplies are breakpoint chlorination and activated carbon, while the most common control technique for groundwater treatment is aeration (Viessman and Hammer, 1985). When breakpoint chlorination, activated carbon, and aeration fail to reduce tastes-and-odors, an alternate process, such as chlorine in combination with chlorine dioxide, can be used.

The first reported application of chlorine dioxide for taste-and-odor control was in 1944 shortly after sodium chlorite was introduced commercially (Synan and MacMahon, 1944). Water utility personnel in Niagara Falls, New York, experimented with chlorine dioxide [2-4 pounds (lb) chlorite / million gallons (MG)] in combination with chlorine in place of breakpoint chlorination. The process combined pretreatment with chlorine for disinfection and post-treatment with chlorine dioxide to remove tastes-and-odors. By applying chlorine dioxide, the utility could eliminate use of activated carbon, thus reducing the costs of treatment by 72.6 percent. The problems were due to "surges" of phenolic tastes-and-odors

and seasonal algal tastes-and-odors (Synan and MacMahon, 1944). The taste-and-odor problems were controlled by the application of chlorine dioxide (Aston, 1947).

Because the experimental process was so successful, full-scale application was started with excellent taste-and-odor control at Niagara's main plant in July, 1944 (Aston, 1947). In September of that same year, the Western New York plant at Woodlawn also implemented a similar process (2.5 lb chlorite/ MG). Excellent control of phenol and oily tastes-and-odors were obtained with the use of chlorine dioxide. To ensure an "unfailing satisfactory supply" and to gain "consumer confidence," chlorine dioxide was applied continuously.

In November, 1944, Tonawanda and North Tonawanda, New York, both adopted treatment with chlorine dioxide to successfully control tastes-and-odors. Tonawanda, similar to other water treatment plants at the time, was not able to provide a free chlorine residual throughout the distribution system. Thus, the implementation of chlorine dioxide (3-3.5 lb chlorite / MG) had a twofold effect. One was the relief of taste-and-odor problems and the other was the production of a free chlorine residual throughout the distribution system. Some tastes-and-odors were observed in the distribution system during the first week of application, but the cause was attributed to the oxidation of slime growths in pipes what had not previously carried a chlorine residual.

In January, 1945, the water utility personnel in

Chicopee, Massachusetts, applied chlorine dioxide (2.5 lb chlorite/MG) for the reduction of musty- and vegetable tastes-and-odors (McCarthy, 1944). Immediate reduction of the odors was observed; threshold odor numbers were reduced from 10 to 1.5. To remove the musty odor, the chlorine dioxide dose was doubled. The musty odor was eliminated, but consumers complained of medicinal, chlorinous, and kerosene tastes. The kerosene taste was assumed to be hydrocarbons entering the water supply, because the taste was not noticed at the treatment plant but at distant points in the distribution system. The chlorine dioxide dose was reduced, and a decrease of tastes-and-odors was achieved.

The use of chloramines, activated carbon, and breakpoint chlorination did not consistently remove tastes-and-odors at Lawrence, Kansas, but successful treatment was achieved by the application of chlorine dioxide in combination with activated carbon and chlorine (Mounsey and Hagar, 1946). The tastes-and-odors were due to organic pollution, algae, decaying vegetation, spring thaws and surface runoffs. Contact of the water with activated carbon for six or more hours followed by the application of chlorine dioxide provided the most economical treatment; higher bacterial quality, attributed only to increased amounts of chlorine, was achieved. In Table 1, the oxidative power of chlorine dioxide and chlorine are shown (Masschelein and Rice, 1979). These oxidation potentials indicate that the overall disinfecting capacity was

Table 1. Redox Potential of Oxidizing Species (Masschelein and Rice, 1979).

SPECIES	OXIDATION POTENTIAL (Volts)
Hypochlorous Acid	1.49
Chlorine	1.36
Chlorine Dioxide (gas)	1.15
Chlorine Dioxide (aq)	0.95
Chlorite	0.78

likely enhanced by the presence of chlorine in combination with chlorine dioxide and residual chlorite ion.

Chlorine dioxide was applied at Valparaiso, Indiana, for the treatment of tastes-and-odors derived from algal blooms and turnovers in a small, inland lake (Coote, 1950). During June and July, algal blooms were attributed to Anabaena, Asterionella, Ceratium, Cyclops, Melosira, Synura, and Vorticella. During the cold temperature periods, the lake would turnover and the tastes-and-odors would be more offensive. In June, 1948, chlorine dioxide treatment (8 lb chlorite/MG) was applied as pretreatment for the reduction of a musty odor and a bitter taste. The tap water TON was reduced from 12 to 5 (Table 2) within three hydraulic detention times thus improving the water. Areas provided with water through wooden pipes were relieved of wood tastes-and-odors immediately upon chlorine dioxide application.

In the fall of 1948, a bloom of Synura occurred causing a very bitter taste in the water supply. Treatment with chlorine dioxide (3-8 lb chlorite/MG) reduced the taste within a few hours to low levels. In October, two of the intakes for the plant were broken during a windstorm that caused a rapid change in the water quality. The appearance of a sour, weedy odor at the plant justified the application of chlorine dioxide (10 lb chlorite/MG). Within an hour, the odor was very slight in the hot water and not detectable in the cold water of the plant (Coote, 1950). During spring turnover, the

Table 2. Threshold Odor Numbers With and Without Chlorine Dioxide Treatment at Valparaiso, Indiana (after Coote, 1950).

COLD TAP WATER TASTE-AND-ODOR	RAW (TON)	TAP (TON)	CHLORINE RESIDUAL (mg/L)
Very Musty Odor Very Bitter Taste	40	12	---
Slight Cl_2 Odor No Taste	40	5	1.5

application of chlorine dioxide kept the TON level between 5 and 7, but at the higher dose, a bitter taste was observed. Additional laboratory testing of chlorine dioxide application as a post-treatment decreased the TON from 7 to 3. A medicinal odor and a "sickening" oily taste developed with post-treatment; therefore, chlorine dioxide was applied as a pretreatment and not as a post-treatment. The overall improvement of tastes-and-odors at Valparaiso is summarized in Figure 1.

Chlorine dioxide was used effectively for the control of algae odors caused by Anabaena at the Eden Creek Filtration Plant, McNeil Island, Washington. The use of chlorine dioxide also had the added advantage of longer filter runs and the removal of manganese (Harlock, 1953). The cost of the treatment was the same as that of breakpoint chlorination.

Chlorine dioxide was tested in laboratory, bench-scale experiments at the Philadelphia Suburban Water Company. The chemical was applied for the removal of musty and woody tastes-and-odors from Crum Creek. A Gram-positive filamentous bacterium, known as actinomycetes, and some blue-green algae are now known to cause musty and woody odors in water. The application of chlorine dioxide (up to 12mg/L) did not remove the tastes-and-odors; the TON was reduced from 40 to only 22 at the highest dose (Shull, 1962). The application of activated carbon in combination with chlorine produced a satisfactory product. The failure of chlorine dioxide in this

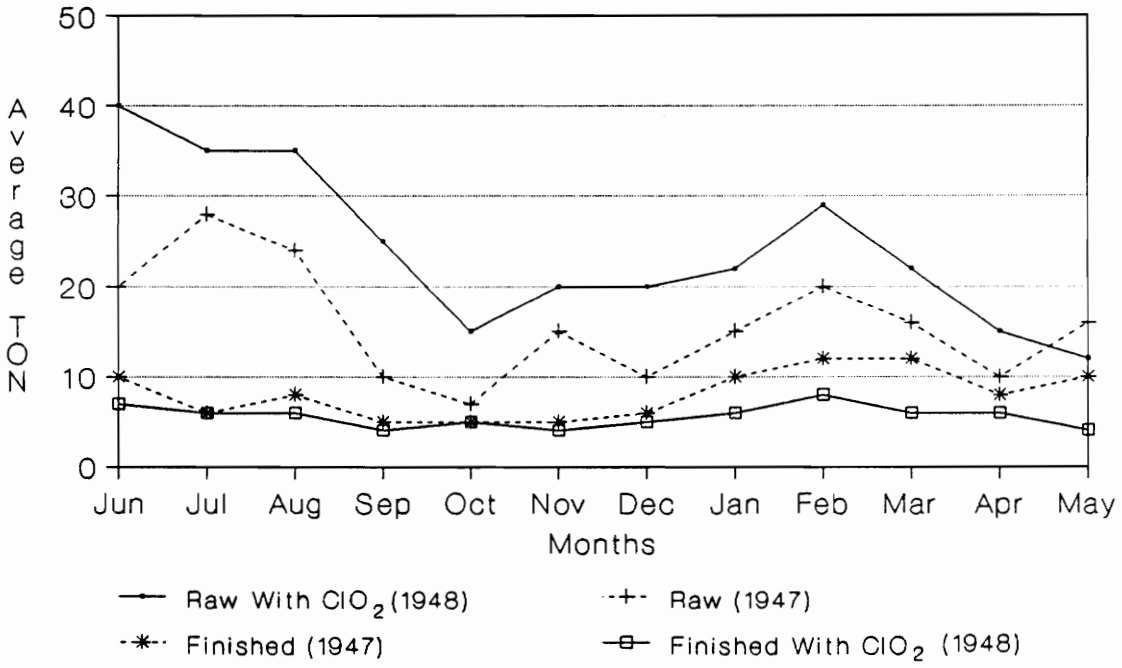

Figure 1. Average Monthly Threshold Odor Numbers (TON) for 1947 when Chlorine Dioxide was Not in Use and 1948 when Chlorine Dioxide was In Use at Valparaiso, IN (Coote, 1950).

case may have been due to inadequate generation of chlorine dioxide. Current Laboratory studies have shown that the efficiency of chlorine dioxide generation by reaction of aqueous chlorite with aqueous chlorine (HOCl) probably was only 30-40 percent (Walker, 1985).

Chlorine dioxide was applied for the reduction of a phenolic taste in the water supply of Medmenham, England (Brett and Ridgeway, 1981). Phenol was leached from an industrial source to the raw water supply during periods of heavy rainfall. After treatment of the raw water with chlorine, severe chlorophenolic tastes were created, inducing "numerous complaints." The application of chlorine dioxide generated from chlorite and chlorine completely removed the taste.

Water treatment personnel in Edmonton; located in the province of Alberta, Canada; successfully applied chlorine dioxide for the reduction of tastes-and-odors (Walker et al., 1986). Chlorine dioxide (0.15-1.2 mg/L) was applied at the head of the plant for the removal of five classes of tastes-and-odors: chlorophenols, hydrocarbons, chlorinous, musty/earthy, and fishy.

The first, chlorophenols, accounted for most of the customer complaints (75-300) during the spring thaw (TON=20-40). Upon application of chlorine dioxide, the "medicinal" or "chemical" tastes-and-odors were no longer observed (Walker et al., 1986). The second group was hydrocarbons such as

"gasoline" and "kerosene." Which were thought to be derived from street runoff. They were not completely removed by chlorine dioxide application either alone or in combination with activated carbon. The third group was dichloramine odors such as "chlorinous" and "bleach-like." These tastes-and-odors were not totally removed by the addition of chlorine dioxide. The fourth group was metabolites of actinomycetes causing "musty" and "earthy" tastes-and-odors that were alleviated by the application of chlorine dioxide. The fifth group was metabolites of algae thought to cause a "fishy" taste-and-odor in the water. This taste-and-odor was also removed with the use of chlorine dioxide (Walker, 1986).

Five compounds known to cause earthy-musty tastes-and-odors were oxidized by chlorine, chlorine dioxide, ozone, or manganese dioxide adsorption in laboratory, bench-scale reactors (Lalezary et al., 1986). Chlorine dioxide was the most effective for removing all five of the compounds: trans-1,10-dimethyl-trans-9 decalol (geosmin); 2,3,6-trichloro-anisole (TCA); 2-isopropyl-3-methoxy pyrazine (IPMP); 2-isobutyl-3-methoxy pyrazine (IBMP); and 2-methyl-isoborneol (MIB). At practical chlorine dioxide doses (3.8 mg/L) and contact times, the removals of IPMP, IBMP, and TCA were greater than 50 percent. Under the same conditions, the removals of MIB and geosmin were less than 30 percent. Although these results suggest that chlorine dioxide is the best oxidant of earthy-musty tastes-and-odors, the complete

removal of geosmin and MIB is probably enhanced by the coupling of activated carbon and preoxidation at most water treatment plants.

To comply with federal THM criteria and reduce taste-and-odor complaints, the Galveston County Water Authority, Texas City, Texas, began pretreatment with chlorine dioxide. A new generator was installed to provide a good conversion efficiency (> 98 percent) of chlorite to chlorine dioxide (Myers et al., 1986). Upon installation of the generator, the THM levels were below the MCL and no taste-and-odor complaints were received. Before the use of chlorine dioxide complaints had occurred with the intermittent bloom of blue-green algae in the raw water. Chlorine dioxide application further enhanced treatment by providing a decrease in filter fouling, improved finished-water turbidities, and excellent bacterial removal.

TASTE-AND-ODOR ENHANCEMENT WITH CHLORINE DIOXIDE

Unlike the other studies mentioned thus far, chlorine dioxide was recently found to be the source of odors in the distribution at Lexington, Kentucky, and Charleston, West Virginia (Hoehn et al., 1990). Low levels of chlorine dioxide were found in the distribution system at both cities. Chlorine dioxide was thought to be regenerated in the distribution system by one of the following reactions:

$$ClO_2^- + HOCl \rightarrow \text{Oxychlorine Intermediates}$$

$$\text{Oxychlorine Intermediates} \rightarrow ClO_2 + Cl^- \quad [1]$$

$$ClO_2 + 1e^- + H_2O\text{-demand} \rightarrow ClO_2^-$$

$$ClO_2^- + HOCl \rightarrow ClO_2 + Cl^- \quad [2]$$

When the customer opened a water faucet, chlorine dioxide would volatilize and react with precursor organic compounds (possibly derived from new carpeting) in the household air. Odors were described as "cat urine" and "kerosene." The researchers concluded that the odors may be prevented by reducing residual chlorite or by ammoniation to form chloramines. The latter would remove a principal reactant in the equations shown previously.

In a draft report to AWWARF, the possible link with new carpeting was cited, but no mechanism for odor generation was proposed (George, 1989). George noted that since the use of chlorine dioxide had begun (1983), personnel at the WTP in Mobile, Alabama, reported several complaints of disagreeable odors from customers in homes or businesses that had recently installed new carpeting.

Many water utilities have indicated that the combination of chlorine dioxide and new carpeting causes odor complaints to increase (Hoehn et al., 1990). The company, number of complaints, and common odor descriptions are summarized in Table 3.

Table 3. Company's Reporting Odors Directly Correlated with New Carpeting in Homes of Customers (Hoehn et al., 1990).

COMPANY	ODOR COMPLAINTS (Total Number)	ODOR DESCRIPTORS
Duck River Utility Commission Tullahoma, TN	19	Cat Urine, Kerosene, Merthiolate
Deans Mill WTP Mystic, CT	3	Kerosene, Plastic
Southern Nevada Water System Boulder City, NV	5	Kerosene
Kansas City, KS	ALL	Kerosene, Strong Body Odor
Latham Water District, Colonie, NY	54	Kerosene, Cat Urine, Gas-like, Grassy, Chemical, Strong Chemical, Permanent Wave Solution, Septic, Skunk, Pine Sap, Rotten Eggs, Sulfide, Strong Body Odor

CHEMISTRY OF CHLORINE DIOXIDE

PHYSICAL AND CHEMICAL PROPERTIES

Chlorine dioxide is a yellow-green gas which forms an orange-red color as the concentration increases (Gall, 1978). The formula for chlorine dioxide is ClO_2 and the molecular weight is 67.46 grams (g)/mole. Chlorine-oxygen bonds show a double-bond character and form an angle of 117.5°, and, the chlorine-oxygen bond length is approximately 1.47 Å, and, chlorine dioxide has a dipole moment of 1.69 Debye units (Gordon, 1972). The freezing point is -59°C and the boiling point is 11°C (Masschelein and Rice, 1979).

The solubility of chlorine dioxide in water, like that of all gases, is dependent on temperature and pressure. At room temperature, 25°C, and 40 millimeters (mm) partial pressure, its solubility is 2.9 g/Liter (L; Gall, 1978). In chilled water, the solubility increases to more than 10 g/L (Sussman and Rauh, 1978). Chlorine dioxide is sensitive to temperature and pressure changes with explosive qualities observed above -40°C, thus making compression and storage of chlorine dioxide gas commercially unsuccessful. Therefore, chlorine dioxide is manufactured at the site where it is used (Aieta and Berg, 1986).

GENERATION OF CHLORINE DIOXIDE

In drinking water treatment, chlorine dioxide is always generated from sodium chlorite (Aieta and Berg, 1986).

Chlorite is oxidized by hydrochloric acid or chlorine gas, as shown by the following reactions (Masschelein and Rice, 1979):

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + 2H_2O \quad [3]$$

$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl \quad [4]$$

The generation of chlorine dioxide by acid and chlorite is not commonly practiced because the maximum conversion of chlorite to chlorine dioxide is only 80 percent (Aieta and Berg, 1986). The excess chlorite inherent in this system is known to be converted to chlorate (ClO_3^-) by the following reaction (Masschelein and Rice, 1979):

$$4NaClO_2 + 2HCl \rightarrow 2ClO_2 + NaClO_3 + 3NaCl + H_2O \quad [5]$$

The most common method of chlorine dioxide generation is by reacting chlorite with chlorine (Reaction 4), because 100 percent conversion is feasible. Sodium chlorite is either mixed with an aqueous chlorine solution or chlorine gas (Aieta and Berg, 1986). At high pH values, chlorate formation could occur by the following reaction:

$$NaClO_2 + Cl_2 + OH^- \rightarrow NaClO_3 + HCl + Cl^- \quad [6]$$

In practice, chlorine dioxide is impure and is accompanied by chlorine and sometimes by chlorates (Masschelein and Rice,

1986).

OXIDATIVE CAPACITY

"Available chlorine" is a term used to define the oxidizing capacity of any compound relative to chlorine (Gall, 1978). The oxidizing capacity is measured by the release of free iodine from potassium iodide (Sussman and Rauh, 1978). The reduction of chlorine species are monitored by one of the following reactions with iodide (Aieta et al., 1984):

$$Cl_2 + 2I^- \rightarrow I_2 + 2Cl^- \quad [7]$$

$$2ClO_2 + 2I^- \rightarrow I_2 + 2ClO_2^- \quad [8]$$

$$2ClO_2 + 10I^- + 8H^+ \rightarrow 5I_2 + 2Cl^- + 4H_2O \quad [9]$$

$$ClO_2^- + 4I^- + 4H^+ \rightarrow 2I_2 + Cl^- + 2H_2O \quad [10]$$

$$ClO_3^- + 6I^- + 6H^+ \rightarrow 3I_2 + Cl^- + 3H_2O \quad [11]$$

The available chlorine is calculated by the following equation (Sussman and Rauh, 1978):

$$\frac{\Delta \# e^- * 35.5}{\text{Molecular Weight}} * 100 = \text{Percent Available Chlorine}$$

By this definition, if chlorine dioxide is completely reduced to chloride, then it has an available chlorine content of 263 percent compared to 100 percent for chlorine, and 53 percent for chlorite. Although, chlorine dioxide usually reacts by a one electron transfer and forms residual chlorite which, therefore, has an available chlorine content of only 53

percent. The oxidative capacity of chlorine dioxide has been applied for the oxidation of manganese, iron, and humic precursors of THM's. These applications of chlorine dioxide in water treatment are the topic of the following sections.

OXIDATION OF MANGANESE

Low levels of manganese (> 0.05 mg Mn/L) in the distribution causes black water which is associated with staining clothes and fixtures (White, 1972). Chlorine dioxide oxidizes manganese (II) to manganese (IV) by forming an insoluble precipitate manganese dioxide. Theoretically, chlorine dioxide is fully reduced to chloride during the oxidation of manganese by the following reaction (Aieta and Berg, 1986):

$$2ClO_2 + 5Mn^{2+} + 6H_2O \rightarrow 5MnO_{2(s)} + 12H^+ + 2Cl^- \quad [12]$$

The complete reduction of chlorine dioxide to chloride requires a five-electron transfer. The reduction occurs in two distinct steps as follows (Masschelein and Rice, 1979).

$$ClO_2 + 1e^- \rightarrow ClO_2^- \quad [13]$$

$$ClO_2^- + 4H^+ + 4e^- \rightarrow Cl^- + H_2O \quad [14]$$

Both reactions will occur at pH values less than 2, but only reaction [13] will occur at a pH of 7; therefore, the oxidation of manganese by chlorine dioxide under drinking

water conditions occurs as follows (White, 1972):

$$2ClO_2 + MnSO_4 + 4NaOH \rightarrow MnO_{2(s)} + 2NaClO_2 + Na_2SO_4 + 2H_2O \quad [15]$$

In a recent laboratory study (Knocke et al., 1987) a stoichiometric dose for manganese oxidation was calculated based on chlorite as the reduction product of chlorine dioxide. The researchers found that a dose at least twice the stoichiometric requirement was needed to reduce the level of manganese to the drinking water secondary MCL (< 0.05 mg Mn/L) in a reasonable time. The oxidation of manganese with chlorine dioxide was good over a range of pH values (Figure 2) but was prolonged at high concentrations of total organic carbon (TOC; Figure 3).

OXIDATION OF IRON

Low levels of iron (>0.3 mg Fe/L) in the distribution system directly cause staining of plumbing fixtures and laundered clothes, and indirectly cause tastes-and-odors. The tastes-and-odors are generated from the distribution system growths of iron bacteria, which eventually decay causing tastes-and-odors. Chlorine dioxide alleviates these problems by oxidizing iron (II) to iron (III). The oxidation forms a brown precipitate iron hydroxide [$Fe(OH)_{3(s)}$] which can be removed by subsequent sedimentation and filtration. The oxidation of iron by chlorine dioxide at drinking water conditions occurs by the following reaction (White, 1972):

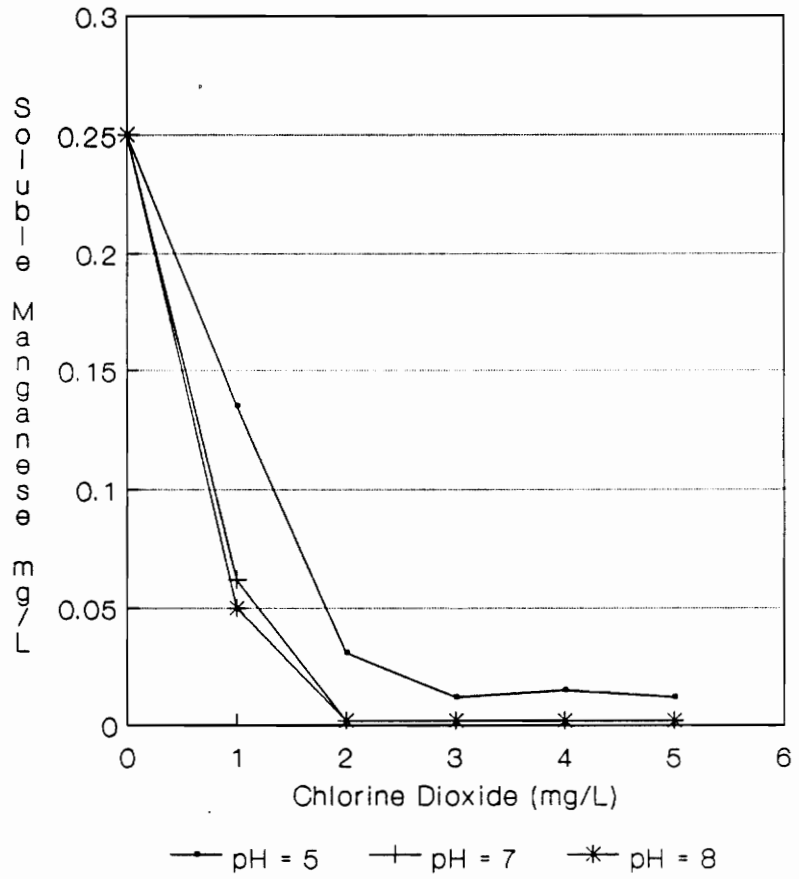

Figure 2. Effect of Solution pH and Oxidant Dosage on the Oxidation of Soluble Manganese by Chlorine Dioxide (after Knocke et al., 1987).

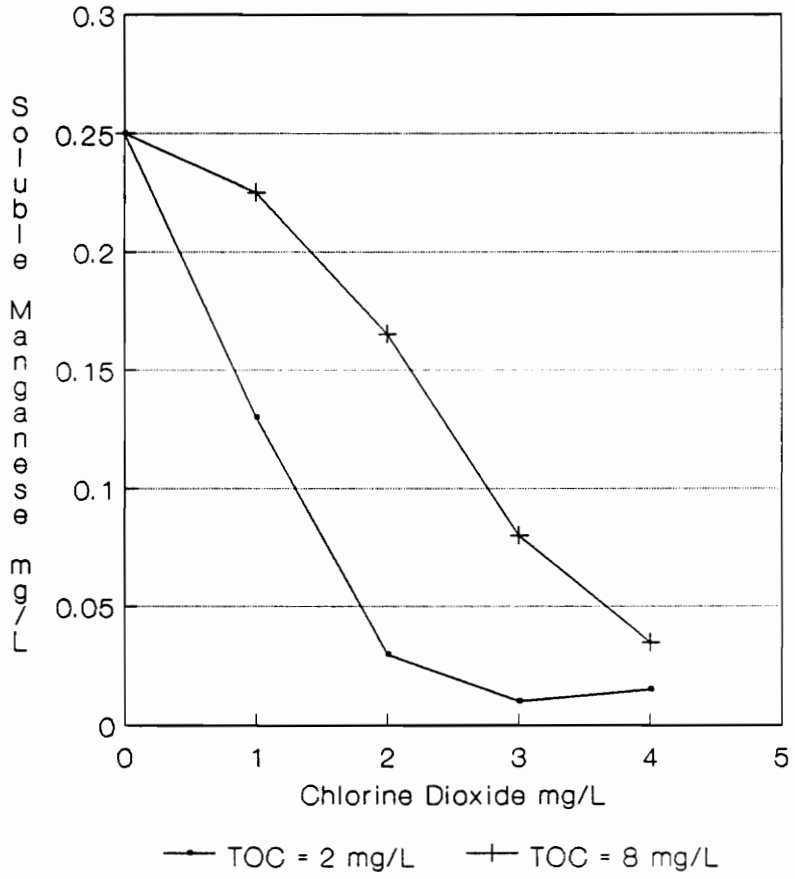

Figure 3. Effect of Solution TOC on the Oxidation of Soluble Manganese by Chlorine Dioxide (after Knocke et al., 1987).

$$ClO_2 + FeO + NaOH + H_2O \rightarrow Fe(OH)_{3(s)} + NaClO_2 \qquad [16]$$

REACTIONS WITH HUMIC SUBSTANCES

Nearly all chlorine containing chemicals in water supplies originate from chlorination during water treatment, runoff, and wastewater discharges (Fleischacker and Randtke, 1983). In 1974 the chlorination of water was found to form trihalomethanes (Rook, 1974). In 1976, trichloromethane (chloroform) was found to cause an increased incidence of tumor formation (National Cancer Institute, 1976). Since that time, the USEPA has set a MCL of 0.10 mg/L for total THM's. As a means to reduce the concentration of THM's in water, one of the USEPA suggestions was to use chlorine dioxide as a preoxidant, alternative, or as a supplemental oxidant to chlorine (USEPA, 1983).

In experiments by Werdehoff and Singer (1987), extracted fulvic acid from Lake Drummond (TOC=4.5 mg/L), Virginia was pretreated with chlorine dioxide (2mg/L) for two hours and then chlorinated (20 mg Cl_2/L) for seven days. Samples were then analyzed for THM and total organic halide (TOX) formation potential (FP). Samples that were pretreated with chlorine dioxide showed a 27 percent reduction in THMFP and TOXFP. These reductions were dependent on a ClO_2:TOC weight ratio greater than 0.4. The reduction of THM's indicated that chlorine dioxide was reacting with THM precursor compounds making them unavailable for THM formation. Chlorine dioxide

reacted by a one-electron transfer forming chlorite as the principal end-product (Werdehoff and Singer, 1987).

In related experiments, water high in humic matter was treated with chlorine dioxide or chlorine, and the treated water quality compared (Mallevialle et al., 1978). Water collected from the forest near Fontainebleau, France, was separated by ultrafiltration. Organic matter retained by membranes with a molecular weight sizing greater than 10,000 were designated as "humic acids," while those greater than 2,000 but less than 10,000 molecular weight were designated as fulvic acids. In this case, 70 percent of the organic carbon content was considered humic acids while the other 20 percent was "fulvic acids." Chlorine dioxide and chlorine (2, 20, or 400 mg/L) were contacted with the water for 1, 4, or 22 hours. No differences were noted between the oxidants for removals of color, TOC, or fluorescence. Chlorine dioxide did not induce any formation of halogenated compounds, whereas chlorine did.

To control THM's, Evansville, Indiana, started preoxidation with chlorine dioxide in August, 1983 (Lykins and Griese, 1986). Chlorine dioxide effected a 60 percent reduction in THM's as compared to chlorine with an average total THM concentration between 50 and 80 μg/L in the finished water. Although the THM's were reduced, the average concentration of TOC remained the same. To maintain a residual disinfectant throughout the distribution system and control THM's, chlorine dioxide was used as a preoxidant and

chlorine as a postoxidant. The addition of chlorine dioxide as a preoxidant for a city in South Carolina effected a water bill increase of $1.77/residence/year (Lykins and Griese, 1986).

FATE OF CHLORINE DIOXIDE

In drinking water treatment, chlorine dioxide usually reacts by a one-electron oxidative pathway (Equation 13) forming the inorganic by-product chlorite. Postoxidation of chlorite by chlorine results in the formation of chlorate or chlorine dioxide, depending on the pH of the solution (Aieta and Roberts, 1984). At acidic pH values, chlorine is present mainly as dissolved molecular chlorine and it can react with chlorite by one of the following reactions (Aieta and Roberts, 1984).

$$Cl_2 + 2ClO_2^- \rightarrow 2ClO_2 + 2Cl^- \quad [17]$$

$$Cl_2 + ClO_2^- + H_2O \rightarrow ClO_3^- + 2Cl^- + 2H^+ \quad [18]$$

At near-neutral pH, chlorine is present mainly as hypochlorous acid and reacts with chlorite by one of the following reactions (Aieta and Roberts, 1984; Singer and O'Neil, 1987):

$$HOCl + 2ClO_2^- + H^+ \rightarrow 2ClO_2 + Cl^- + H_2O \quad [19]$$

$$HOCl + ClO_2^- + OH^- \rightarrow ClO_3^- + Cl^- + H_2O \quad [20]$$

At alkaline pH, chlorine is present mainly as hypochlorite ion

and reacts very slowly as follows (Aieta and Roberts, 1984).

$$OCl^- + ClO_2^- \rightarrow ClO_3^- + Cl^- \quad [21]$$

HEALTH EFFECTS

CHLORINE

The toxicological effects of the inorganic species used during chlorination (chlorine, hypochlorous acid, and hypochlorite ion) of drinking water have not been specifically shown (Condie, 1986). For example, mice given free available chlorine (HOCl) in drinking water for 30-50 days did not show any abnormalities upon autopsy and histologic examination. In another study, seven generations of rats were exposed to chlorinated drinking water. The number of malignant tumors were the same in the exposed rats and in the control group.

Since 1974, studies have focused on the by-products of chlorination. Specifically, the reaction of organic material naturally present in source water (humic and fulvic acids) with chlorine have gained national and international attention by the water industry. The effect of some of the identifiable chlorination by-products are listed in Table 4. The reaction of naturally occurring organics with chlorine are so diverse that the chemicals responsible for more than 90 percent of the mutagenic activity have not yet been identified (Condie, 1986). The presence of the strong Ames mutagen 3-chloro-4-

Table 4. Health Effects Related to Chlorination By-Products (Condie, 1986).

CHEMICAL CLASS	BY-PRODUCT	TOXICOLOGICAL EFFECT
Trihalomethanes	Chloroforms	Carcinogenic, Hepatotoxic, Renal Toxic
	Dichlorobromo-methane	Hepatotoxic, Renal Toxic
	Dibromochloro-methane	Hepatotoxic, Renal Toxic
Haloacetonitriles	Chloro-acetonitrile	Genotoxic Developmental
	Dichloro-acetonitrile	Mutagenic, Genotoxic, Developmental
Chlorophenols	2-Chloro-phenol	Fetotoxic, Tumor Promotor
	2,4,6-Tri-chlorophenol	Carcinogenic Fetotoxic Tumor Promotor

(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX) has recently been identified as increasing mutagenic activity in extracts of chlorinated humic water (Kronberg et al., 1988). This is currently an active area of research.

CHLORINE DIOXIDE

Condie (1986) presented an excellent overview of the toxicological studies of chlorine dioxide. A summary is provided in the following paragraphs. Chlorine dioxide was found to produce hemolytic anemia by causing oxidative damage to the membranes of red blood cells in mice. Monkeys were treated with increasing doses of chlorine dioxide; therefore, each monkey served as its own control. Chlorine dioxide caused decreased thyroxine levels in the blood of the monkeys. Thyroxine is active in stimulating the metabolism of the liver and muscles (Lehninger, 1982). Thyroxine levels were also reduced in 21-day-old rats whose parent was exposed to chlorine dioxide through drinking water (100 mg/L). The 21-day-old rats also had delayed brain development and behavior.

Human volunteers were exposed to increasing doses of chlorine dioxide for one day. No effect was observed in blood parameters, serum or urine values, or adverse physical symptoms. In a similar experiment, no effects were detected after 84 days of exposure of human volunteers to 5 mg/L chlorine dioxide in drinking water. Consumers were exposed to chlorine dioxide (0.25-1.1 mg/L) in their drinking water for 12 weeks. No changes were observed in the following clinical

parameters: hematocrit, hemoglobin, red blood cell count, mean corpuscular volume, methemoglobin, blood urea nitrogen, serum creatinine, total bilirubin, reticulocyte count and osmotic fragility.

COMPARISON OF CHLORINE AND CHLORINE DIOXIDE MUTAGENICITY

Water from lake Kinnereth in Israel was tested for the presence of mutagenic activity by the Ames test (Salmonella typhimurium tester strains, TA 104 and TA 100) and a luminescent genotoxic assay (LGA, Guttman-Bass et al., 1987). Experiments were conducted on lake-water samples, humic substances extracted from sediments in the lake, and on commercial humic acids. Samples were either untreated or disinfected with chlorine or chlorine dioxide. Treatment with chlorine dioxide decreased the mutagenic ratio of the lake water and the humic materials (Table 5). Thus, chlorine dioxide oxidized some mutagens to inactive products. The humic material extracted from the sediment in the lake provided a similar mutagenic response as the lake water (Table 5). Therefore, testing humics extracted from the natural system in question may provide a better mutagenic guide than using commercially available humic acids (Guttman-Bass et al., 1987).

CHLORITE

Condie (1986) also provided an overview of health effects associated with chlorite. Chlorite is the most potent by-product of chlorine dioxide disinfection, causing hemolytic

Table 5. Effect of Disinfectants on Mutagenicity. TA 104 and TA 100 are Salmonella typhimurium tester strains for the Ames test. LGA is the Luminescent Genotoxic Assay (Guttman-Bass et al., 1987).

TREATMENT	TA 104	TA 100	LGA
UNTREATED			
Lake Water	NM	M	M
HA Lake Sediment	M	M	M
HA Commercial	M	NM	M
CHLORINE			
Lake Water	NM	M	M
HA Lake Sediment	M	NM	M
HA Commercial	M	M	M
CHLORINE DIOXIDE			
Lake Water	NM	NM	NM
HA Lake Sediment	NM	NM	NM
HA Commercial	M	NM	M

HA - Humic Acids M - Mutagenic NM - Not Mutagenic

oxidative stress in animals. Female mice were exposed to chlorite from the time of breeding to the time of weaning. The growth rates and body weight of the pups were lower than a control group not exposed to chlorite. In another study, female mice were exposed to extreme levels of chlorite causing an increase in stillbirths. When chlorite (100 mg/Kg) was applied twice weekly to the shaved backs of Sencar mice for 51 weeks, no tumors were detected. Consumers were exposed to chlorite (3.2-7 mg/L) in their drinking water for 12 weeks. No changes were observed in the clinical parameters listed: hematocrit, methemoglobin, red blood cell count, mean corpuscular volume, blood urea nitrogen, serum creatinine, total bilirubin, reticulocyte count, and osmotic fragility.

CHLORATE

Condie (1986) also provided an overview of health effects associated with chlorate. Chlorate was found to cause hemolytic anemia in the red blood cells of rats and monkeys. The mutagenic potential of chlorate was evaluated by mouse micronucleus assay and mouse bone marrow chromosomal aberration assay. No mutagenic activity was observed. Rats were exposed to 1 percent solutions of $NaClO_3$ and $KClO_3$ in their drinking water for 25 weeks. No renal carcinogenic effect was observed.

Chlorate has been used to control weeds, the following results were obtained from accidental human exposure to the chemical during use for weed control (Condie, 1986). A dose

of 3400 mg/Kg ingested by humans will cause cyanosis, methemoglobinemia, renal failure, congested kidneys, hypothermia, convulsions, and coma. The lowest lethal dose is known to be 220 mg/Kg in adults and 250 mg/Kg in infants.

Consumers were exposed to chlorate (0.87-1.8 mg/L) in their drinking water for 12 weeks. No changes were observed in the clinical parameters listed: hematocrit, methemoglobin, red blood cell count, mean corpuscular volume, blood urea nitrogen, serum creatinine, total bilirubin, reticulocyte count, and osmotic fragility (Condie, 1986).

POTENTIAL AMELIORATION TECHNIQUES

Chlorine dioxide, chlorite, and chlorate, can be formed as a result of the application of chlorine dioxide for drinking water treatment. Because of potential health effects, the USEPA recommends that the residual, combined-oxidant concentration (the combined total of residual chlorine dioxide, chlorite ion and chlorate ion) be no greater than 1 mg/L (National Research Council, 1980). Because most chlorine dioxide is directly converted to chlorite, the current application of chlorine dioxide in water treatment is limited to approximately 1.0-1.4 mg/L. Current opinion is that the USEPA likely will place more stringent guidelines ($\leq$ 0.5 mg/L) on the total combined-residual oxidants.

In response to the USEPA requirement to eliminate total combined-residual oxidants, the following techniques need further development to determine their potential for residual

oxidant removal. First, the application of sulfur dioxide (SO_2) shows potential to remove chlorite ion in the pH 5.5-7.5 range by the following reaction (Slootmaekers et al., 1986):

$$SO_3^{2-} + ClO_2^- \rightarrow SO_4^{2-} + Cl^- \quad [22]$$

Second, generators used to manufacture chlorine dioxide on-site at drinking water treatment plants must be properly adjusted to alleviate the formation of chlorate. Third, the presence of iron has shown potential to remove residual chlorite by the following reaction:

$$5Fe^{2+} + ClO_2 + 13H_2O \rightarrow 5Fe(OH)_{3(s)} + Cl^- + 11H^+ \quad [23]$$

Fourth, the use of activated carbon has shown potential for the removal of residual chlorite in drinking-water-treatment applications (Jackson et al., 1987; Voudrias et al., 1983). The application of powdered activated carbon (PAC) for the removal of chlorite was investigated as part of this thesis research.

INTERACTIONS OF CHLORINE SPECIES WITH ACTIVATED CARBON

PREVIOUS ADSORPTION STUDIES

The adsorption capacity of granular activated carbon (GAC) for four, polar compounds (nitromethane, methyl ethyl

ketone, n-butanol, and 1,4-dioxane) was decreased after oxidation of the carbon surface by sodium hypochlorite (McGuire and Suffet, 1984). The reduction in capacity was thought to occur by a pore-blockage mechanism. Oxidized surfaces of the carbon were found to consist of polar functional groups which interact with water, which is the most polar compound in the system, and, therefore, block the entrance sites for adsorption of other compounds. Column studies showed also that an increase in chlorine dose effected a decrease in the adsorption capacity of the GAC. In another study, ozone and potassium permanganate caused a decrease in the adsorption capacity of several organic compounds with an increase in oxidant dose.

McCreary and Snoeyink (1981) adsorbed peat extracted humic substances to GAC. A solution of free chlorine was applied to the column of peat-adsorbed-GAC. No organochlorine compounds were detected, indicating that the chlorine reacted with the GAC instead of the organics adsorbed on the carbon. No differences were observed in the type of compounds in the influent and the effluent (as monitored by gas chromatography), except that the effluent concentrations were lower. Hence, adsorbed compounds did not form any new detectable chlorination products.

Powdered activated carbon (PAC), enmeshed in alum floc, showed a higher rate of adsorption after 24 hour of exposure when compared to PAC alone. The solutes tested were 2,4-

dichloro-phenoxy-acetic acid, 2-nitrophenol, nitro-benzene, phenol, cresol (Lettinga et al., 1978). The results suggest that diffusion through the liquid layer surrounding the activated carbon particles may be the main barrier to mass transport instead of "floc particle diffusion." The transport mechanism also may be governed by the reversal of adsorption and the solubility or molecular dimension of the solute (Lettinga et al., 1978).

Because chlorite can produce adverse health effects, the German standard for chlorite in finished water is 0.2 mg/L (Oehler and Schuettler, 1986). Water containing high concentrations of organic material have a high chlorine dioxide demand; high concentrations of residual chlorite result. Oehler and Schuettler reported applying several types of PAC to chlorite solutions in batch reactors to determine the feasibility of residual oxidant removal by PAC. When Hydraffin AP PAC (400 mg/L) was contacted with chlorite (9 mg/L), 98 percent of the chlorite was removed from solution within two hours. In a similar experiment, Hydraffin 800 effected a removal of 50 percent in three hours. An increase in temperature caused an increase in chlorite removal. These results suggest that the removal may not have been by a pure adsorption process because many chemical reactions have been shown to occur faster at higher temperatures, on the other hand, diffusion also occurs faster at increasing temperatures. The removal was not well described by the equations of

Freundlich.

In studies by Dielmann (1981), batch experiments were conducted over a 24 hour period in which GAC columns (Calgon Filtrasorb 400) were used to remove chlorite to determine if chlorite removal was by adsorption. He found that chlorite removal by GAC was in the range of 7.27 to 195.19 mg per g GAC. Residual chloride was found to be the main reaction product to within 10 percent of the theoretical mass balance (Table 6). Theoretical increases in chlorite concentration were calculated from the amount of chlorite destroyed, and experimental values were measured in terms of increased chloride concentrations (Voudrias et al., 1983). Therefore, chlorite was found to be reduced to chloride by GAC (Dielmann, 1981). All chlorite dosages below 70 mg/g carbon resulted in complete chlorite removal.

Bench-scale, column (0.5 g GAC) studies by Dielman (1981) indicated also that chlorite (11 mg/L) initially was completely removed, but after the addition of 85-90 mg chlorite per gram of carbon, a rapid increase of chlorite in the effluent was observed, followed by a gradual increase in effluent chlorite concentrations until they became constant. At that time, the chlorite concentration passing through the column was 94 percent of the applied. He proposed that chlorite was reacting with particular functional groups on the surface of the carbon, and, once the sites had been used, chlorite would pass through the column unreacted. The six

Table 6. Chloride Mass Balance for Chlorite GAC Reaction (Dielmann, 1981).

ClO_2^- Dosage (mg ClO_2^- / g GAC	Theoretical Cl GAIN (mg)	Experimental Cl GAIN (mg)	Percent Difference
7.27	0.38	0.37	2.6
9.05	0.38	0.58	0.0
12.13	0.38	0.37	2.6
18.39	0.38	0.35	7.9
36.77	0.38	0.35	7.9
70.66	0.36	0.32	11.1
120.39	0.29	0.27	6.9
24.40	6.90	6.60	4.3
28.03	6.90	6.50	5.8
32.50	6.90	6.20	10.1
39.32	6.90	6.40	7.2
48.85	6.90	6.30	8.7
65.31	6.90	6.60	4.3
97.77	6.80	6.20	8.8
195.19	5.10	4.80	5.9

percent removal was attributed to a reversal of the reaction, thus freeing some sites for continued reaction.

Chlorine dioxide application was investigated as a potential oxidant at a 1.0 MGD pilot water-reuse plant in Denver, Colorado (Lohman and Rogers, 1987). The capacity of Calgon Filtrasorb 300 GAC (1 g) to reduce chlorite (100 or 500 mg total chlorite in solution) was determined over a 24- or 72-hour period. On average, 92 mg chlorite/g of GAC was removed with no significant increase in removal efficiency between the 24- and 72-hour experiments. Bench-scale, column (10 g GAC) studies indicated that a high loading of chlorite, > 68 mg chlorite / g GAC, slowed reduction. Good chlorite removal was affected when chlorite was contacted for adequate reaction times. For instance, good removal of chlorite (4 mg/L) was achieved on the column at feed rates below 15 mL/min. A plateau of chlorite removal (70 percent chlorite reduction) was achieved at 7920 bed volumes (equivalent to 6.4 months of plant operation). These results suggest that chlorite does not react by a single mechanism at specific sites, but by a reversible reaction, therefore causing equilibrium to be established (Lohman and Rogers, 1987).

The identity of products formed by the reaction between chlorine dioxide and hydrocarbons (ethylbenzene, indan, tetralin, diphenylmethane, and fluorene) adsorbed on GAC surfaces were investigated by Chen et al. (1982). In aqueous solution, the reaction of chlorine dioxide with hydrocarbons

having benzylic hydrogen atoms (listed above) formed mainly ketones and alcohols. In another experiment, the hydrocarbons listed above were reacted with chlorine dioxide for 2.9 minutes and then passed through a GAC (HD3000) bed. Chlorinated compounds such as chloroindan were identified in the effluent.

Chen et al. (1982) also conducted batch experiments with chlorine dioxide (2.3 g) contacting GAC (HD3000, 1 g carbon) for 10 days. Purge-and-trap analyses identified no volatile organic compounds. Chlorate, which was determined by the o-tolidine method, represented 22-37 percent of the initial chlorine dioxide concentration; the only other inorganic species found in solution was chloride. In a similar experiment, a lower dose of chlorine dioxide (0.03 g) was passed through a GAC (1 g) column. No volatile organic compounds were released into the effluent. The only inorganic product found in the effluent was residual chloride.

The reactions between chlorine and chlorine dioxide with resorcinol both in aqueous solution and adsorbed on GAC (HD3000) were investigated to determine the types of products that are formed (Jackson et al., 1987). In aqueous solution, the three-hour reaction of chlorine (1:3 and 1:5 mol ratio) with resorcinol ($5X10^{-4}$ M) mainly formed chlorinated resorcinols and chlorinated cyclopentene-1,2-diones. When chlorine dioxide (1:2 and 1:1 mol ratio) was reacted for 24 hours with resorcinol ($5X10^{-4}$ M), the main reaction product

formed were dichlorocyclopentene-1,3-dione. Chlorine and chlorine dioxide were reacted with resorcinal preadsorbed on GAC. Both oxidants produced 5,5-dichlorocyclopent-3-ene-1,2-dione as a main reaction product, indicating that similar, free-radical intermediates may be formed on the carbon surface by both oxidants. No products were found when aqueous resorcinol was applied to GAC columns following contact of the column with chlorine or chlorine dioxide.

A batch reaction between chlorite (10.4 mg/L) and vanillic acid (2.6 mg/L) for 5 min, 1 hour, or 24 hours showed that no reaction occurred (Voudrias et al., 1983). In a similar experiment, the same concentration of chlorite (20 L) and vanillic acid (20 L) were contacted for 0.5 minutes and then passed over a GAC (1.6 g, 6.4 mLs/min) column. The reaction products detected by gas chromatography/mass spectrometry (GC/MS) were several methoxyhydroxy benzene compounds, 2-methyl-3-furancarboxylic acid methylester, 1,1,3-trichloro-2-butanone, and a methylated vanillic acid (Voudrias et al., 1983). The identity of several compounds detected by the analysis was unknown. The products discovered when GAC was present indicate that reactions occurring at the carbon surface include: decarboxylation and hydroxylation of the aromatic ring, demethylation of methoxy-substituents, and carbon dioxide fixation on the aromatic ring (Voudrias et al., 1983).

A similar experiment was conducted using indan. The

reaction products (indan-1-one, indan-1-ol, unknown MW=148) were the same whether the reaction was carried out in solution or in the presence of carbon (Voudrias et al., 1983).

ADSORPTION OR REDUCTION

Powdered activated carbon has two advantages over GAC. First, PAC costs three times less than GAC (Lettinga et al., 1978). Second, compounds adsorb faster on PAC because the surface area of PAC is greater than that of GAC (Lettinga et al., 1978). These two advantages attract the water industry to research the mechanisms by which carbon removes pollutants from water. The summary in the previous section indicates that researchers have found that other mechanisms besides adsorption may be responsible for chlorite reduction by GAC. To date, no one has researched either the fate of chlorite in the presence of PAC or determined the reaction rate at practical, water-treatment concentrations.

PULSED-BED, SOLIDS-CONTACT CLARIFIER

PROCESS DESCRIPTION

The Superpulsator® Clarifier is designed to perform three functions in one tank during water treatment. First the water is flocculated and then clarified. Finally the sludge is concentrated and removed (Hartman and Jaccarino, 1987). Initially, coagulated water is evenly distributed over the bottom of the tank, and the water rapidly flocculates due to

a pressure differential generated by a vacuum pump. Water then flows upward and moves through the floc blanket contact zone where sludge concentrations are from 2000 to 7000 mg/L. A series of fiberglass plates, positioned at sixty degree angles to the horizontal, forms an inclined channel which is the solids/liquid separation zone. Clarified water (turbidity = 0.5 - 3.0 NTU depending on raw water conditions) flows through this zone to perforated collection laterals and floc flows down the plates and back into the blanket. A vacuum-release valve is opened causing a "surge" of water to be distributed, thereby, lowering the hydraulic head within the clarifier and allowing the cycle to repeat itself (Hartman and Jaccarino, 1987).

APPLICATIONS OF THE SUPERPULSATOR®

In the spring of 1985, a pilot plant (4.0 MGD) Superpulsator® was installed at Red Lion, Pennsylvania (Hartman and Jaccarino, 1987). The purpose of the study was to determine the effect of rise rates on effluent turbidity. The results showed that the effluent turbidity in the Superpulsator® was equal to or better than that obtained in the existing clarifier which had a rise rate of 0.3 GPM/ft^2 (Table 7, Hartman and Jaccarino, 1987). During an increase in turbidity of 91 percent over a 4 day period, the maximum turbidity of the Superpulsator® effluent was 3.8 NTU (Table 8, Hartman and Jaccarino, 1987).

A pilot plant (0.035 MGD) Superpulsator® was installed at

Table 7. Comparison of Conventional Clarification and the Superpulsator® (Hartman and Jaccarino, 1987).

RAW WATER Influent Turbidities, NTU	4.1	3.1	3.5	3.9
CONVENTIONAL CLARIFICATION				
Rise Rate, GPM/ft^2	0.3	0.3	0.3	0.3
Effluent Turbidity, NTU	1.2	1.3	0.94	0.9
SUPERPULSATOR®				
Rise Rate, GPM/ft^2	2.5	3.0	3.5	4.0
Effluent Turbidity, NTU	0.79	0.88	1.1	0.9

Table 8. Effect of the Superpulsator® on the Removal of Turbidity at Fluctuating Influent Conditions (Hartman and Jaccarino, 1987).

DATA	INFLUENT TURBIDITY (NTU)	EFFLUENT TURBIDITY (NTU)
6/14/85	18	0.9
6/17/85	91	2.7
6/18/85	197	2.5
6/18/85	147	3.8
6/18/85	207	1.9
6/18/85	17	1.7

Newport News, Virginia, in 1985 to determine operating conditions for the full-scale clarifier scheduled to go on-line in 1988 (Hoehn et al., 1987). Studies were conducted to determine the effectiveness of PAC (Aqua Nuchar and Nuchar SA) for reducing turbidity and THM precursors. The Superpulsator® removed turbidity to less than 1 NTU with high rise rates up to 4.0 GPM/ft^2 .

The enmeshment of PAC (15-25 mg/L) in the sludge blanket provided a very high concentration of PAC in the system which effected a 70 percent decrease in THMFP; no carbon appeared in the effluent. Preoxidation with ozone did not increase the removal of either THM precursors or TOC in trials involving the coagulant alone or PAC enmeshed in the coagulant (Hoehn et al., 1987).

CHAPTER 3

METHODS AND MATERIALS

SURVEY

A survey was developed as a part of the AWWARF project (Appendix A). The survey was sent to companies identified by the American Water Service Company (AWSCo) and AWWARF. The author of this thesis distributed the survey by mail to 37 water utilities throughout the United States and analyzed the data.

SUMMARY OF THE SURVEY

The survey consisted of eighteen questions in four general sections: source description, treatment provided, chlorine dioxide use, and history of taste-and-odor problems. The "source description" was designed to acquire data concerning the type of raw water source, population served, and raw and finished water quality parameters. The section entitled "treatment provided" was designed to acquire data concerning the type of pretreatment (coagulants and oxidants), clarification, and filtration. The third section entitled "chlorine dioxide use" was utilized to determine the primary and secondary purpose for applying chlorine dioxide. Also, the month of application was described, along with the type of equipment and general operations such as application point and target dose. The final section of the survey was designed to acquire specific data concerning tastes-and-odors. Thirty-

nine specific tastes-and-odors were provided and respondents ranked the specific taste-or-odor between never occurring (value=1) and frequently occurring (value=5).

TOTAL DESIGN METHOD

The purpose of the total design method is to produce high-quantity and high-quality responses to a survey (Dillman, 1978). To achieve this goal, several letters were sent to those participating in the survey. The first letter with the survey (Appendix B) was utilized to convince people within the water industry that a problem existed and that their help was needed to find a solution. One week after the initial letter and survey were mailed, a post card was sent to those participating in the survey. The postcard (Appendix B) thanked those who had returned their survey or served as a reminder to those who had not. A third mailing was sent five weeks after the initial contact. Another survey was enclosed with a letter (Appendix B) that restated the appeal in the first letter. After six months of data input and analysis, all those participating in the survey were sent a thank-you letter and a brief summary of findings from the survey (Appendix B).

INTERPRETATION OF THE SURVEY

The data gathered from the survey was used to determine why odors were occurring with the application of chlorine dioxide. First, tastes-and-odors were correlated with raw and finished water quality parameters. Second, tastes-and-odors

were correlated with dose of chlorine dioxide. Third, chlorinous, cat-urine, and kerosene tastes-and-odors were correlated with the point of application. Fourth, comparisons were made between the final disinfectants chlorine and chloramine to determine if differences in kerosene, cat urine, and chlorinous tastes-and-odors were related to the type of final disinfectant. Fifth, comparisons were made between chlorine dioxide on and chlorine dioxide off for each taste-and-odor. Sixth, the association of tastes-and-odors to one another were determined using cluster analysis.

DESIGN OF THE DATABASE

Each survey consisted of 396 potential responses. Each response was given a variable name, these variables were entered into a database on the mainframe computer and then, the responses from each survey were entered as a block of data. Respondents were given a code number to maintain anonymity. The database contained about 14000 individual records. If a respondent left an answer blank a period, ".", was put in the database. This is read by the Statistical Analysis System (SAS) as a missing value. If a respondent indicated not applicable, then a "-1" was put in the database, these were "filtered out" before analysis.

STATISTICAL METHODS

Descriptive Statistics. The Statistical Analysis System (SAS release 5.18) at VPI&SU Computing Center was used to perform the statistical analyses. The frequency of response

was determined for each field. Bar graphs were constructed to display discrete data by use of the "proc chart" and "vbar" commands. The mean, standard deviation, and the minimum and maximum values were determined by use of the "proc means" command for continuous data. The taste-and-odor responses were counted by use of the "proc freq" command followed by the "tables" command.

Statistical Tests. As part of the survey design, the thirty-nine tastes-and-odors were grouped into seven classes (Table 9) by the VPI&SU research team. All correlations were conducted using classes of tastes-and-odors not the individual responses to the tastes-and-odors. Pearson's correlation coefficient (r) was used to determine differences between the classes and other parameters. For example, the comparison of classes of tastes-and-odors, which were ranked from never observed to frequently observed, with water quality parameters such as color, turbidity, pH, and threshold odor number were determined. In statistical analysis, correlation coefficients range between 1 and -1; numbers closer to either extreme indicate correlation actually exists between the two variables being compared (i.e. are significant). The values were determined by use of the "proc corr" command followed by the variable names of interest.

Pearson's Chi-square (X^2) statistic was used to determine if differences in kerosene, cat urine, or chlorinous taste-and-odors were related to the type of final disinfectant

Table 9. Classes of Tastes-and-Odors as Determined by the Research Team. The Classes were Generated from the Thirty-Nine Original Taste-and-Odor Descriptions on the Survey Sent to Water Treatment Companies that Use Chlorine Dioxide.

CLASS	ORIGINAL DESCRIPTIONS
Cat Urine	Cat Urine
Disinfection	Antiseptic, Bleach, Chlorinous, Chlorox, Medicinal, Phenolic, Purex, Swimming Pool
Hydrocarbon	Diesel Fuel, Gasoline, Hydrocarbon, Kerosene, Lighter Fluid, Natural Gas, Organic Solvent, Plastic, Plastic Pipe, Rubber, Varnish
Musty	Earthy, Moldy, Potato, Potato Bin, Varnish, Wet Paper, Woody
Pleasant	Floral, Fragrant, Sweet
Rotten	Decayed Vegetation, Fishy, Marshy, Pig Pen, Septic, Sewage, Swampy
Vegetation	Cucumber, Grassy, Haylike

applied. A contingency table was generated to test the independence of tastes-and-odors with the type of disinfectant.

To test if the presence of chlorine dioxide enhanced tastes-and-odors, the Wilcoxon paired-sample test was used to compare responses of chlorine dioxide in use and chlorine dioxide not in use for each taste-and-odor (Zar, 1984). The Wilcoxon paired-sample test is applicable when one can not assume that the differences between pairs of responses are from a normal population, hence the test is nonparametric.

Clusters were created to determine if some odors or tastes were commonly associated with one another. For example, if a respondent's water frequently smelled like chlorox, did it also smell like swimming pool or bleach which are associated odors? The "proc varclus" command was used to divide the tastes-or-odors into non-overlapping clusters. The procedure begins with all variables in one cluster. Variation within a cluster was determined by a correlation matrix. If the variation between elements in the cluster was high, then the cluster was split into two clusters. Clusters were then plotted as flow charts to depict the way clusters were split.

GENERAL ANALYTICAL TECHNIQUES

GLASSWARE

Glassware used in the research was soaked in 10 percent nitric acid for 24 hours, then rinsed in distilled water three times. In experiments conducted to determine the fate of chlorite at the carbon surface, the glassware was rinsed three more times in Milli-Q water.

INSTRUMENTATION

Field Instruments. Chlorine dioxide, chlorite, and chlorine were analyzed by the amperometric method of Aieta et al., 1984. Residual chlorine species were determined by adjusting the pH, adding potassium iodide and then titrating with phenylarsine oxide (PAO) on a Fisher-Porter (Warminster, PA) Model 17T1010 Amperometric Titrator.

Researchers from Miami University (Oxford, OH) had previously developed the flow injection analysis (FIA) for determining the concentrations of residual oxidants (chlorine, chlorine dioxide, chlorite, and chlorate) at very low levels. These experts were part of the AWWARF research team and analyzed residual oxidant concentrations in the same samples that were analyzed by the author of this thesis. The flow injection analysis method is described fully elsewhere (Themelis et al., 1989). Basically, FIA uses the Aieta method in small sample sizes and under controlled kinetic conditions. This method yields highly reproducible and sensitive results.

Laboratory Instruments. To determine the fate of chlorite at the carbon surface chlorite, chloride, and chlorate were monitored on a Dionex Ion Chromatograph (Dionex Corporation; Sunnyvale, CA) Model 2010i equipped with an IonPac AS9 column or the AS4A column. Both columns are capable of separating chlorite, chloride, and chlorate ions, but the AS9 column has been specifically designed to do this in the presence of other anions. For analyses with the AS9 column, the eluent was composed of 2.0 mM Na_2CO_3 and 0.75 mM $NaHCO_3$. The suppressant was a 0.25 N H_2SO_4 solution. The flow rate was 1.0 mL/min. Duplicate samples were express-mailed to Miami University (Oxford, OH) for analysis by FIA to confirm concentrations determined by ion chromatography. The flow injection analysis method is described fully elsewhere (Themelis et al., 1989). In another experiment, chlorite was contacted with various concentrations of carbon for 7 days. For analyses with the ASA4 column, the eluent was composed of 1.8mM Na_2CO_3 and 1.7 mM $NaHCO_3$. The flow rate was 2.0 mL/min.

In the flocculation and floc-blanket experiments chlorine dioxide, chlorite, and chlorine were measured by amperometric titration. Residual chlorine species were determined after pH adjustment and the addition of potassium iodide by titration with PAO. A Computer Aided Titrator (Fisher Scientific; Raleigh, NC) Model 465 equipped with a platinum-platinum electrode was used for the analysis.

The pH was determined using a Fisher Scientific Model 230

meter. Turbidity was determined using a Hach (Ames, IA) Turbidimeter Model 2100A. TOC was determined using a Dohrmann TOC Analyzer (Santa Clara, CA) Model DC-80. Manganese and iron were determined using a Perkin Elmer (Norwalk, CT) flame Atomic Adsorption Spectrophotometer Model 703.

CHEMICALS

Inorganic Salts. Pure (99.7 percent) sodium chlorite (Novatek; Oxford, OH) was used to determine the fate of chlorite at the carbon surface. Sodium chlorite (Novatek; Oxford, OH), potassium chlorate (Fisher Scientific; CAS Number 3811-04-9), and sodium chloride (Fisher Scientific; CAS Number 7647-14-5) standards were made up in water from a Milli-Q ion-exchange system (Millipore Corporation; Milford, MA). Milli-Q water was used in all experiments to determine the fate of chlorite at the carbon surface, except the 7 day experiment in which distilled water was used.

Sodium chlorite (Eastman, Kodak Company; Rochester, NY) was used in flocculation and floc-blanket experiments to provide 1.6 to 10 mg/L chlorite in solution. Aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$; CAS Number 7784-31-8) from Fisher Scientific was used for coagulation. A standard (0.00564 N) solution of phenylarsine oxide (Fisher Scientific; CAS Number 637-01-6) was used in all amperometric titrations. Potassium Iodide (Aldrich; Milwaukee, WI) was used as an indicator. Phosphate buffer consisting of sodium phosphate monobasic (Fisher Scientific; CAS Number 10028-24-7) and sodium phosphate

dibasic (Fisher Scientific; CAS Number 7558-79-4) were used to adjust the pH before titration. Hydrochloric acid (Fisher Scientific; CAS Number 7647-01-0) was also used for pH adjustment. For flocculation studies, a laboratory-constituted water consisting of 100 mg/L bicarbonate (Fisher Scientific) and 1.6 to 1.7 mg/L chlorite (Eastman Kodak) was utilized.

Alkalinity was determined by using a 0.02 N solution of sulfuric acid (Fisher Scientific; CAS Number 7664-93-9). Color was determined by using cobalt-platinum standards (Lot Number 851455-24) from Fisher Scientific. The pH 4 buffer (Fisher Scientific) and the pH 7 buffer (Fisher Scientific) were used to adjust the pH meter.

Chlorine Dioxide. Stock chlorine dioxide was generated by adding 20 mLs of dilute H_2SO_4 to a 20g sodium chlorite solution ($NaClO_2$; Eastman Kodak), thus forming chlorine dioxide gas (Figure 4). The gas was scrubbed through a saturated solution of sodium chlorite to eliminate the potential for chlorine contamination. To ensure solution stability, the gas was trapped in an amber bottle filled with water drawn from a Milli-Q system and cooled to 10°C. Chlorine dioxide gas that did not dissolve was neutralized by reaction with a saturated solution of potassium iodide. The stock solution of chlorine dioxide was stored at 10°C.

Carbon. The carbon selected for this study was Cecarbon Powdered Activated Carbon 20B (PAC) produced by Autochem,

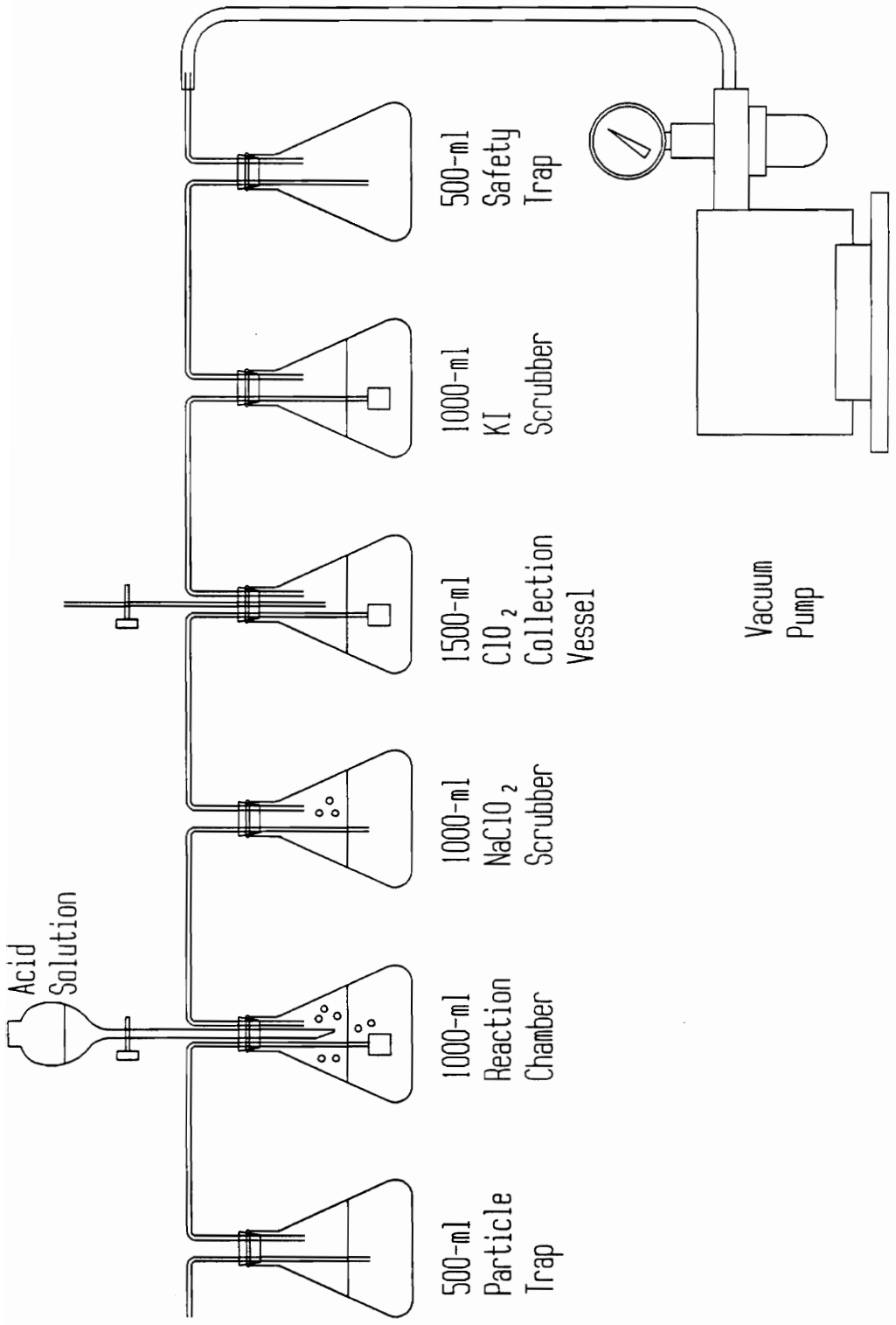

Figure 4. Schematic Diagram of the Chlorine Dioxide Generator.

Inc., Glen Rock, New Jersey. It is manufactured from coal by a steam-activation process and has an ash content of 12.5%. Carbon was removed from solution by using a Gelman Supor-200 0.2 micrometer (μm) filter.

CHARACTERIZATION OF RIVER WATERS

The two river waters used in this study were characterized as per Standard Methods for color, pH, alkalinity, and turbidity (APHA, 1985). Color was determined using platinum cobalt, Method 204. The pH was determined by Method 423. The alkalinity was determined by Method 403. Turbidity was determined by Method 214A.

Total Organic Carbon (TOC) was measured by ultra-violet promoted persulfate oxidation (Dohrmann; Santa Clara, CA). Iron and manganese were measured by flame atomic adsorption spectrophotometry.

FIELD STUDIES

The AWWARF research team traveled to two sites that were experiencing the offensive odors during the application of chlorine dioxide. The sites were the Kentucky American Kentucky River Water Treatment Plant (WTP) and the West Virginia American Kanawha Valley WTP. Samples were taken in the plant and distribution system to monitor the level of residual oxidants. Samples were analyzed also by flavor profile analysis (FPA) and for volatile organic compounds.

This thesis addresses only the inorganic analyses. Details of other aspects were presented by Hoehn et al., 1990.

The Kentucky River WTP is a 40 MGD plant. Chlorine dioxide (1 mg/L) was added to the raw water (Kentucky River). Aldrich purification units are used at the plant. These units are designed to provide mixing, flocculation, settling, and filtration within themselves. Polymer is added for coagulation. Potassium permanganate and chlorine dioxide are added as preoxidants. Chlorine is added at the clearwell.

The West Virginia WTP is a 40 MGD plant. The plant is divided into two identical treatment trains that have their own rapid mixer and two circular clarifiers. To control THM formation, chlorine dioxide (2 mg/L) is added to one train, typically during the warmer months of the year. Chlorine is added to the other side of the plant. Filtration through dual media is followed by blending in a common clearwell and chlorination to provide a residual in the distribution system.

SAMPLING STRATEGY

On October 11, 1988, samples were collected for analysis from the Kentucky River WTP. Inorganic samples included: treated water after chlorine dioxide application, and the clearwell after chlorination. Samples were taken also from the distribution system at a single-family residence where an individual (Customer A) had complained of cat-urine odors. Across the street, samples were taken at another customer's home (Customer C, control site) where no odors had been

detected. Samples were taken also at the water meters of the two homes. Sampling at the meters provided intermediate checkpoints between the WTP and the customers' homes to help determine if the odor-causing compounds were being generated in the customers' piping. Later that same day, samples were taken at an apartment where another individual (Customer B) had complained of "coal-oil" odors, but sampling at the meter was not possible.

On November 3-4, 1988, samples were collected for analysis from the Charleston WTP. Inorganic samples included: settled water after chlorination, settled water after chlorine dioxide addition, chlorinated water below filter, chlorine dioxide treated water below filters, and the mixed effluent. Samples were also taken in the distribution system at a single-family residence (Customer D) where the consumer had complained of kerosene-like odors. Samples were taken also at a neighboring home (Customer E, control site) where no odors had been recently observed. Customer E reported, however, that odors had been experienced in the past. Samples were taken at the meters of both homes the next morning.

CONFIRMING EXPERIMENTS

Once the link between chlorine dioxide and new carpeting had been established (based on survey and field sampling) a control experiment was designed to further investigate gas phase reactions of chlorine dioxide and carpet compounds. Chlorine dioxide was imparted to the air of a local

establishment (Blacksburg, VA) that had recently installed new carpeting. A chlorine dioxide solution (0.1 - 7.0 mg/L) was discharged rapidly from a glass syringe into a beaker to vaporize the chlorine dioxide, and observations of the odors above the beaker were noted. A chlorine solution was vaporized in the same manner, and observations of the odors above the beaker were noted. Detection and description of odors were performed by part of the AWWARF research team and by an independent group.

LABORATORY STUDIES

FATE OF CHLORITE AT THE CARBON SURFACE

A chlorite solution (20 mg/L in Milli-Q water) was treated by addition of 0, 5, 10, 20, 30, 40, 50, and 100 mg/L PAC for 15 and 30 minutes. Residual chlorite, chloride, and chlorate were monitored by ion chromatography using the AS9 column. For comparative purposes, samples were sent to Miami University (Oxford, OH) for evaluation by FIA. Typically, there was a two to five day delay in sample analysis, thus accounting for some of the variability between the two laboratories. Residual chlorite was also evaluated by amperometric titration.

A chlorite solution in distilled water was treated by addition of 0, 5, 10, 20, 25, 30, and 35 mg/L PAC for 7 days. Residual chlorite was evaluated by amperometric titration.

Residual chloride and chlorate were evaluated by ion chromatography using the ASA4 column. The chlorate concentration was not quantified during the initial analyses, although the chlorate peak was present on the chromatogram. A few months later, chlorate standards were run on the ASA4 column under the same chromatographic and instrumental conditions used for the original samples. These standards were used to quantify the chlorate peaks on the original chromatograms; thus these chlorate concentrations are approximate.

Milli-Q water was spiked with 20 mg/L chlorite and 50 mg/L PAC in a nine-liter, batch reactor. To determine the fate of chlorite at the carbon surface, 300 mL samples were removed from the reactor after contact times of 0, 0.25, 0.5, 0.75, 1.0, 1.5, 2, 3, 4, 8, 16, 24, 36, and 48 hours. The PAC was removed by filtration of the samples through a Gelman Supor-200 0.2 (μm) filters, thus halting the PAC/chlorite interactions. Residual chlorite, chloride, and chlorate concentrations were analyzed by ion chromatography using the AS9 column. For comparative purposes, samples were sent to Miami University (Oxford, OH) for analysis by FIA. Residual chlorite was also evaluated by amperometric titration.

KINETIC STUDIES WITH PAC IN LABORATORY-CONSTITUTED WATER

The laboratory-constituted water (500 mL in each of 7 jars) was rapidly mixed (on a standard jar-tester apparatus) for two minutes at >100 rpm during which time alum (50mg/L),

PAC (10 or 50 mg/L), or a combination of alum and PAC were added. Experiments were conducted in triplicate. The pH of the laboratory-constituted water was determined during the rapid-mix phase. Individual jars were removed from the jar-tester for chlorite analysis initially and after flocculation for 15, 30, 60, 120, 180 or 240 minutes. To prevent the reaction from continuing, the PAC was removed from the flocculated samples by filtration. Residual chlorite was measured by amperometric titration. To serve as the control, the laboratory-constituted water was not treated with alum or PAC and was exposed for the same reaction times as the treated water.

KINETIC STUDIES WITH PAC IN PO RIVER WATER

Po River water was obtained from Spotsylvania County, Virginia and characterized by Standard Methods. The alkalinity of the water was increased by the addition of bicarbonate (100 mg/L). Triplicate samples were dosed with chlorine dioxide (mean dose: 7.24 mg/L) for 30 minutes. Following preoxidation the water was rapid mixed for 2 minutes (on a standard jar-tester apparatus) at >100 rpm during which alum (105 mg/L), PAC (50 mg/L), or a combination of alum and PAC were added. The pH of the water was determined during the rapid mix phase. Each jar containing 500 mL of sample was withdrawn from the jar-tester apparatus for chlorite analysis initially and after flocculation for 15, 30, 60, 120, 180, or 240 minutes. The samples were then filtered as described

above. Residual chlorite and chlorine dioxide were determined by the amperometric method. To serve as the control, Po River water was dosed with chlorine dioxide and then not treated with alum or PAC but residuals were monitored with time.

SIMULATION OF A FLOC-BLANKET CLARIFIER

A completely stirred tank reactor (8.5 L) with a side clarifier (1.5 L) was used to simulate conditions in a pulsed-bed, solids-contact clarification process (Infilco Dregremont, Inc. Superpulsator®). A floc-blanket was developed in distilled water by adding bicarbonate (23.18 g), alum (28.79 g), and PAC (28.79 g). A chlorite solution (9.43 mg/L) was fed into the reactor at 95 mL/min to provide a hydraulic detention time of 90 minutes. The floc with PAC enmeshed was gently stirred during the entire experimental period. Effluent chlorite was determined every hour for 24 hours.

In a parallel set of experiments, a floc-blanket was developed in Mattaponi River water (New Kent County, Virginia). River water was used to make up the floc-blanket in to determine if a natural water source with a high TOC concentration would deplete the potential of the carbon to react with chlorite. A chlorite solution (9.73 mg/L) was fed into the reactor at 95 mL/min to provide a hydraulic detention time of 90 minutes.

CHAPTER 4

RESULTS

The results section is composed of three main parts: survey, field studies, and laboratory studies.

SURVEY

Descriptive statistics were first used to characterize the survey with attention given to the source water, treatment, chlorine dioxide use, and history of tastes-and-odors. Statistical tests were then conducted to compare tastes-and-odors with other water-quality variables surveyed. Descriptive statistics and statistical tests are presented below.

DESCRIPTIVE STATISTICS

Overview. The eighteen-question survey consisted of four main sections: source description, treatment provided, chlorine dioxide use, and history of taste-and-odor problems. Thirty-seven surveys were sent and thirty-five (95 percent) were returned. Three of the thirty-five were not completed because chlorine dioxide was no longer in use. Eighteen states were represented in this survey. Respondents spent, on average, 1.82 hours filling out the survey. The range was 0.25 to 5.5 hours.

The survey provided both discrete and continuous data. A discrete variable can only take on certain values, for example the odors in this survey were described using integer values from never occurring (value=1) to frequently occurring

(value=5). A continuous variable can take on any conceivable value within the observed range, for example pH. The answers to questions providing discrete data were summarized by frequency and percent of responses. Continuous data were summarized by mean, standard deviation, minimum, and maximum values. These data are listed in Appendix C. Descriptive results from the four sections are presented below.

Source Description. The most-common, raw-water source was rivers (Figure 5). The population served was at neither extreme with most facilities serving between 10,000 and 50,000 people (Figure 6). The annual average of the water quality characteristics are listed in Tables 10 and 11.

Treatment Provided. During treatment, most facilities apply either alum or a polymer as the coagulant (Figure 7). Chlorine (81.3 percent) and chlorine dioxide (87.5 percent) were the most commonly used oxidants. Clarification was effected by conventional flocculation followed by settling at 71.0 percent of the installations; the others used sludge-blanket clarifiers. Filters most commonly were either rapid sand or dual media (Figure 8).

Chlorine Dioxide Use. The major purpose for adding chlorine dioxide was for THM control with the secondary purpose being predisinfection (Figure 9). Chlorine dioxide was used year-around by most facilities with only a slight increase noted in July, August, and September (Figure 10). The most common generator (34.4 percent) used by the utilities

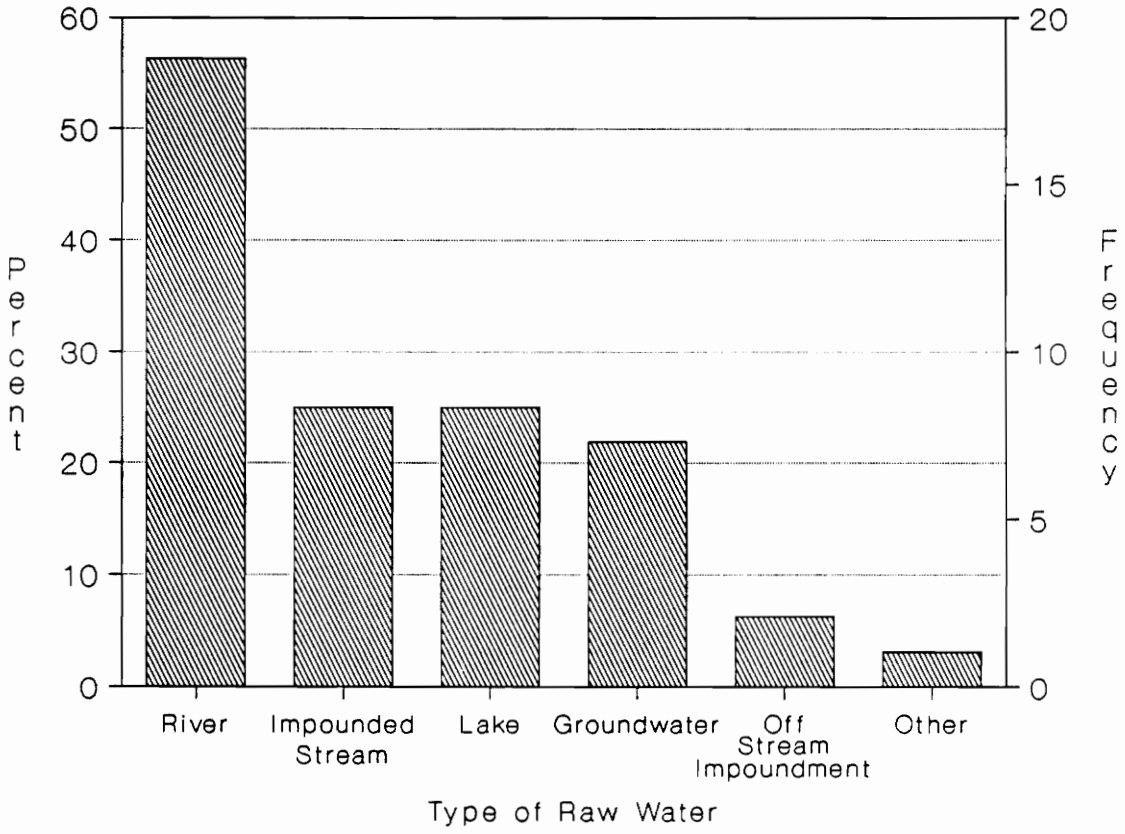

Figure 5. Distribution of Raw Water Sources Used by Companies Surveyed.

Note: The Percentages Do Not Sum to 100 Because Many Companies Indicated that They Use More than One Type of Raw Water Source.

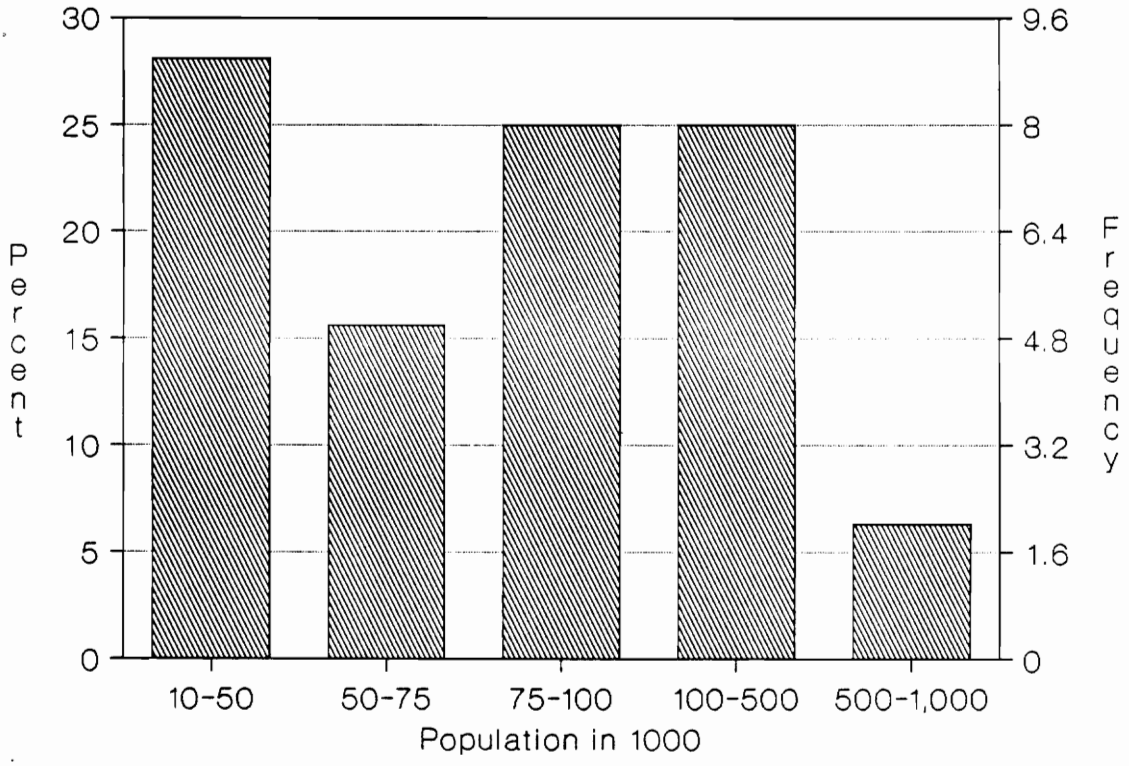

Figure 6. Distribution of Populations Served by Companies Surveyed.

Table 10. Annual Raw Water Quality Data as Reported by Water Utilities Responding to the Chlorine Dioxide Survey.

CHARACTERISTIC	N	MEAN	SDEV	MIN	MAX
Color Units, Number	17	41.65	45.46	2.5	200.0
TOC, mg/L	7	7.65	7.84	2.0	25.0
Fe, mg/L	24	1.26	2.81	0.019	13.0
Mn, mg/L	21	0.13	0.13	0.004	0.45
Turbidity, NTU	29	20.11	27.82	0.44	138.0
pH	29	7.4	0.7	5.7	8.2
Ammonia-N, mg/L	8	0.25	0.17	0.02	0.49
Odor, TON	14	5.07	6.13	1.00	24.0
TDS, mg/L	16	248.9	159.1	26.0	558.0
Bromide, mg/L	5	0.24	0.35	0.0	0.86
Chloride, mg/L	22	43.23	41.57	4.9	200.0
Coliforms, Number / 100 mL	25	3942	8315	1	37300
TKN, mg/L	4	1.09	1.18	0.23	2.80

Table 11. Annual Finished Water Quality Data as Reported by Water Utilities Responding to the Chlorine Dioxide Survey.

CHARACTERISTIC	N	MEAN	SDEV	MIN	MAX
Color Units, Number	19	2.02	1.82	0.0	5.0
TOC, mg/L	7	3.88	2.21	1.0	8.0
Fe, mg/L	28	0.05	0.06	0.01	0.30
Mn, mg/L	27	0.03	0.01	0.0	0.09
Turbidity, NTU	30	0.32	0.21	0.1	1.0
pH	30	7.8	0.6	6.8	9.0
Ammonia-N, mg/L	7	0.34	0.36	0.06	1.0
Odor, TON	18	1.76	1.59	0.0	0.38
TDS, mg/L	21	273.1	203.5	48.0	1000
Free Chlorine, mg/L	29	1.25	0.87	0.0	2.9
Combined Chlorine, mg/L	21	1.29	0.87	0.0	3.0
Chlorine Dioxide, mg/L	20	0.17	0.32	0.0	1.0
Chlorite, mg/L	12	0.32	0.28	.001	0.8

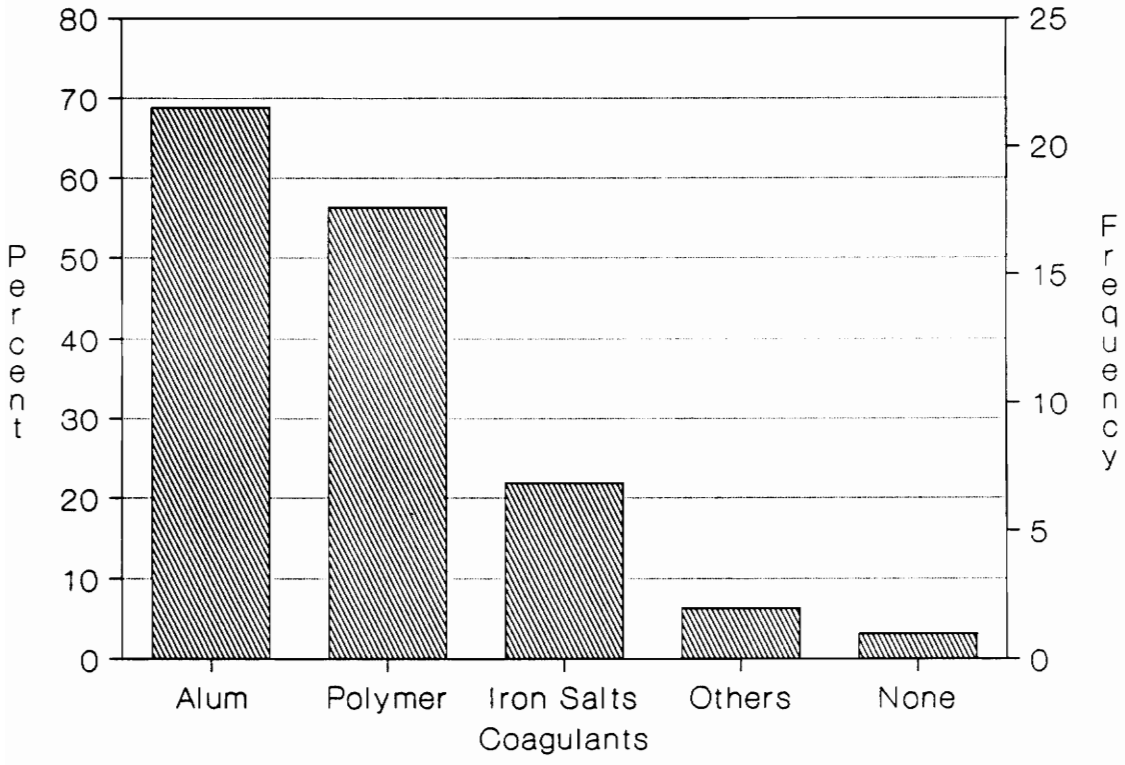

Figure 7. Distribution of Coagulants Used by Companies Surveyed.

Note: The Percentages Do Not Sum to 100 Because Many Companies Indicated that they Used More Than One Coagulant.

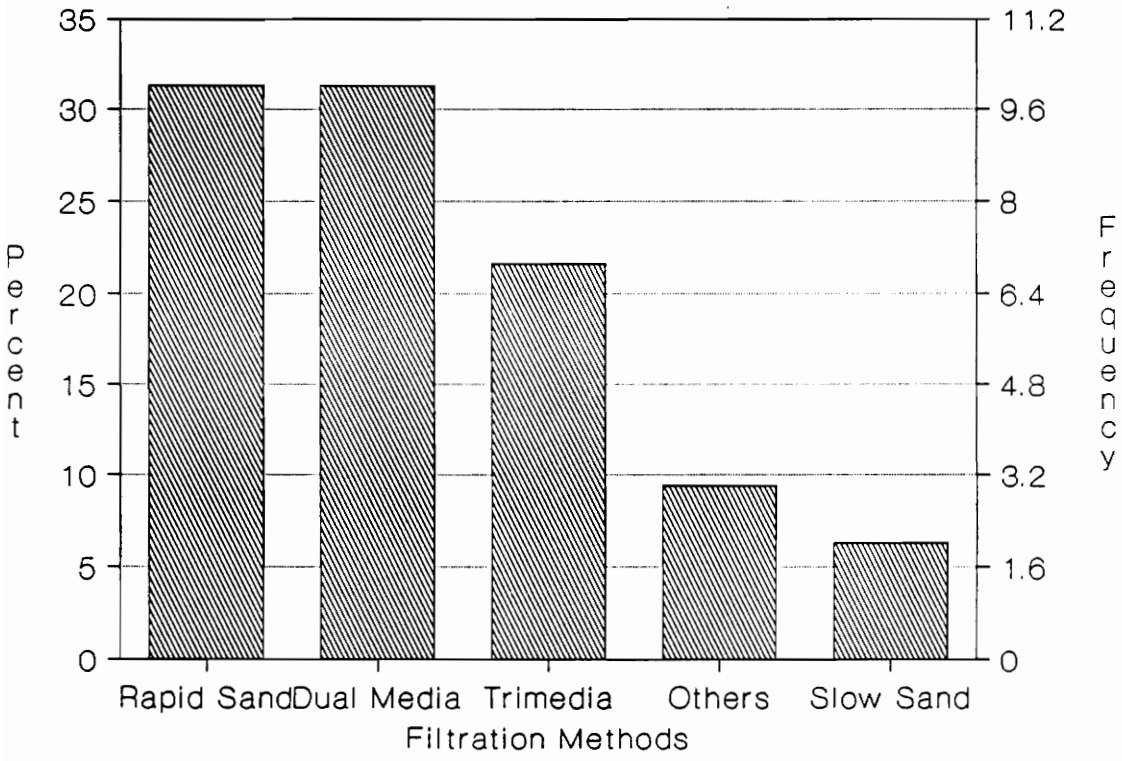

Figure 8. Distribution of Filtration Methods Used by Companies Surveyed.

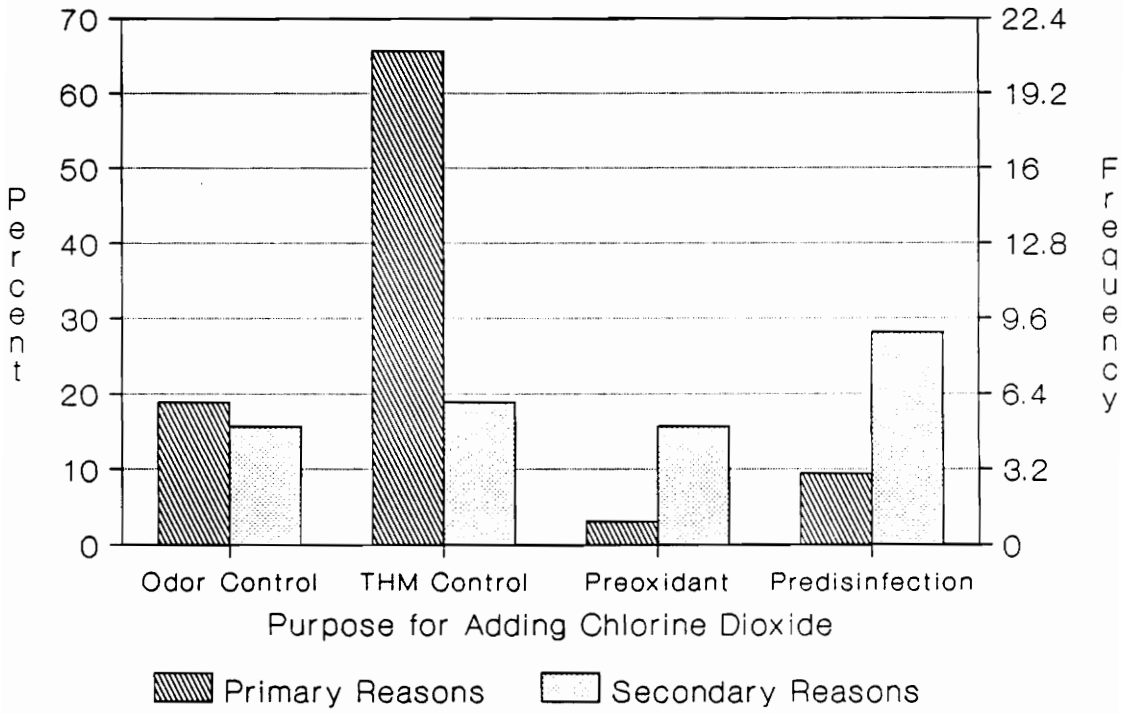

Figure 9. Distribution of Major and Secondary Reasons Given in the Chlorine Dioxide Survey for Applying the Oxidant.

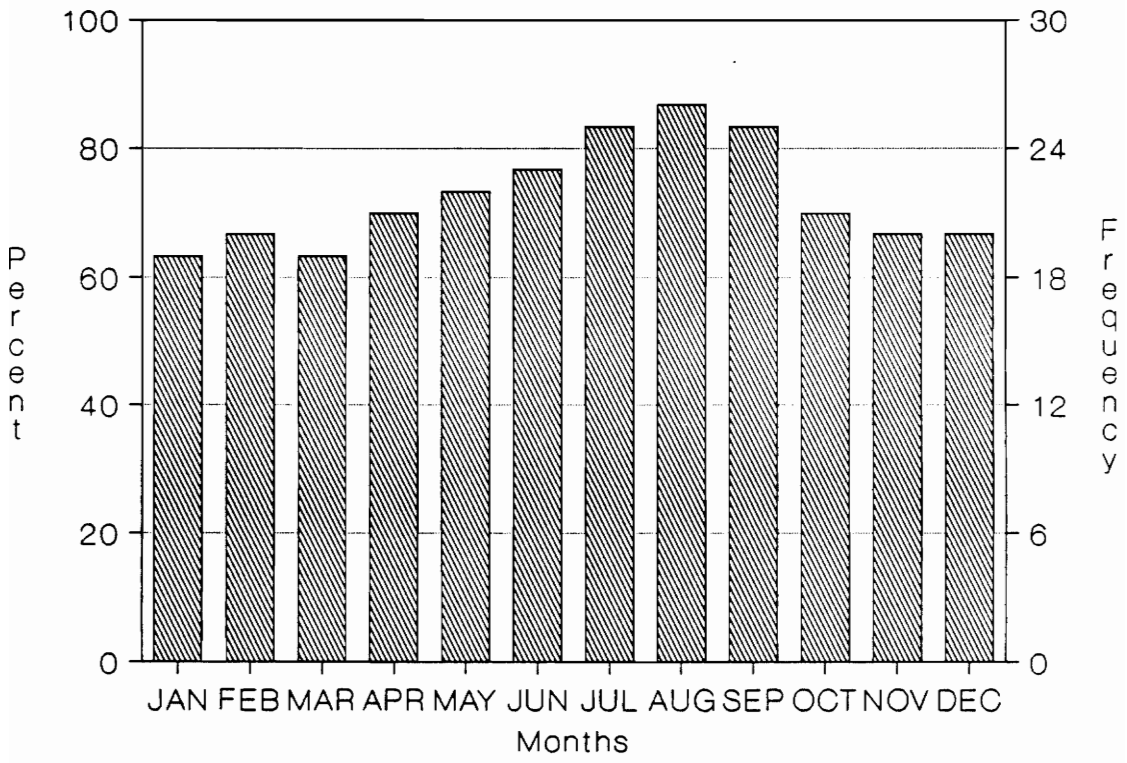

Figure 10. Monthly Chlorine Dioxide Use as Indicated by Companies Answering the Chlorine Dioxide Survey.

surveyed was manufactured by Rio Linda, although eleven types were represented in the survey. Some chlorine dioxide generators were installed as early as 1960, but 90 percent have been installed since 1980 (Figure 11). During the generation process liquid chlorite was usually fed (88.2 percent). Acid was never used in the generation process. The generator efficiency was 88.8 percent with a standard deviation of 13.1 percent. The generator efficiency was commonly determined weekly (Figure 12). Chlorine dioxide was usually applied at the intake (40.6 percent) or the flash mixer (46.9 percent). The target dose of chlorine dioxide was on average 1.24 mg/L with a standard deviation of 1.18 mg/L. At the control point, chlorine dioxide was usually monitored and the mean residual was 0.46 mg/L. Oxidants were commonly measured by the DPD method (56.7 percent) or the amperometric method (46.7 percent).

History of Taste-and-Odor Problems. Odors reported during times of chlorine dioxide addition were usually observed in the air and water (Figure 13). The mean number of complaints reported by customers to water treatment personnel when chlorine dioxide was added was 5.34. The mean number of complaints when chlorine dioxide was not added was 2.95. The complaints in the distribution system originated at random locations throughout the system (73.3 percent). Complaints were usually registered with the water companies throughout the day (90.0 percent). Of the 34.5 percent that noted an

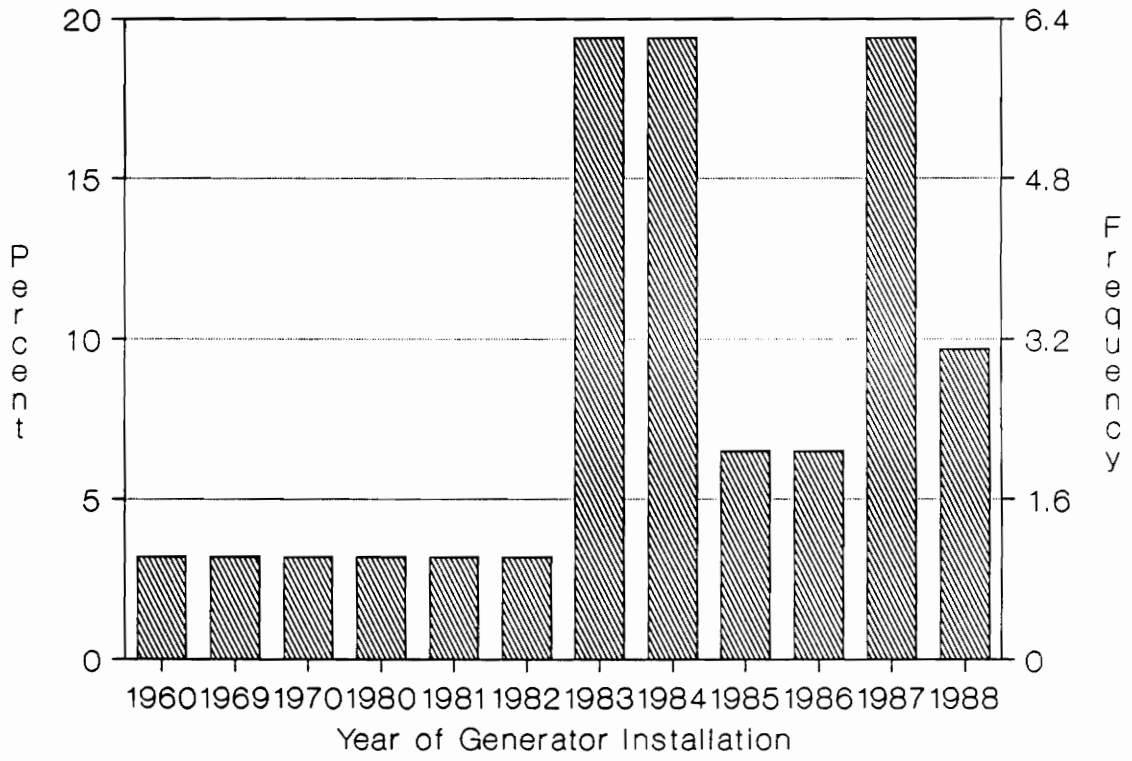

Figure 11. Distribution of Years of Generator Installation by Companies Surveyed.

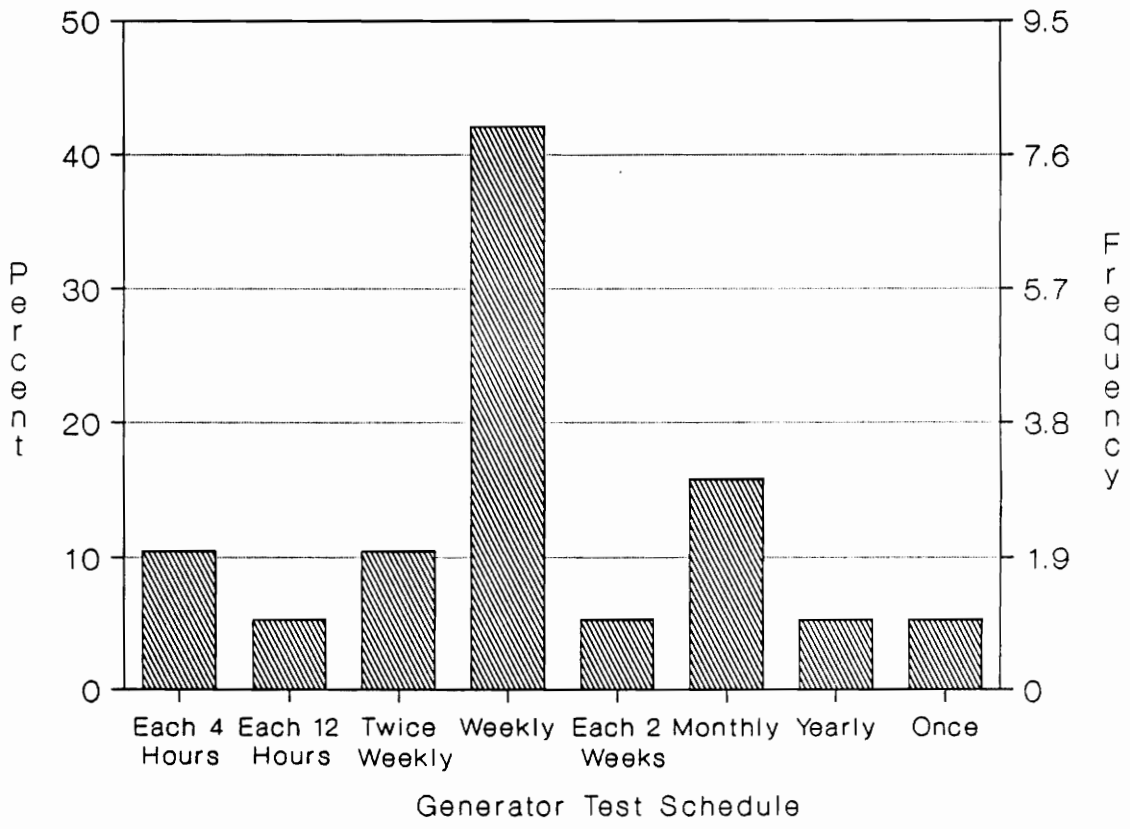

Figure 12. Test Schedule of Chlorine Dioxide Generator Efficiencies as Determined Through the Survey.

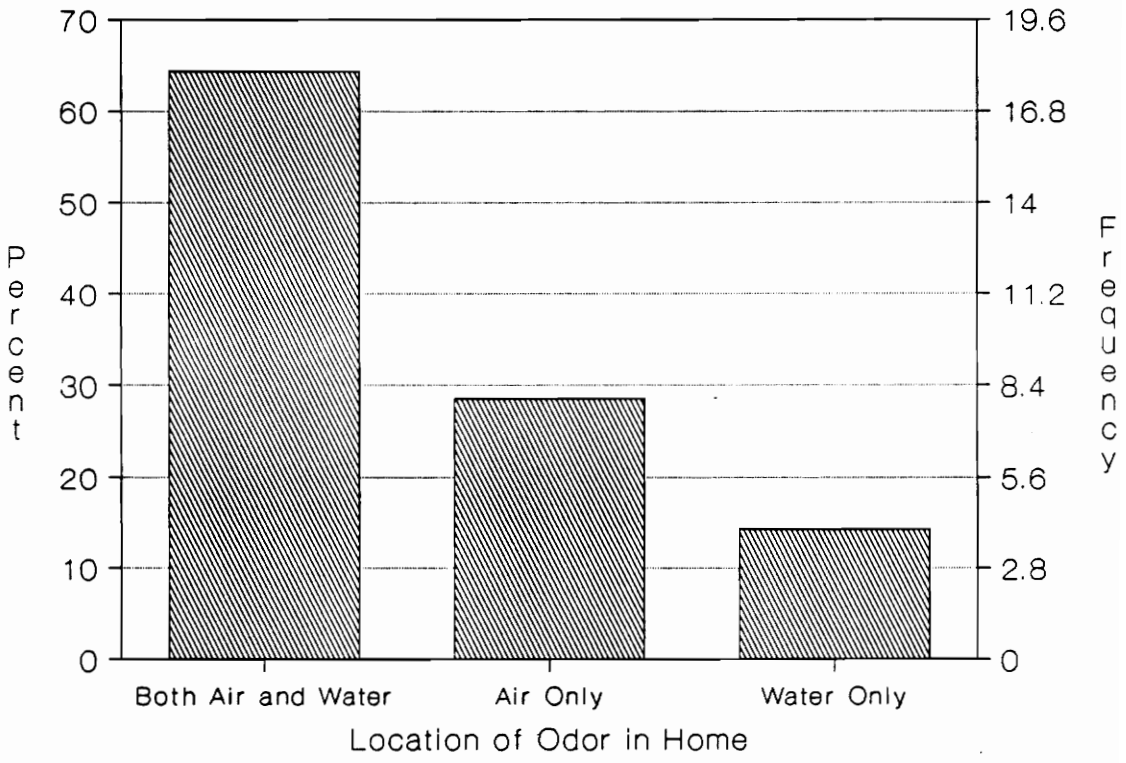

Figure 13. Location of Odors in Homes of Customers Represented by the Companies Surveyed.

increase in complaints with an increase in chlorine dioxide dose, a mean dose of 1.5 mg/L with a standard deviation of 0.95 mg/L was stated to cause an increase in complaints.

Customers who had recently installed new carpeting complained more frequently than those who had not (Figure 14). The mean number of complaining customers identified by water treatment personnel that had new carpeting was 46.0 percent, values ranged from 1 percent to 100 percent. Thus, at some locations, every complaining customer had new carpeting, and at another only 1 percent of customers who complained had new carpeting (at some locations, water treatment personnel asked all complaining customers if they had new carpeting, at other locations, water treatment personnel did not ask their customers if they had new carpeting). Customers who recently redecorated or painted complained less than those that had recently installed new carpet (Figure 14). The mean number of complaints was 40.6 percent, values ranged from 5 percent to 100 percent. Tastes-and-odors were most commonly detected in the kitchen (86.7 percent) and bathroom (73.3 percent). Threshold odor number (75.9 percent) was the most commonly used method for quantifying tastes-and-odors.

STATISTICAL TESTS

Four statistical tests were used to compare the survey data. In all cases, the chosen level of significance was 95 percent (alpha = 0.05). The results of these tests are presented in the following sections.

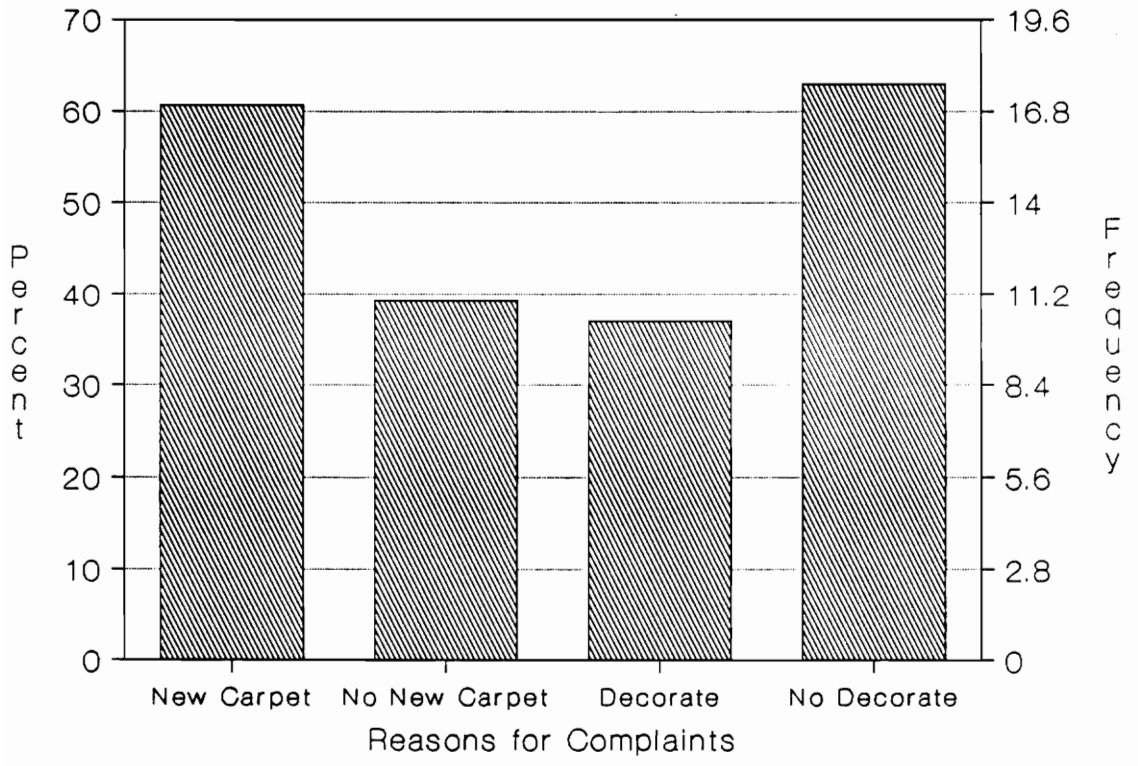

Figure 14. Mean of Customer Complaints Attributed to New Carpeting or Recent Decoration by Companies Surveyed.

Correlation. Correlations were utilized to determine if tastes-and-odors were related to water quality parameters, dose of chlorine dioxide, and point of application. Before any tests were performed, the thirty-nine individual tastes-and-odors were grouped into seven classes by the VPI&SU research team (Previous Chapter Table 9). Pearson's correlation coefficient (r) was then determined by comparing the class name with the variable of interest.

None of the classes of tastes-and-odors correlated with either raw or finished water-quality characteristics (Appendix D). None of the classes of tastes-and-odors correlated with the target dose of chlorine dioxide (Appendix D). The point of application was not correlated with cat urine, chlorinous, or kerosene tastes-and-odors (Appendix D).

Chi Square (X^2). Chi Square tests were performed to determine if the choice of final disinfectant applied by the utility was related to the formation of cat urine, chlorinous, and kerosene tastes-and-odors. An example of a contingency table is shown as Table 12. The analysis indicated that none of the odors appeared more frequently when either chlorine or chloramine were applied as the final disinfectant (Appendix D).

Wilcoxon Paired-Sample Test. Wilcoxon's paired-sample test was used to compare responses to questions regarding taste-and-odor complaints both when chlorine dioxide was in use and when it was not for each individual taste-and-odor

Table 12. Example of a Contingency Table Used In Chi-Square Analyses to Evaluate Responses to Intensity of Kerosene Odors (if value=1 then the odor was never observed, if value=5 then the odor was frequently observed) when Chlorine versus Chloramine was Used as a Final Disinfectant. The values below the Intensity Numerals are the Total Number of Responses to Each Intensity Level by the Companies Participating in the Chlorine Dioxide Survey.

	INTENSITY OF KEROSENE ODOR				
	Never				Frequent
DISINFECTANT TYPE	**1**	**2**	**3**	**4**	**5**
Chlorine	10	6	3	1	3
Chloramine	2	1	0	0	1

description. Sum of the ranks with a plus sign (T_+) and ranks with a minus sign (T_-) are listed in Appendix D. Odors that were different in the presence compared to the absence of chlorine dioxide are listed in Table 13. The odors listed were more intense when chlorine dioxide was added at the treatment plant. No tastes were different in intensity when chlorine dioxide was used at the treatment plant.

Clustering. Clusters based on a correlation matrix were established to determine if some odors or tastes were commonly associated with one another. When chlorine dioxide was in use, seven clusters of odors were generated (Table 14). Since the clustering routine begins with all thirty-nine odors in one cluster, the separation of clusters (i.e. how the odors are related) throughout the process is of interest. These data are presented as a flow chart (Figure 15). When chlorine dioxide was not in use, one cluster of odors was formed by the analysis (i.e. all odors were in one group). When chlorine dioxide was in use, five clusters of tastes were formed (Table 15). These data are also presented as a flow chart (Figure 16). When chlorine dioxide was not in use, two clusters were formed (Table 16).

Table 13. Odors that were Statistically Different in the Presence Compared to the Absence of Chlorine Dioxide as Determined by Responses from Companies Participating in the Chlorine Dioxide Survey. The Odors Listed were more Common in the Presence of Chlorine Dioxide. There were no Differences Observed for Tastes. The Wilcoxon Paired-Sample Test was Used to Determine Differences.

ODORS
Cat Urine
Diesel Fuel
Fishy
Gasoline
Kerosene
Natural Gas
Organic Solvent

Table 14. Responses to Odor Descriptions Reported by Companies Participating in the Chlorine Dioxide Survey were Correlated to One Another By Using a Computerized Cluster Analysis. The Groups of Odors that Companies Responded Similarly to as Determined by the Correlation Matrix are Listed Numerically. Chlorine Dioxide was in Use.

CLUSTER NUMBER	ODOR DESCRIPTION USED IN SURVEY
One	Decayed Vegetation, Earthy, Grassy, Haylike, Marshy, Moldy, Septic, Sewage, Swampy, Woody
Two	Organic Solvent, Phenolic, Plastic, Plastic Pipe, Rubber, Varnish
Three	Floral, Fragrant, Pig Pen, Wet Paper
Four	Antiseptic, Cucumber, Fishy, Medicinal, Potato, Potato Bin, Sweet
Five	Bleach, Chlorinous, Chlorox, Purex, Swimming Pool
Six	Diesel Fuel, Gasoline, Kerosene, Natural Gas
Seven	Cat Urine, Hydrocarbon, Lighter Fluid

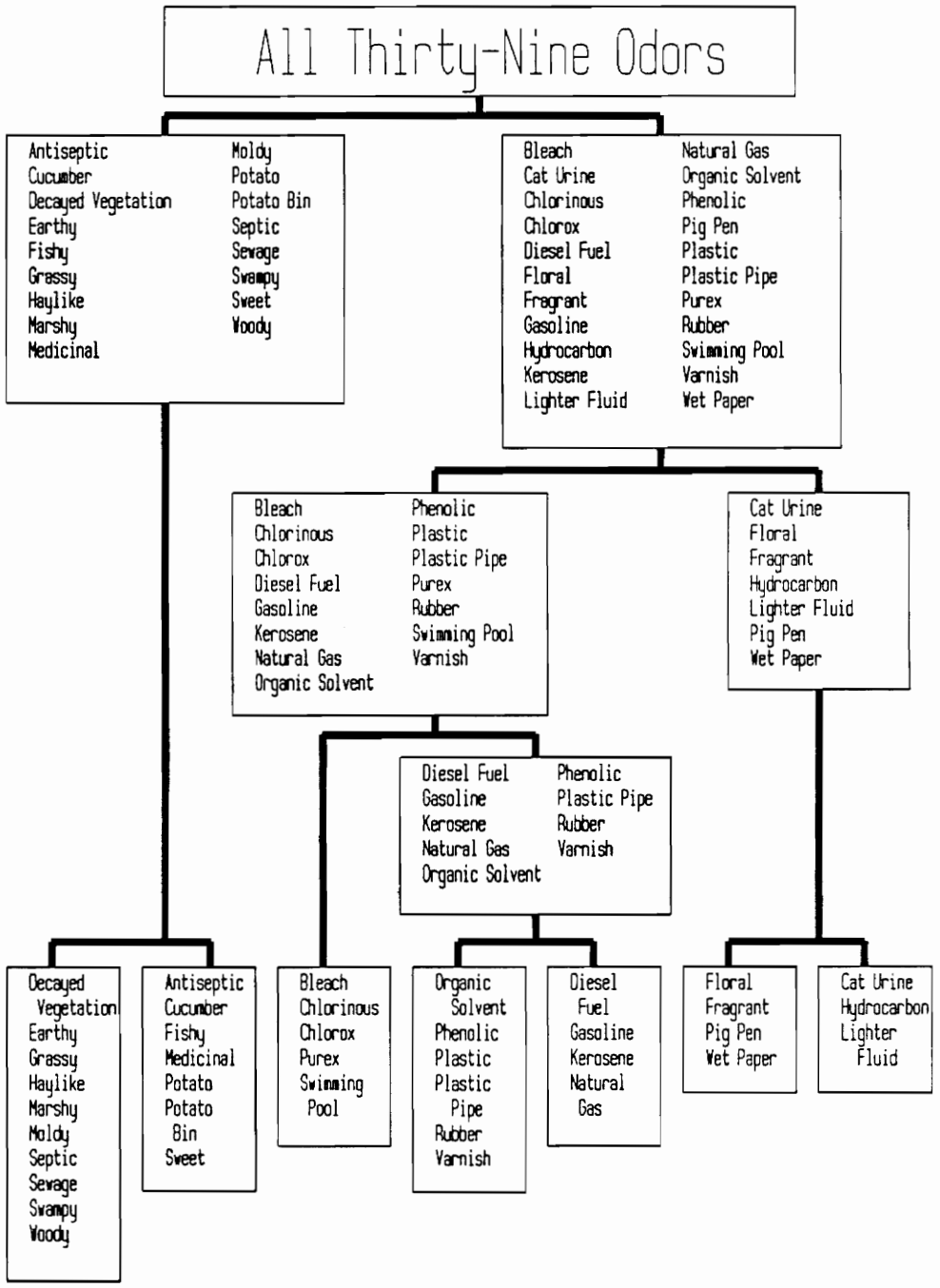

Figure 15. Odor Grouping as Determined by Computerized Clustering of Responses to Odor Descriptions Given by Companies Answering the Chlorine Dioxide Survey. Similar Responses are Grouped Together Through a Correlation Matrix. Clusters are Surrounded by Boxes; Ultimately, Seven Clusters were Produced for Odors.

Table 15. Responses to Taste Descriptions Reported by Companies Participating in the Chlorine Dioxide Survey were Correlated to One Another By Using a Computerized Cluster Analysis. The Groups of Tastes that Companies Responded Similarly to as Determined by the Correlation Matrix are Listed Numerically. Chlorine Dioxide was in Use.

CLUSTER NUMBER	TASTE DESCRIPTION
One	Bleach, Chlorox, Diesel Fuel, Gasoline, Kerosene, Lighter Fluid, Natural Gas, Organic Solvent, Phenolic, Plastic, Plastic Pipe, Purex, Rubber, Swimming Pool, Varnish
Two	Cucumber, Fishy, Haylike, Potato, Potato Bin, Septic, Sweet
Three	Antiseptic, Floral, Fragrant, Hydrocarbon, Pig Pen, Wet Paper
Four	Decayed Vegetation, Earthy, Marshy, Moldy, Sewage, Swampy, Woody
Five	Cat Urine, Chlorinous, Grassy, Medicinal

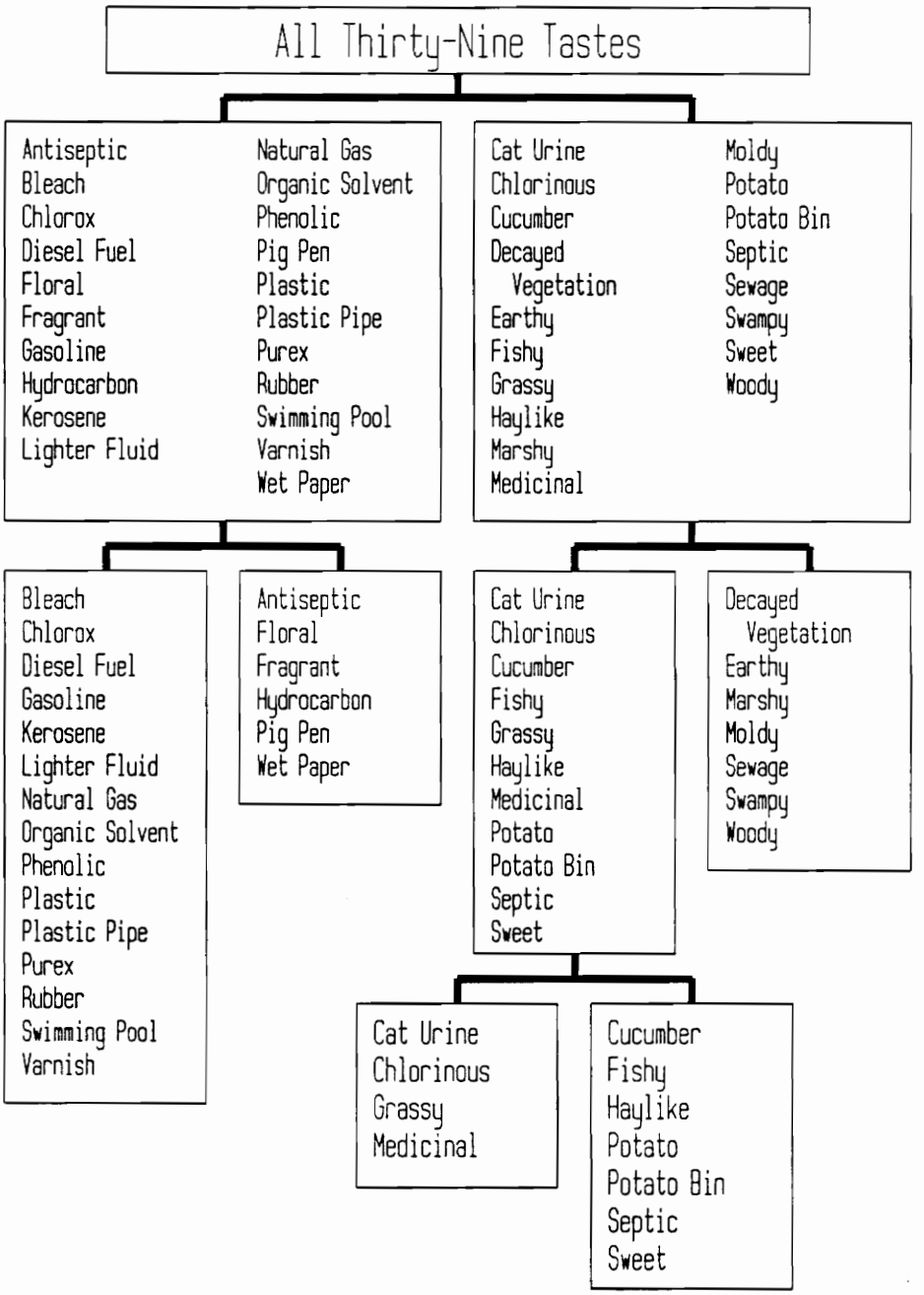

Figure 16. Taste Groupings as Determined by Computerized Clustering of Responses to Taste Descriptions Given by Companies Answering the Chlorine Dioxide Survey. Similar Responses are Grouped Together Through a Correlation Matrix. Clusters were Surrounded by Boxes; Ultimately, Five Clusters were Produced for Tastes.

Table 16. Responses to Taste Descriptions Reported by Companies Participating in the Chlorine Dioxide Survey were Correlated to One Another By Using a Computerized Cluster Analysis. The Groups of Tastes that Companies Responded Similarly to as Determined by the Correlation Matrix are Listed Numerically. Chlorine Dioxide was Not in Use.

CLUSTER NUMBER	TASTE DESCRIPTION
One	Antiseptic, Cat Urine, Cucumber, Decayed Vegetation, Diesel Fuel, Fishy, Floral, Fragrant, Gasoline, Haylike, Hydrocarbon, Kerosene, Lighter Fluid, Marshy, Natural Gas, Organic Solvent, Phenolic, Pig Pen, Plastic, Plastic Pipe, Potato, Potato Bin, Purex, Rubber, Septic, Sewage, Swampy, Sweet, Swimming Pool, Varnish, Wet Paper, Woody
Two	Bleach, Chlorinous, Chlorox, Earthy, Grassy, Medicinal, Moldy

FIELD STUDIES

Samples for residual oxidants were taken at the plant, and at customer's homes where the odors were detected and homes where odors were not detected (i.e. neighbors of the customers not experiencing the odors). The results of the two sampling trips are presented first. Once the association of new carpeting and chlorine dioxide was established as the odor causing mechanism (through the survey and trips to two sites having odor events), a confirming experiment was conducted. The confirming experiment is presented second.

KENTUCKY

Low levels of chlorine dioxide were detected by amperometric titration of samples from the distribution system at Lexington, Kentucky (Table 17). Inorganic analyses of water from Customer C's home (where odors were not observed) were not conducted because, at the time, it was not considered necessary. Results of the analyses by FIA were not accurate because a quenching agent required in the analysis had been inadvertently left at the laboratory; therefore, they are not reported here. All members of the research team described odors in the air and water of the odor home as being either "kerosene-like" or "cat-urine-like".

Table 17. Chlorine, Chlorite, and Chlorine Dioxide Concentrations (mg/L) Determined by the Amperometric Method in Lexington, Kentucky.

SITE	CHLORINE	CHLORITE	CHLORINE DIOXIDE
Plant: After Chlorine Dioxide but Before Chlorination	0.34	1.05	-0.23
Plant: After Chlorine Application	0.96	1.46	-0.06
Customer A: Cold Water, Washing Machine	1.60	0.68	0.08
Customer A: Meter	1.48	0.69	0.01
Customer B: Cold Water, Kitchen Tap	1.25	0.60	-0.01
Customer B: Hot Water, Kitchen Tap	0.87	0.34	0.07

WEST VIRGINIA

Low levels of chlorine dioxide were detected both by amperometric titration and FIA in the distribution system at Charleston, West Virginia (Table 18). The standard deviation for chlorine dioxide by FIA was 0.02 mg/L at all concentrations. The standard deviation for chlorate by FIA was 0.03 mg/L at concentrations less than 0.5 mg/L and 0.02 mg/L at concentrations greater than 0.5 mg/L (Slootmaekers, 1990). All members of the research team described odors in the air and water of the odor home as either "kerosene-like" or "cat-urine-like".

CONFIRMING EXPERIMENTS

The volatilization of chlorine dioxide in a room with new carpeting produced the offensive "kerosene-like" and "cat-urine-like" odors (Table 19). The odors increased in intensity when the concentration of the chlorine dioxide solution was increased from 0.1 mg/L to 7 mg/L. No odors were observed when chlorine was volatilized in the room.

LABORATORY STUDIES

FATE OF CHLORITE IN THE PRESENCE OF ACTIVATED CARBON

Chlorite in Milli-Q water was contacted with several concentrations of PAC for 15 minutes. At all PAC concentrations, chlorite was reduced to chloride, and no chlorate was formed (Figure 17). In a similar experiment,

Table 18. Chlorine, Chlorite, Chlorate, and Chlorine Dioxide Concentrations (mg/L) Determined by the Flow Injection Analysis (FIA) and Amperometric (AMP) Methods in Charleston, West Virginia.

SITE	Cl_2	ClO_2^-	ClO_3^-	ClO_2
	AMP FIA	AMP FIA	† FIA	AMP FIA
Plant: Settled and Chlorinated	-0.28 0.04	0.03 0.02	‡	0.58 0.09
Plant: Settled and Treated with ClO_2	0.09 0.55	1.03 1.14	‡	0.04 0.14
Plant: Filtered, Chlorinated	0.60 0	0.36 0.31	0.35	-0.05 0
Plant: Filtered and Treated with ClO_2	0.03 0	1.54 1.67	0.14	0.06 0
Plant: Mixed Effluent (Cl_2 & ClO_2)	0.36 1.88	0.65 0.71	‡	0.01 0.12
Customer D: Cold Water	0.15 0.65	0.82 0.90	0.28	-0.06 0.05
Customer D: Hot Water	0.01 0.01	0.67 0.73	0.24	0.005 0.03
Customer D: Meter	1.09 1.41	0.56 0.28	0.26	0 0.09
Customer E: Cold Water	0.22 0.95	0.86 0.93	0.28	-0.52 0.12
Customer E: Hot Water	0.04 0.19	0.72 0.78	0.16	0.008 0.07
Customer E: Meter	1.18 1.41	0.56 0.27	0.26	0 0.09

† Not Determined by Amperometric Titration

‡ Sample Interference during Analysis -- no valid data

Table 19. Odors Generated Upon Volatilizing Chlorine Dioxide in a Room with New Carpeting located in Blacksburg, Virginia.

GROUP PROVIDING DESCRIPTION	ODOR DESCRIPTION USED
AWWARF Research Team	Cat Urine, Kerosene
Independent Group	Cat Urine, Kerosene, Petroleum Products, Strong Body Odor

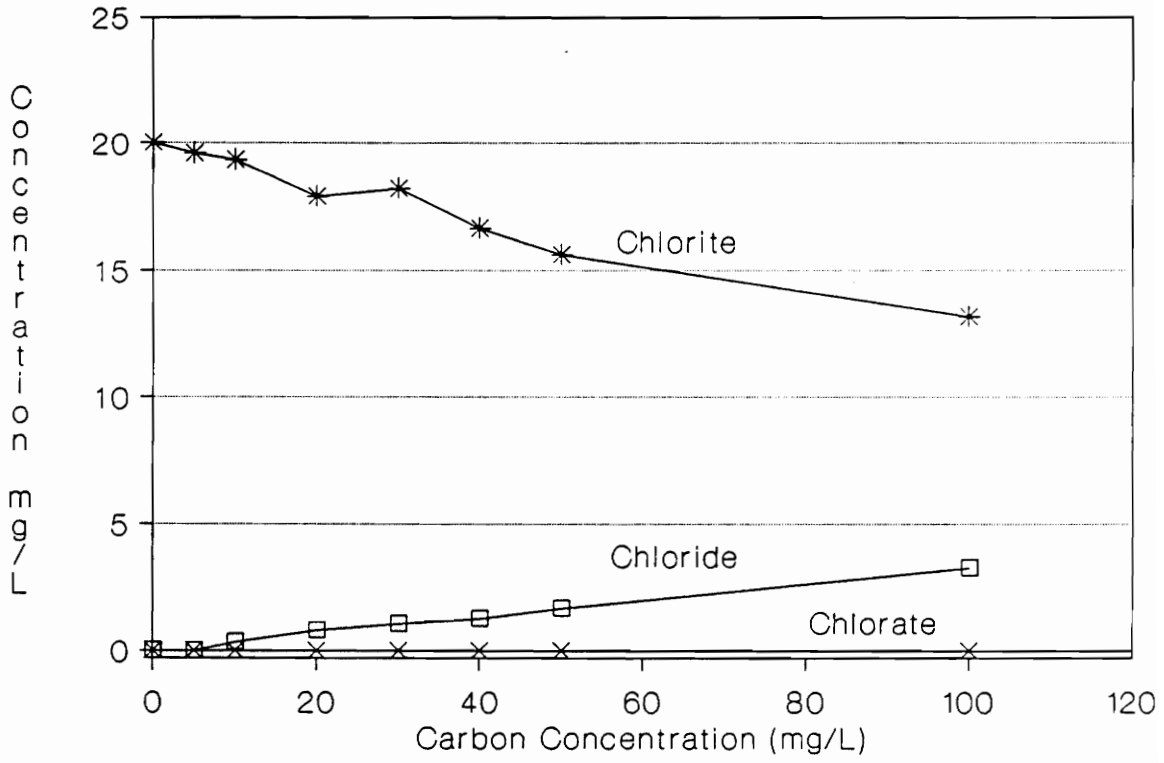

Figure 17. Chlorite Removal in Milli-Q Water Containing Several Concentrations of PAC (15-minute Contact Time).

chlorite was contacted with several concentrations of PAC for 30 minutes. At all PAC concentrations, chlorite was reduced to chloride and also oxidized to chlorate (Figure 18). Similar trends in chlorite reduction and chloride formation were evident in tests involving PAC at both contact times (Figure 19). Chlorate, on the other hand, was detected only when PAC contact period was 30 minutes (Figure 19C). The pH during both experiments ranged from 5.5 to 6.5. A mass balance on chlorine containing species (i.e. chlorite, chlorate, chloride) indicated that 97.1 percent was accounted for in the 15-minute experiment. Similarly, 91.2 percent was accounted for in the 30-minute experiment. Similar results were obtained when samples were analyzed by FIA at another laboratory. Results of chlorite analyses by three methods are presented in Table 20. Results of chlorate determination by two methods are presented in Table 21. As a control, carbon alone was contacted with Milli-Q water for 10 hours. No chlorite or chlorate were extracted from the carbon and less than 0.35 mg/L chloride was observed.

Chlorite was contacted with several concentrations of PAC for seven days. At all PAC concentrations, chlorite was reduced to chloride and oxidized to chlorate (Figure 20). The pH of the experiment ranged from 5.5 to 6.0. A mass balance on chlorine containing species expressed as chlorine indicated that from 95 to 101 percent of the species were accounted for each time a sample was analyzed.

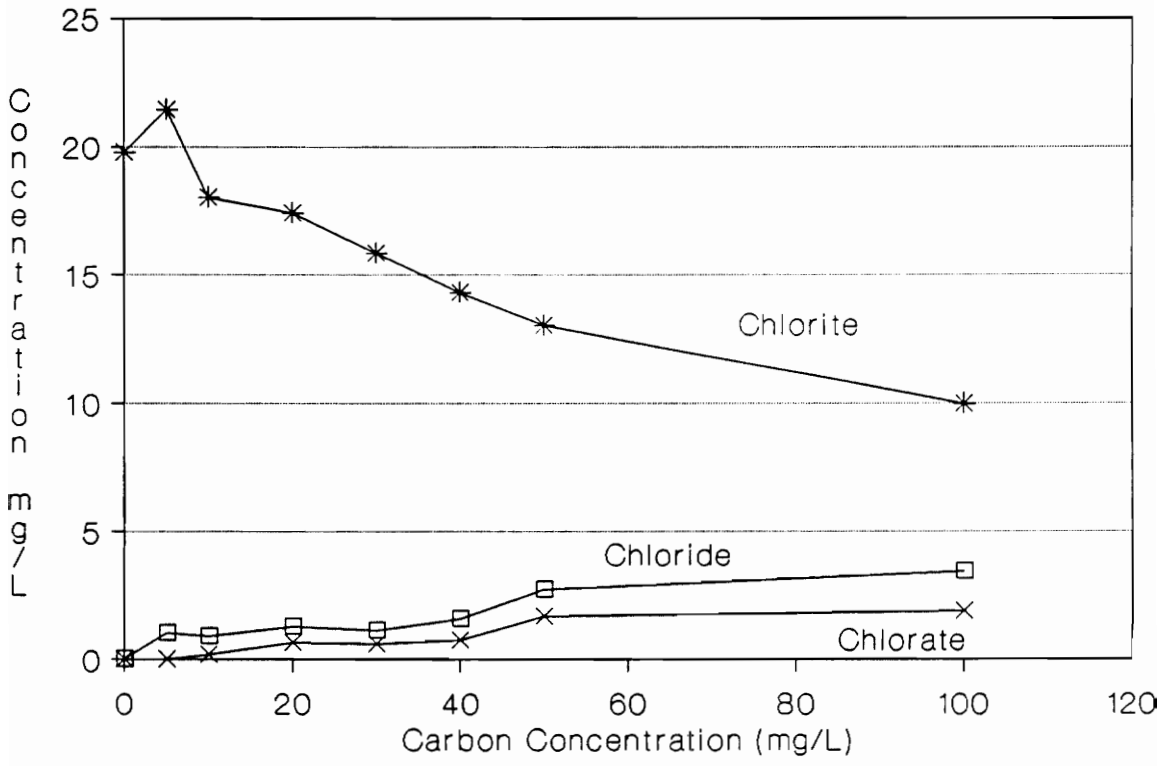

Figure 18. Chlorite Removal in Milli-Q Water Containing Several Concentrations of PAC (30-minute Contact Time).

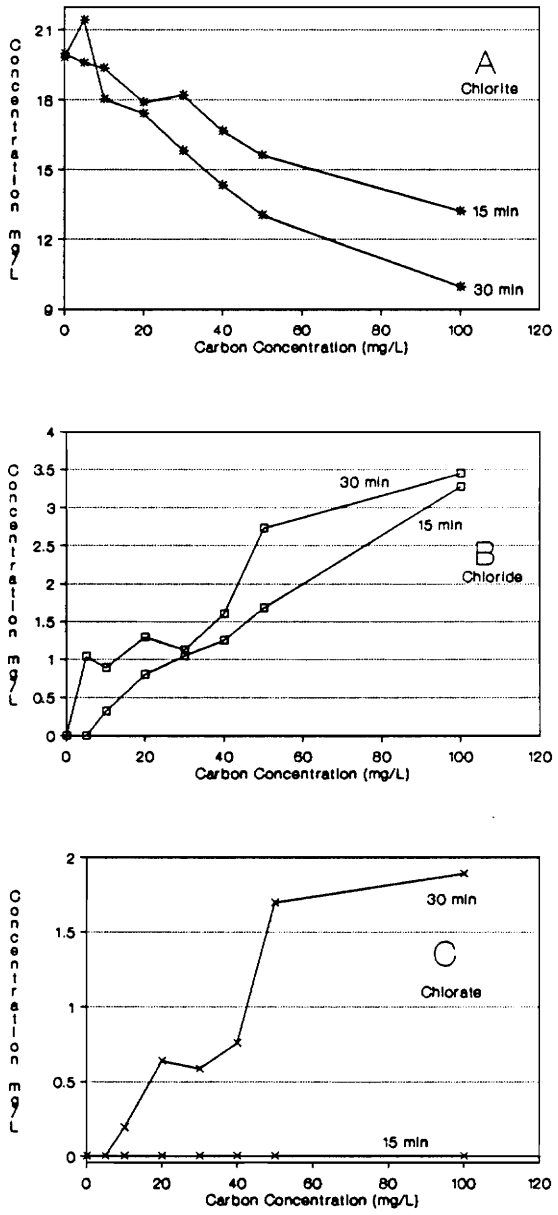

Figure 19. Chlorite (A) Removal, and Chloride (B) and Chlorate (C) Formation after 15 minute and 30 minute Reactions with Several PAC Concentrations in Milli-Q Water.

Table 20. Comparison of Ion Chromatography (IC), Amperometric Titration (AMP) and Flow Injection Analysis (FIA) for the Determination of Chlorite. Chlorite was contacted with Different Concentrations of PAC for 15 minutes and 30 minutes in Milli-Q water.

	Chlorite Concentration, mg/L, at Two PAC-Contact Times					
	15 Minutes			30 Minutes		
PAC (mg/L)	IC	AMP	FIA	IC	AMP	FIA
0	20.00	18.34	25.34	19.79	19.97	24.90
5	19.59	18.72	24.90	21.44	19.06	23.12
10	19.35	18.37	24.19	18.04	18.68	21.69
20	17.91	18.87	22.94	17.43	17.61	21.96
30	18.22	17.54	22.05	15.83	16.98	20.62
40	16.66	17.35	21.16	14.30	15.83	19.20
50	15.63	15.97	19.73	13.01	12.40	12.43
100	13.18	12.17	15.19	9.97	9.47	11.36

Table 21. Comparison of Ion Chromatography (IC) and Flow Injection Analysis (FIA) for the Determination of Chlorate. Chlorite was contacted with Different Concentrations of PAC for 15 minutes and 30 minutes in Milli-Q water.

	Chlorate Concentration, mg/L, at Two PAC-Contact Times			
	15 Minutes		30 Minutes	
PAC (mg/L)	IC	FIA	IC	FIA
0	0.0	0.0	0.0	0.0
5	0.0	0.2		0.2
10	0.0	0.0	0.19	0.5
20	0.0	0.0	0.64	0.3
30	0.0	0.2	0.59	0.4
40	0.0	0.4	0.76	0.6
50	0.0	0.0	1.70	2.5
100	0.0	1.1	1.89	2.3

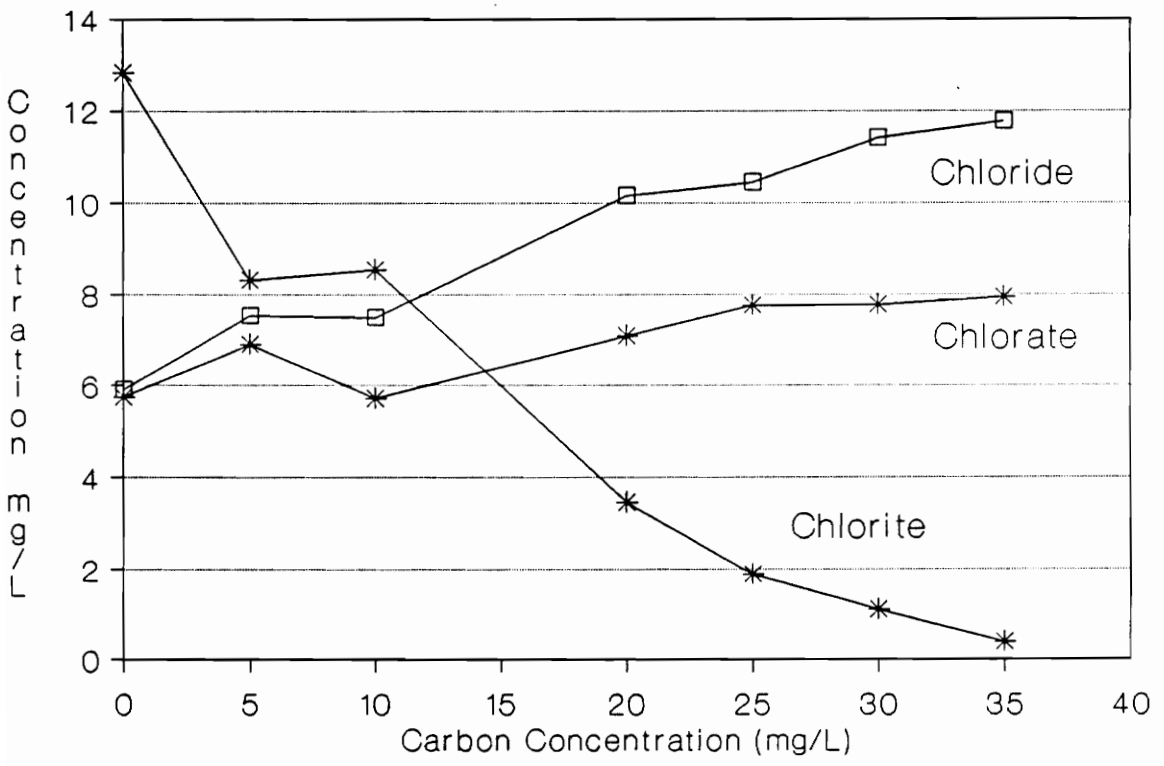

Figure 20. Chlorite, Chloride, and Chlorate Remaining In Distilled Water After Seven-Day's Contact with Varying Concentrations of PAC.

In another experiment, chlorite (20 mg/L) was contacted with PAC (50 mg/L) for 48 hours in a batch reactor. Chlorite was reduced to chloride and oxidized to chlorate (Figure 21). These results were confirmed by FIA (Table 22 and Table 23). The pH of the solution during the experiment ranged from 5.5 to 6.2. A mass balance on chlorine containing species expressed as chlorine indicated that from 88 to 91.6 percent of the species were accounted for each time a sample was analyzed. Chlorite decay followed second-order reaction kinetics as determined by plotting the inverse of the concentration versus time (Figure 22). A linear regression provided an r^2 value of 0.98 which exhibited that the correlation was good for second order; the portion of the variation not explained by the line was 0.02 (two percent). The kinetic constant (slope of the line) was 0.039 hours*L/mg. The overall linear form of the second order expression used to explain the loss of chlorite in Milli-Q water is as follows:

$$1/[ClO_2^-]_t = 1/[ClO_2^-]_o + (0.039*Time) \quad [24]$$

KINETIC STUDIES WITH PAC IN LABORATORY-CONSTITUTED WATER

Laboratory-constituted water was treated with alum alone, PAC alone, or a combination of alum and PAC. For overall comparative purposes, the means of each data point was normalized by dividing by the initial concentration. The combination of alum and PAC (50 mg/L) effected the best

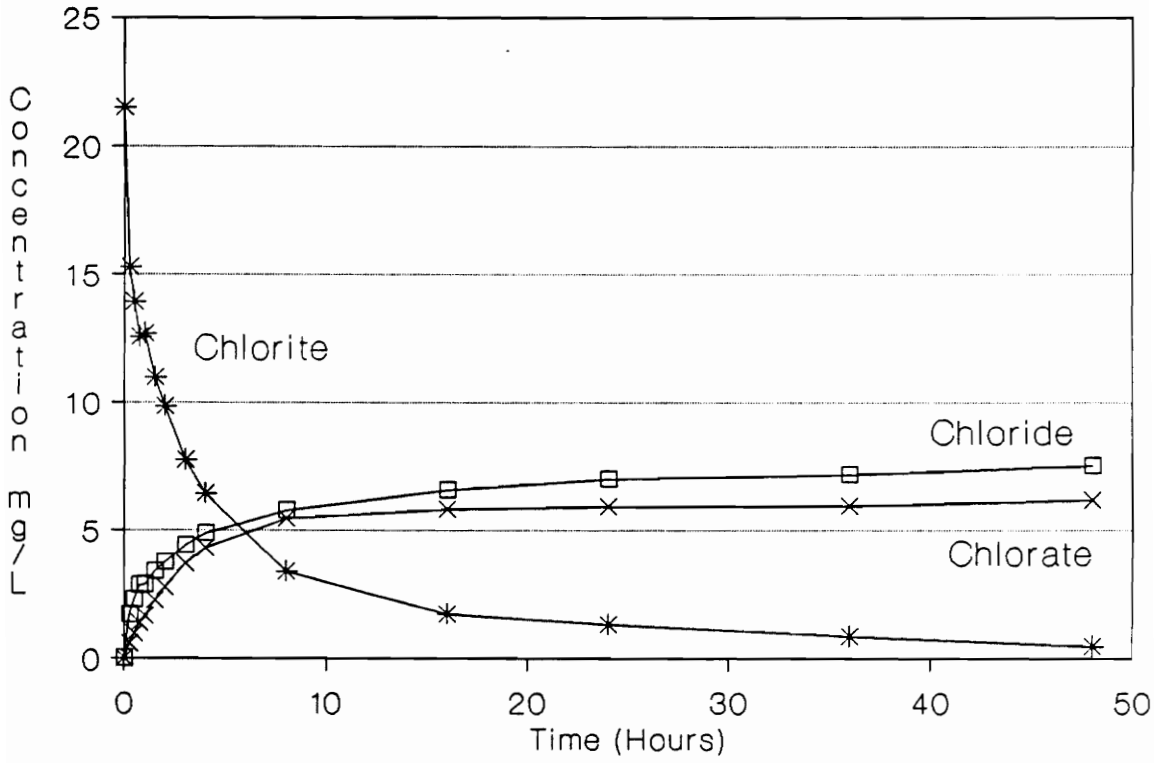

Figure 21. Removal of Chlorite by PAC (50 mg/L) in Milli-Q Water.

Table 22. Comparison of Ion Chromatography (IC), Amperometric Titration (AMP), and Flow Injection Analysis (FIA) for the Determination of Chlorite. Chlorite was Contacted with PAC (50 mg/L) in Milli-Q water for 48 Hours in a Batch Reactor.

	Chlorite Concentration, mg/L		
Time (Hours)	**IC**	**AMP**	**FIA**
0	21.50	19.33	23.74
0.25	15.27	15.71	18.49
0.50	13.92	14.30	16.35
0.75	12.55	13.54	15.10
1	12.67	13.05	14.30
1.5	10.98	11.68	12.78
2	9.84	10.46	11.45
3	7.77	8.60	9.31
4	6.43	7.15	7.71
8	3.38	4.15	4.23
16	1.72	2.23	2.55
24	1.30	1.36	1.63
36	0.84	0.81	0.90
48	0.46	0.49	0.52

Table 23. Comparison of Ion Chromatography (IC) and Flow Injection Analysis (FIA) for the Determination of Chlorate. Chlorite was Contacted with PAC (50 mg/L) in Milli-Q Water in a Batch Reactor for 48 Hours.

	Chlorate Concentration, mg/L	
Time (Hours)	**IC**	**FIA**
0	0.011	1.02
0.25	0.57	1.64
0.50	0.96	2.19
0.75	1.36	2.56
1	1.63	2.73
1.5	2.24	3.24
2	2.77	3.75
3	3.67	4.72
4	4.29	5.22
8	5.47	6.41
16	5.83	6.40
24	5.93	6.53
36	5.94	6.64
48	6.17	6.36

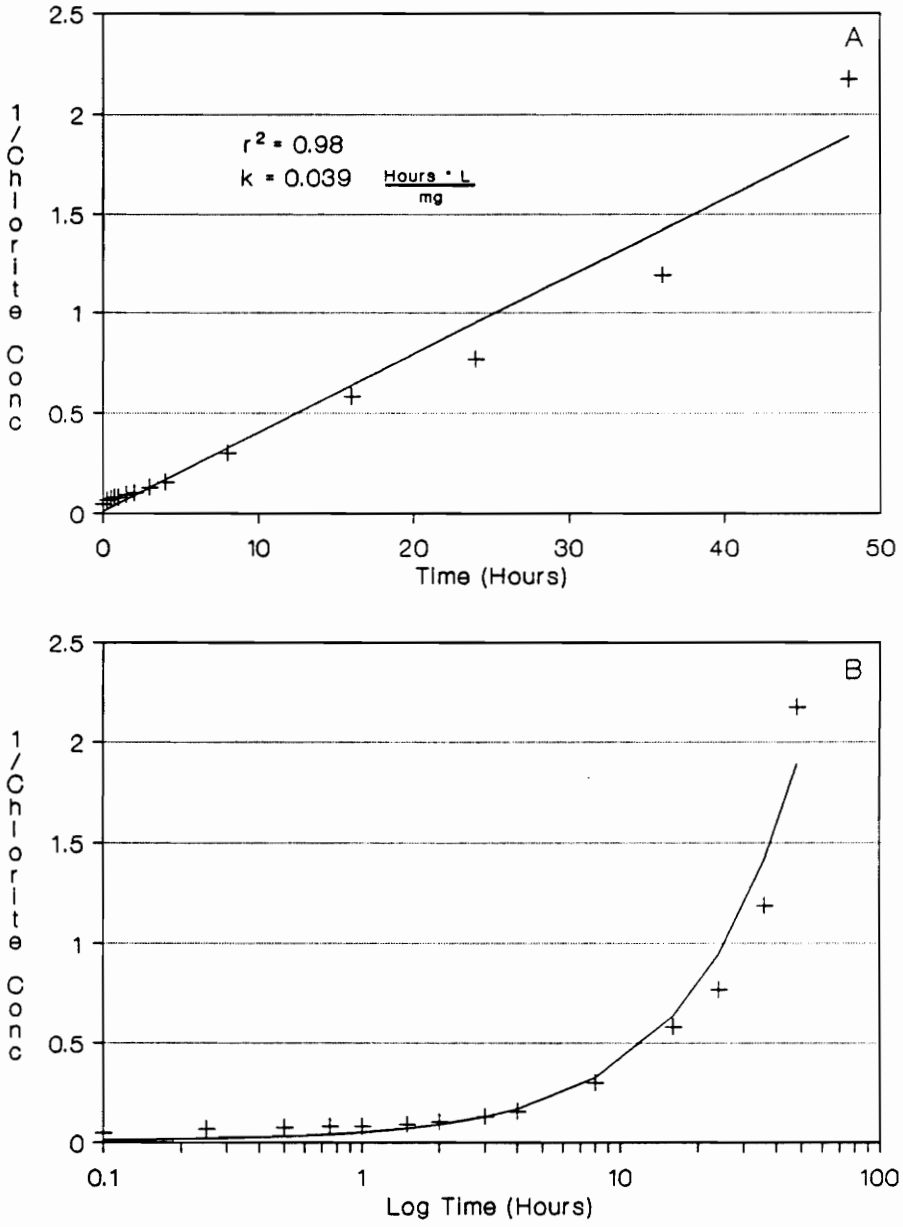

Figure 22. Evaluation of Second Order Kinetics for the Reduction of Chlorite in Milli-Q Water Using PAC (A). The Log of the X-Axis was Taken to Highlight the Early Reaction Times (B).

removal of chlorite (Figure 23). Individual treatments are further explained in the next two paragraphs.

Each experiment was conducted three times, and chlorite concentrations resulting from individual treatments are presented as means with one standard deviation error bars. The pH of the test water was 7.4. No chlorite reduction was evident in solutions containing only chlorite and bicarbonate (Figure 24). Three percent removal of chlorite occurred when alum was contacted with chlorite over a four-hour period (Figure 25). Chlorite removal by two PAC concentrations was evaluated. At 10 mg/L PAC, 17.2 percent of the chlorite was removed over the four hours of contact (Figure 26). At 50 mg/L PAC, 64 percent of the chlorite was removed over the four hour period (Figure 27). The combination of 10 mg/L PAC and alum slightly enhanced removal to 22.2 percent (Figure 28). The best removal of chlorite was effected by the combination of 50 mg/L PAC and alum (Figure 29). The percent removal was 78 after four hours of contact.

The reaction rates (Table 24) during each treatment were determined by using second order kinetics. These kinetics were shown to closely describe the decay of chlorite under ideal conditions (in the previous section). A linear regression was performed, and r^2 values were greater than 0.90 for all treatments.

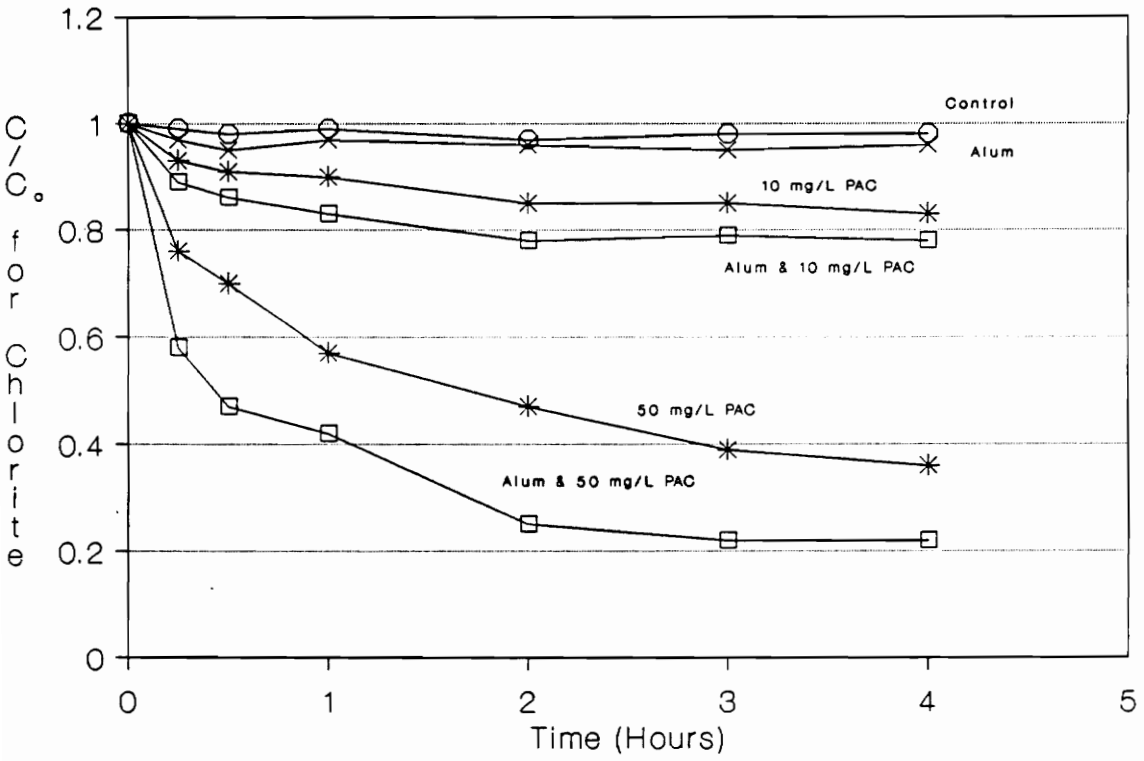

Figure 23. The Reduction of Chlorite in Laboratory-Constituted Water.
Note: The Data Have Been Normalized.

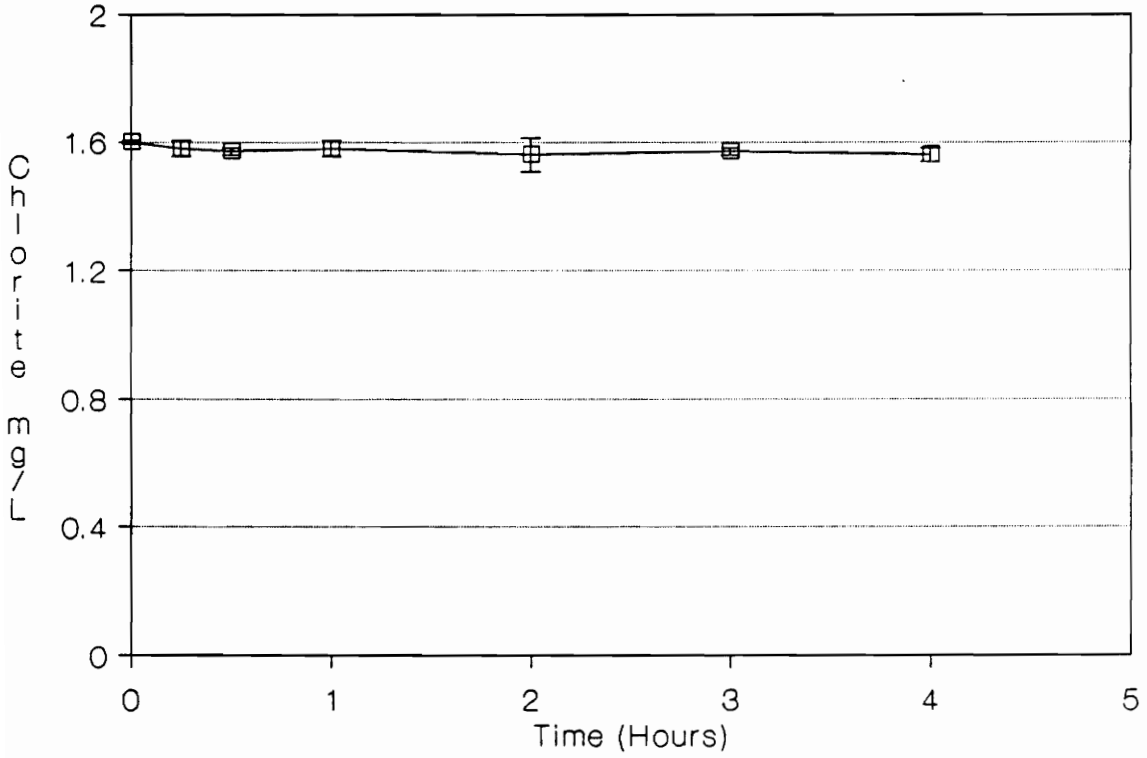

Figure 24. Chlorite Removal in Laboratory-Consituted Water for the Control Run. The Mean Data are Based on Three Different Experiments and Error Bars are One Standard Deviation.

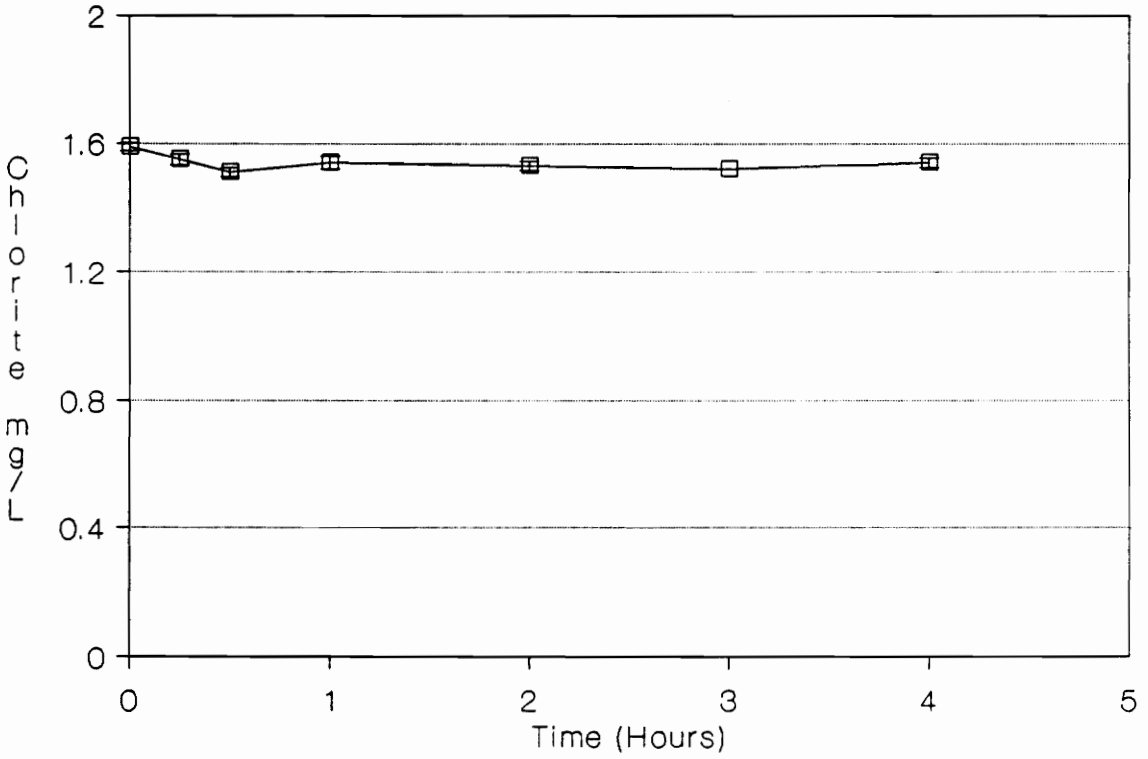

Figure 25. Chlorite Removal in Laboratory-Constituted Water By Alum. The Mean Data are Based on Three Different Experiments and Error Bars are One Standard Deviation.

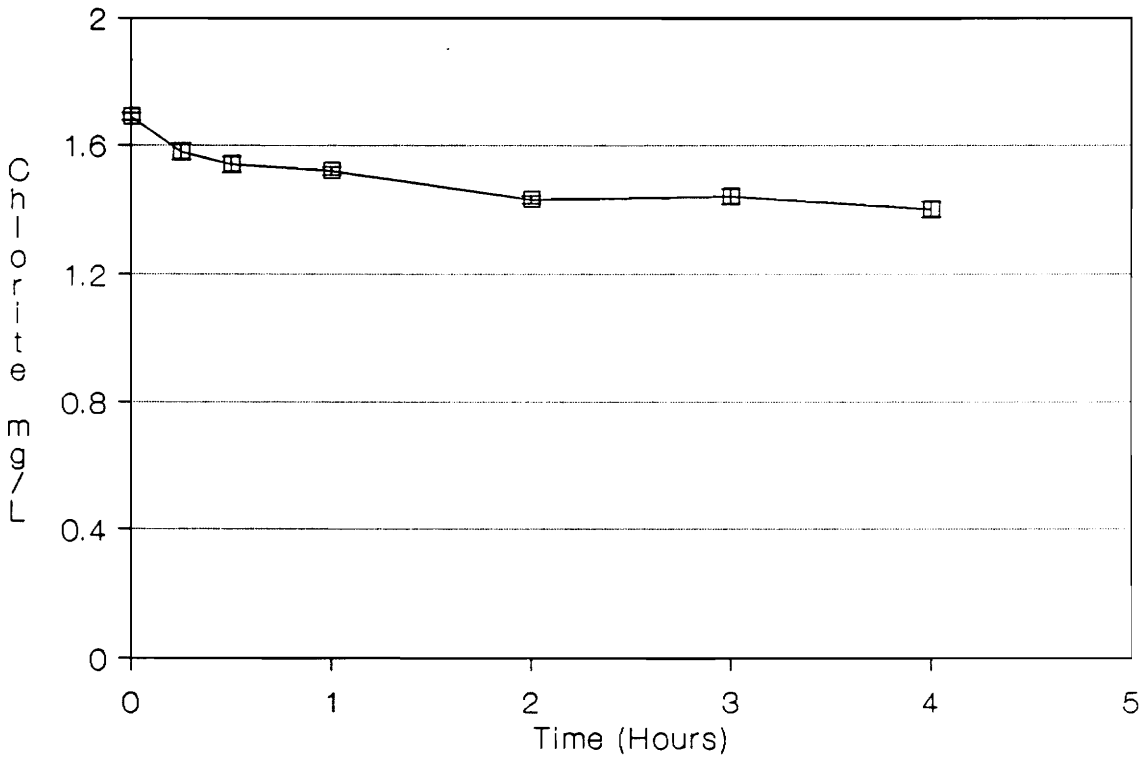

Figure 26. Chlorite Removal in Laboratory-Constituted Water By PAC (10 mg/L). The Mean Data are Based on Three different Experiments and Error Bars are One Standard Deviation.

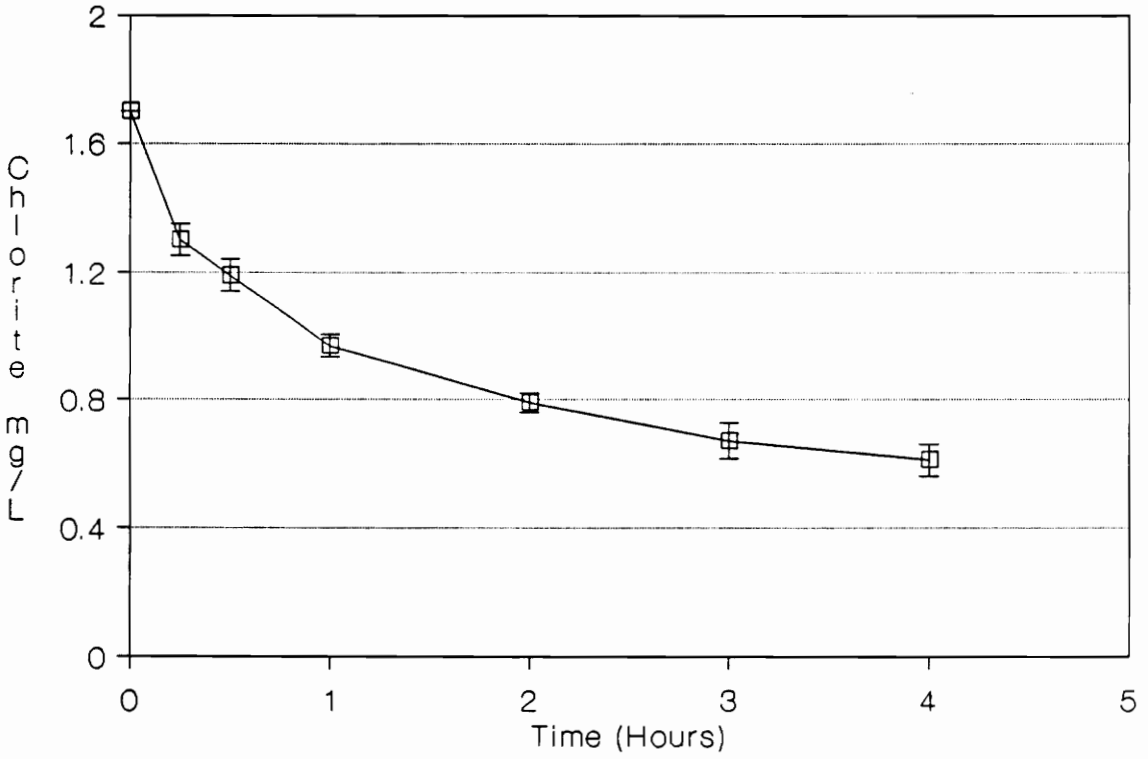

Figure 27. Chlorite Removal in Laboratory-Constituted Water by PAC (50 mg/L). The Mean Data are Based on Three Different Experiments and Error Bars are One Standard Deviation.

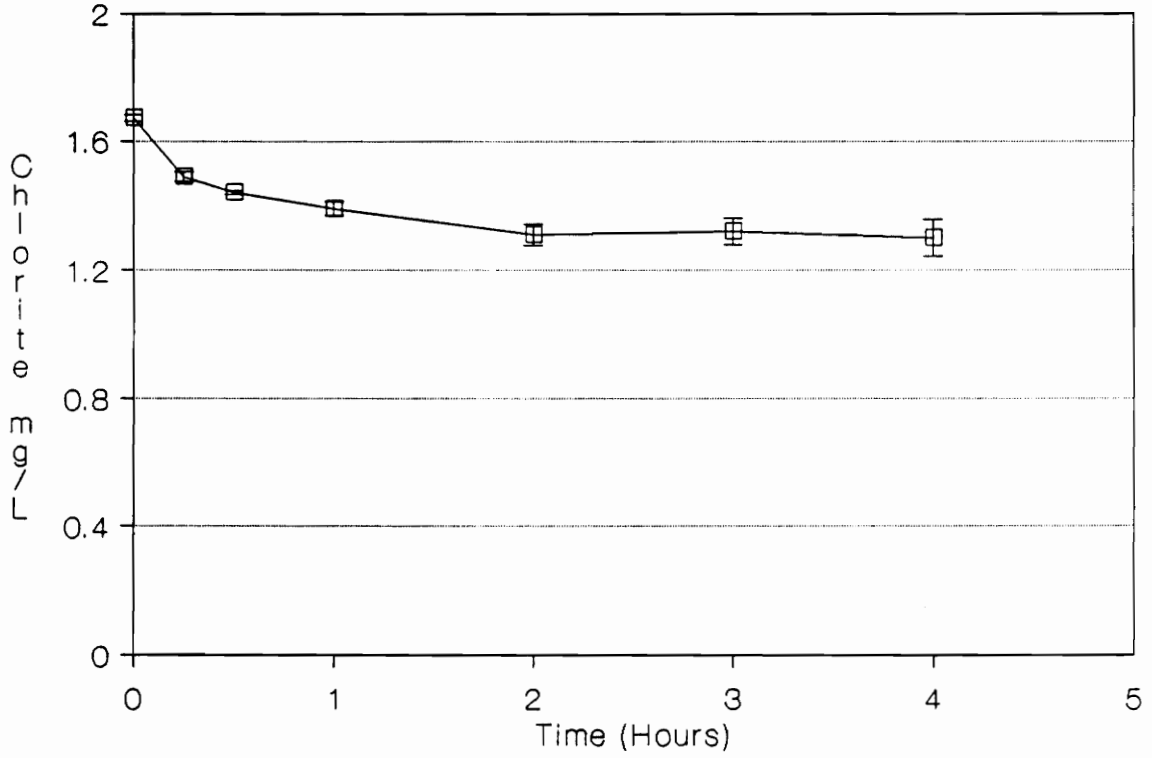

Figure 28. Chlorite Removal in Laboratory-Constituted Water by the Combination of Alum and PAC (10 mg/L). The Mean Data are Based on Three Experiments and Error Bars are One Standard Deviation.

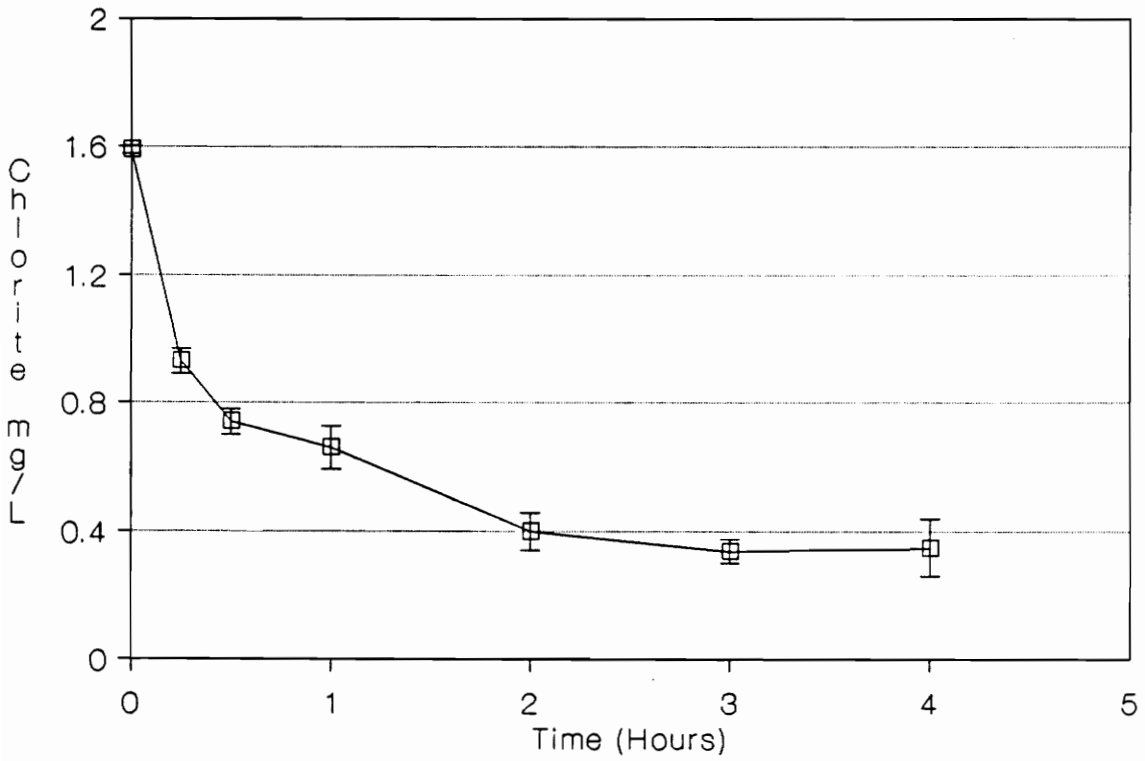

Figure 29. Chlorite Removal in Laboratory-Constituted Water by the Combination of Alum and PAC (50 mg/L). The Mean Data are Based on Three Experiments and Error Bars are One Standard Deviation.

Table 24. Reaction Rates (k) for Each Treatment Applied to Laboratory-Constituted Water for the Reduction of Chlorite.

TREATMENT	RATE (k) (Hours * L)/mg
PAC (10 mg/L)	0.026
PAC (50 mg/L)	0.253
ALUM & PAC (10 mg/L)	0.034
ALUM & PAC (50 mg/L)	0.575

KINETIC STUDIES WITH PAC IN PO RIVER WATER

The total organic carbon (TOC) concentration of Po River water was 7.27 mg/L (Table 25). The pH of each experiment was fixed at 7.4 by the addition of bicarbonate. Po River water was preoxidized with chlorine dioxide, and the concentrations of chlorine dioxide and chlorite were monitored at three intervals during the preoxidation period (Figure 30). The initial concentration (Initial Dose Figure 30) was determined by analysis of a distilled water solution (containing the chlorine dioxide dose) within 30 seconds. The immediate demand was determined by monitoring Po River water within 30 seconds of adding chlorine dioxide. The concentration of chlorine dioxide and chlorite were then measured after 30 minutes contact (i.e. as soon as the preoxidation period was complete). After preoxidation, Po River water was treated with either alum alone, PAC alone, or a combination of alum and PAC to remove residual chlorite. For overall comparative purposes, the data were normalized as was previously described. The best removal of chlorite was by the addition of alum and PAC in combination (Figure 31). Chlorine dioxide rapidly dissipated in water treated with PAC (Figure 32). Individual experiments are further explained in the following paragraphs.

Each experiment was conducted three times, and the mean chlorite concentration presented for each time interval with one standard deviation error bars. Chlorine dioxide was

Table 25. Water Quality Characteristics of Po River Water.

CHARACTERISTIC	CONCENTRATION
pH	6.9
Alkalinity	16 mg/L as $CaCO_3$
TOC	7.27 mg/L
Fe	2.72 mg/L
Mn	0.12 mg/L
Ultra-Violet Absorbance	0.365 (at 254 nm)

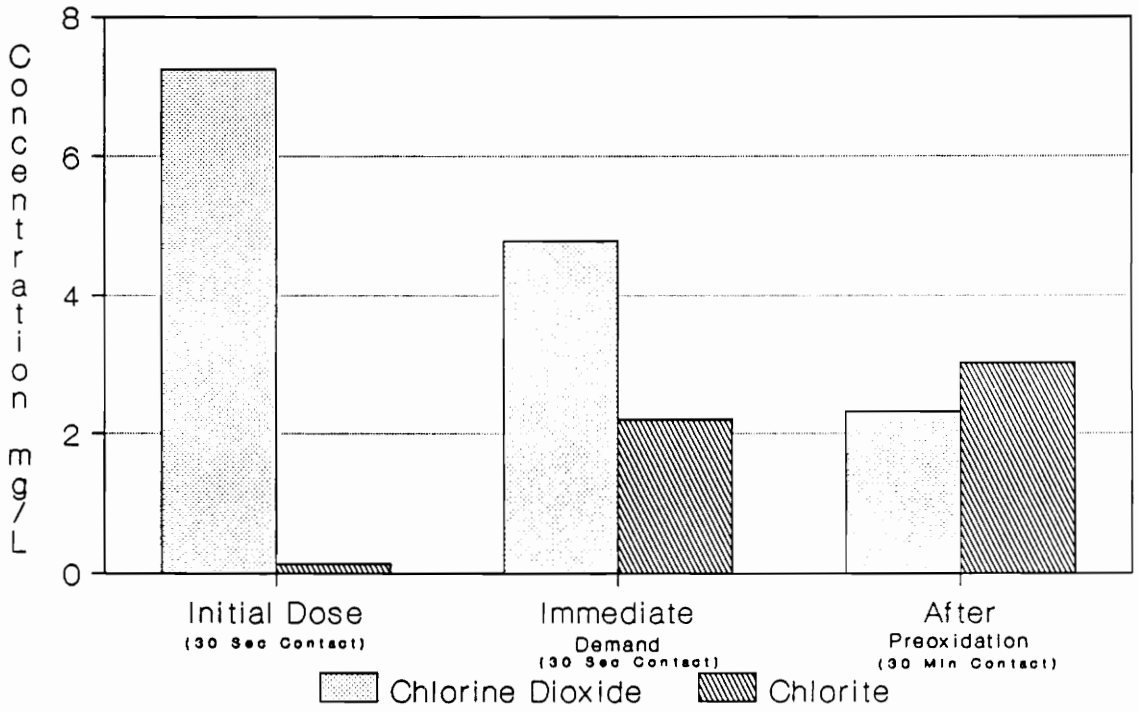

Figure 30. Concentrations of Chlorine Dioxide and and Chlorite During Preoxidation of Po River Water by Chlorine Dioxide. Initial Dose was Determined In Distilled Water.

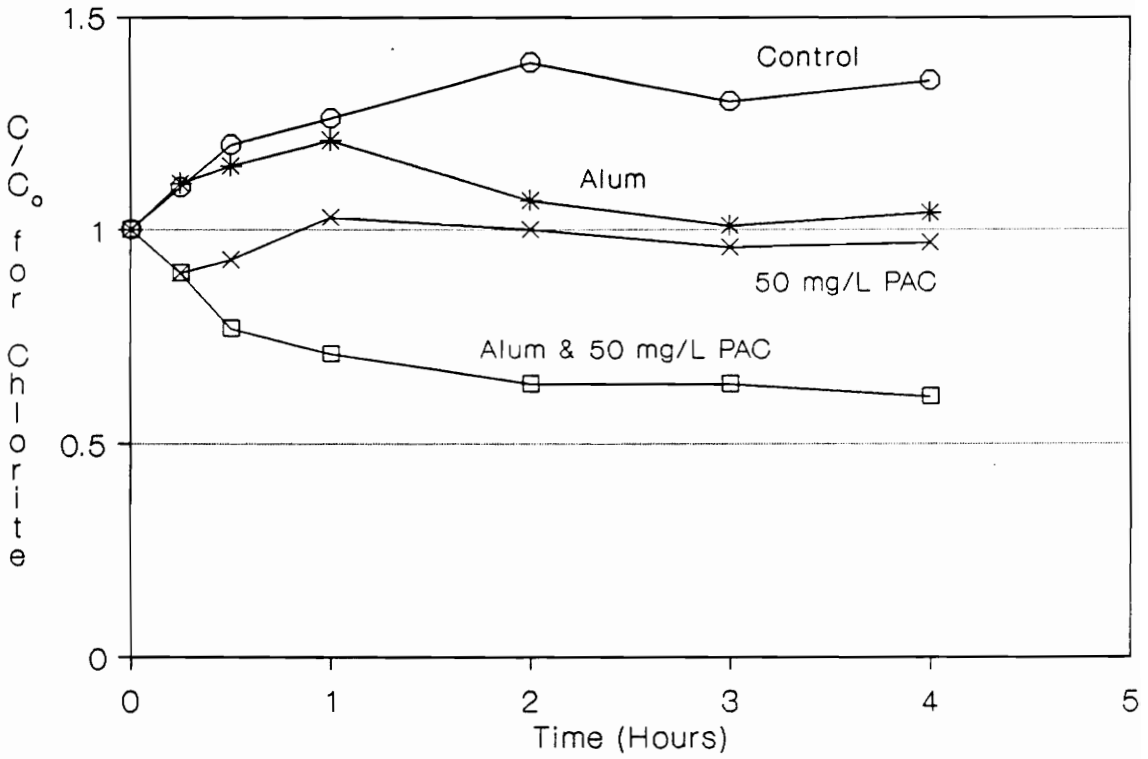

Figure 31. The Reduction of Chlorite in Po River Water.

Note: The Data Have Been Normalized.

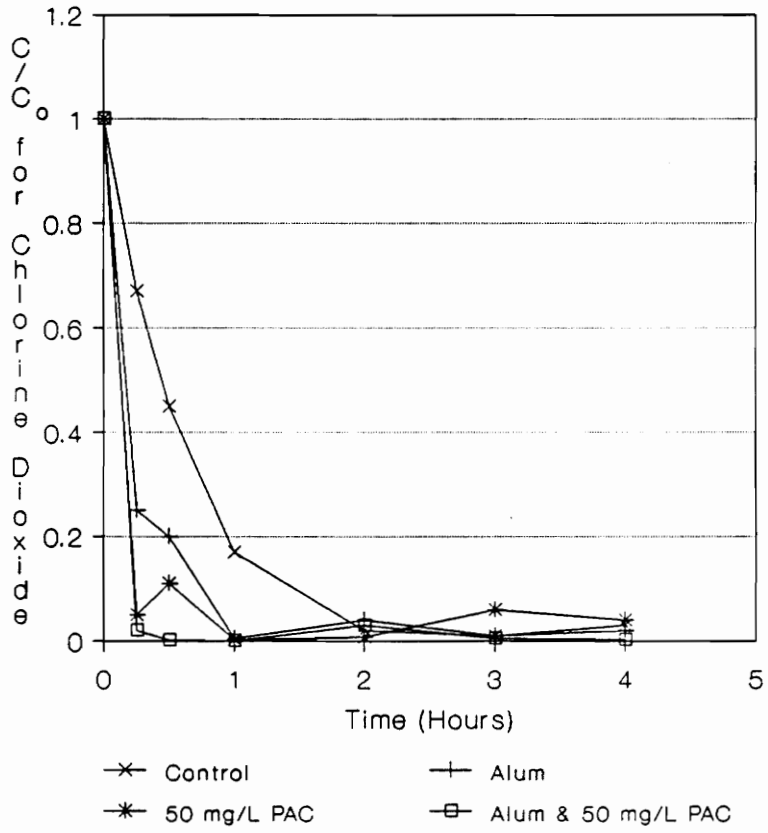

Figure 32. The Reduction of Chlorine Dioxide in Po River Water by One of Four Treatments Listed in the Legend.
Note: The Data have been Normalized.

completely reduced to chlorite after 2 hours of contact with Po River water in the control which had no treatment applied (Figure 33). The chlorite concentration did not change appreciably throughout the rest of the experiment. Chlorine dioxide was removed completely after one hour of contact with alum floc, and thereafter the level of chlorite was continuously reduced (Figure 34). Chlorine dioxide was removed to low levels after 15 minutes of contact with PAC (50 mg/L) and complete removal was observed after one hour of contact. Chlorite reduction occurred after chlorine dioxide was completely reduced (Figure 35).

Chlorine dioxide was completely removed within 15 minutes after treatment with the combination of PAC and alum. Chlorite was removed throughout the entire contact period (Figure 36). The rate of chlorite removal was determined to be 0.047 hours*L/mg through application of second-order kinetics. A linear regression was performed, and the resulting r^2 value was 0.90.

SIMULATION OF A FLOC-BLANKET CLARIFIER

A floc-blanket clarifier was simulated in the laboratory in a completely stirred tank reactor with a side clarifier. Powdered activated carbon was enmeshed in an alum floc in both laboratory-constituted water and Mattaponi River water in separate studies. The raw-water characteristics for Mattaponi River water are listed in Table 26. The resulting mean solids concentration was 2277 mg/L in the reactor containing

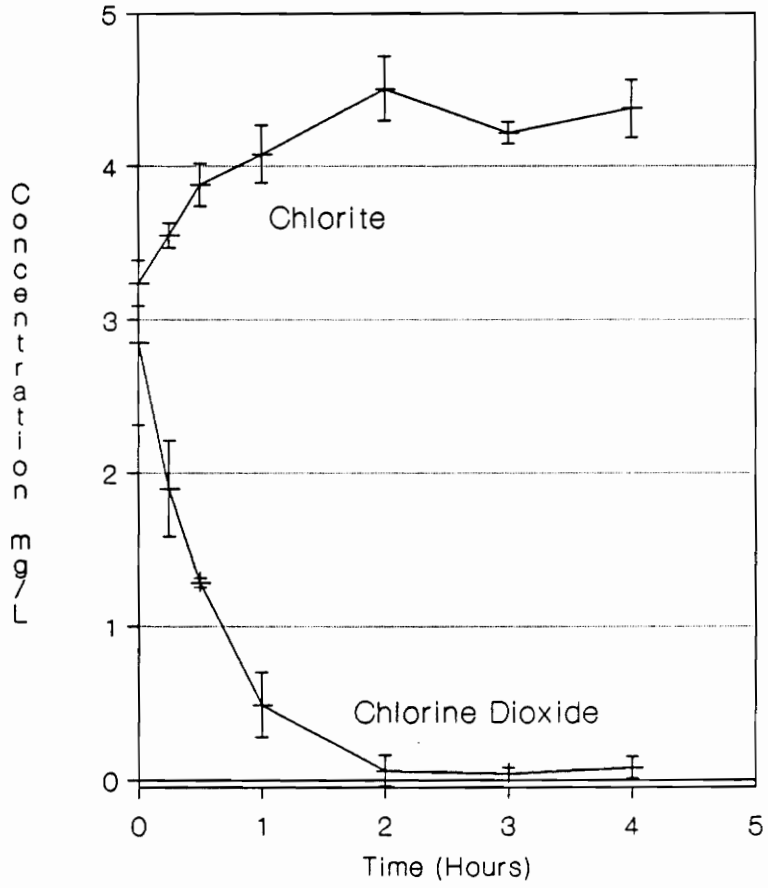

Figure 33. The Reduction of Chlorine Dioxide, and the Subsequent Formation of Chlorite in Po River Water During the Control Run. The Mean Data are Based on Three Different Experiments and Error Bars are One Standard Deviation.

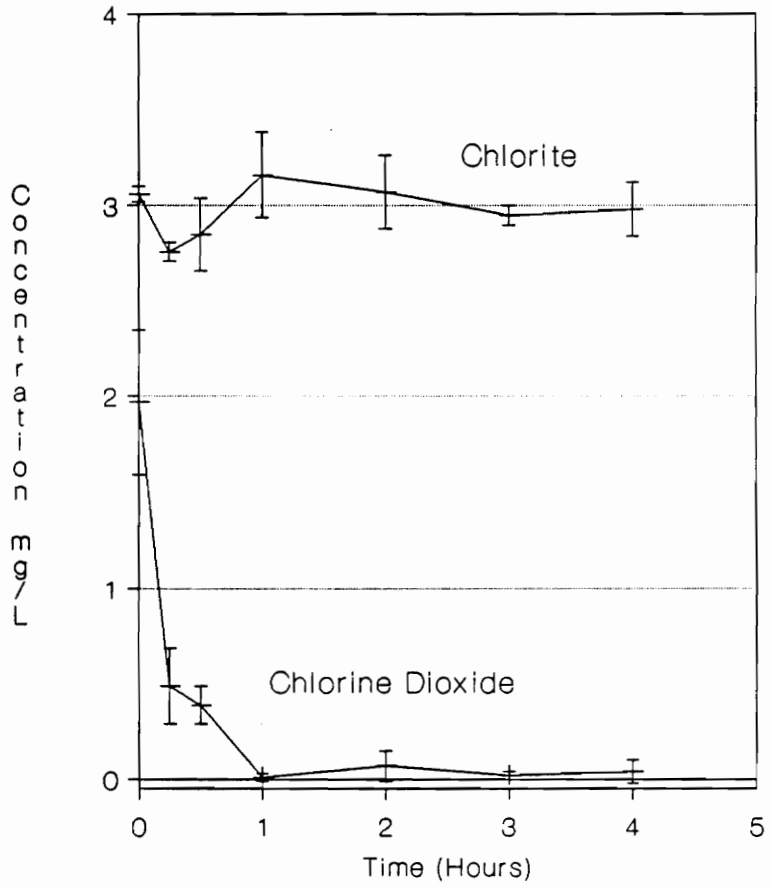

Figure 34. The Reduction of Chlorine Dioxide and the Subsequent Formation of Chlorite in Po River Water During Alum Treatment. The Mean Data are Based on Three Different Experiments and Error Bars are One Standard Deviation.

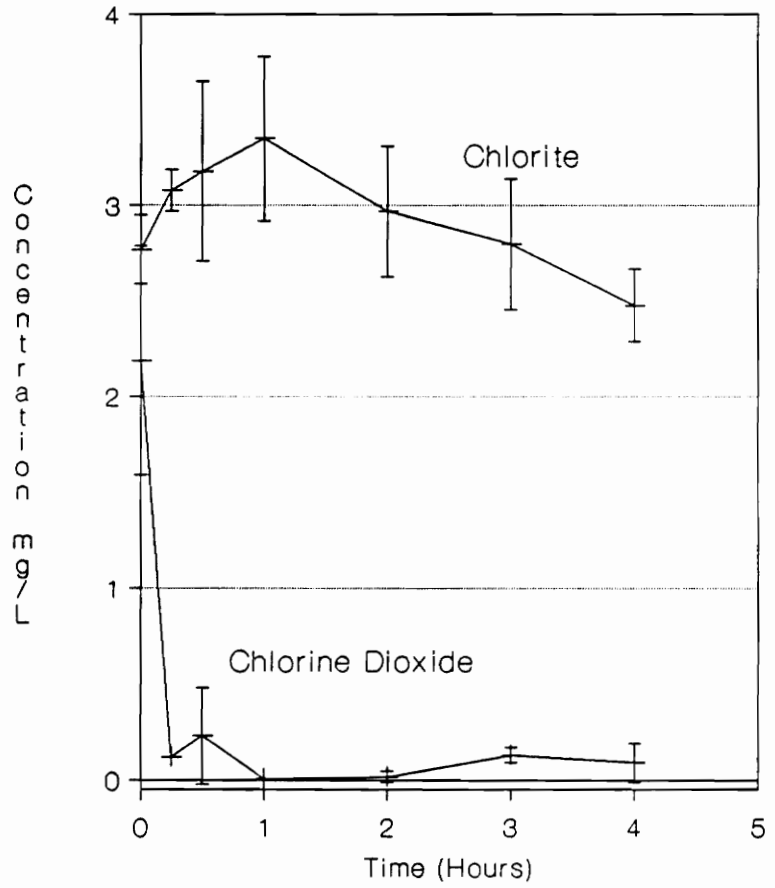

Figure 35. The Reduction of Chlorine Dioxide Followed by Chlorite Reduction in Po River Water During PAC Treatment (50 mg/L). The Mean Data are Based on Three Different Experiments and Error Bars are One Standard Deviation.

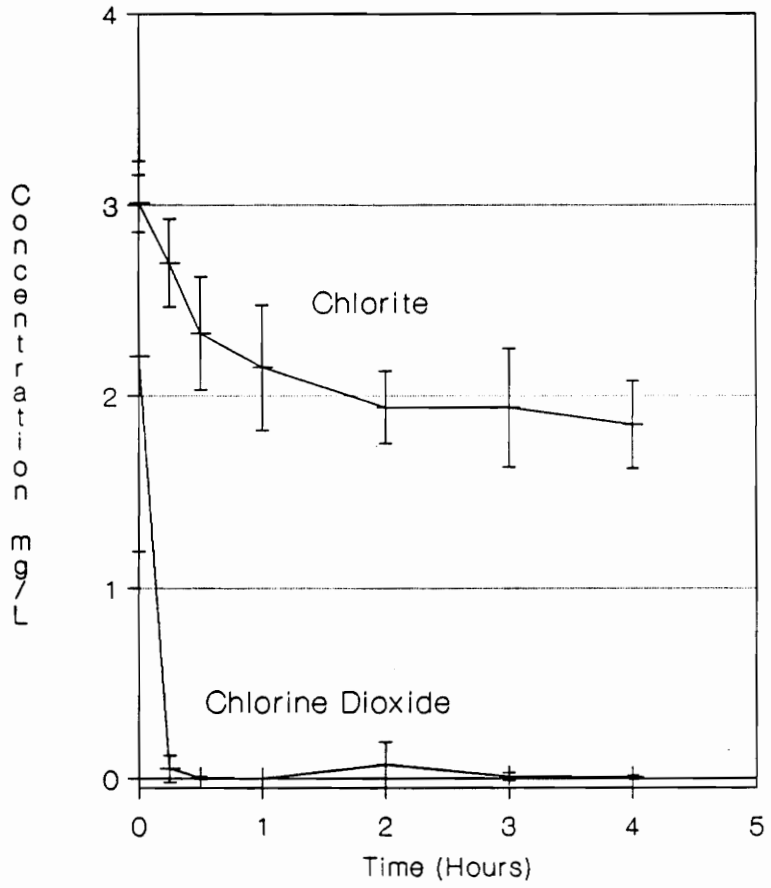

Figure 36. The Reduction of Chlorine Dioxide and Chlorite by Alum and PAC Treatment in Po River Water. The Mean Data are Based on Three Different Experiments and Error Bars are One Standard Deviation.

Table 26. Water Quality Characteristics of Mattaponi River Water.

CHARACTERISTICS	CONCENTRATION
pH	6.8
TOC	7.23 mg/L
Turbidity	5.52 NTU
Ultra-Violet Absorbance	0.056 (at 254 nm)

laboratory-constituted water and 3183 mg/L in the one containing Mattaponi River water. Floc made up in laboratory-constituted water was used as a control, and chlorite removal was greater than 96 percent throughout the experiment (Figure 37). In the reactor containing Mattaponi River water, chlorite removals during the first 11.3 hydraulic detention times were 92 percent (Figure 37). In both experiments, carbon loss from the reactor was evident 12 hours after the study began.

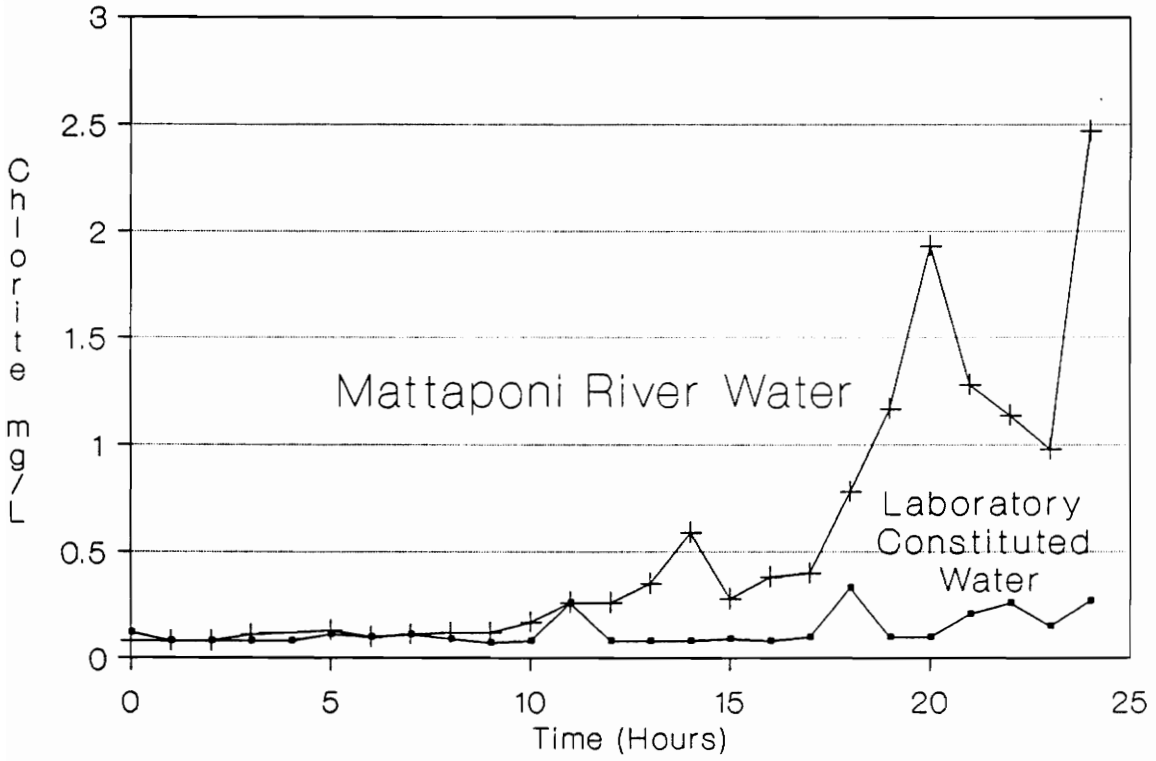

Figure 37. The Removal of Chlorite Through the Simulation of a Floc-Blanket Clarifier. The Feed Concentration of Chlorite was 9.58 mg/L.

CHAPTER 5

DISCUSSION OF THE RESULTS

SURVEY

The survey was sent to several water utilities that use chlorine dioxide but not to a "control group" that did not apply chlorine dioxide. Therefore, inherent in all the results, some bias may exist, though, bias was minimized by asking the utilities to describe their taste-and-odor events when chlorine dioxide was both on and off.

DESCRIPTIVE STATISTICS

The survey encompassed a wide variety of water utilities that use chlorine dioxide. The raw-water sources varied in type, volume, and quality. The raw-water quality characteristics among the utilities varied by orders of magnitude. (e.g. The color ranged from 2.5 to 200.) On the other hand, the finished-water quality did not vary so greatly, especially in those characteristics for which there are maximum contaminant levels (MCL) established.

Since most of the utilities stated that their primary use of chlorine dioxide was for THM-precursor control, one may assume that the companies were working to comply with the USEPA's mandate for the reduction of THM's (0.10 mg/L) in drinking water. This assumption is in agreement with the finding that eighty-five percent of the utilities had

installed their chlorine dioxide generator since 1980. On the other hand, in the earliest literature, most companies had indicated that the primary use of chlorine dioxide was for taste-and-odor control.

In keeping with the trend for the 1980's, eleven utilities applied chlorine dioxide every month of the year, indicating that for 34.3 percent of those surveyed, the use of chlorine dioxide is not just a seasonal treatment used in late summer. Again, one may assume that the utilities are using chlorine dioxide year-around to meet the current THM standard. With the expected lowering of the THM standard in 1991, the dose of chlorine dioxide needed to lower the organic precursors that form THM's may be very high (4-8 mg/L).

Water companies currently add about 1.0-1.4 mg/L chlorine dioxide. When chlorine dioxide reacts in water, chlorite, chlorate, and chloride are produced. Chlorite and chlorate are residual oxidants know to affect the oxygen-carrying capacity of red blood cells (Condie, 1986). Consequently, stringent requirements are proposed for these residual oxidants, with the current recommended limit set at 1.0 mg/L. Thus, methods will have to be developed in the near future for economically reducing the concentrations of chlorine dioxide by-products if the oxidant is to be used successfully.

The efficient generation of chlorine dioxide requires a delicate balance between chlorine and chlorite. A mere 20 percent of the companies surveyed evaluated generator

efficiency on a daily basis. One company tested the efficiency only one time, at "start-up". These results suggest that many companies may not know the true efficiency of their generator and may be producing excess by-products such as chlorate.

Taste-and-odor complaints reported by the utilities increased by 45 percent when chlorine dioxide was in use. The mean number of complainants who that had new carpeting was 46 percent. Several respondents indicated that all customers (100 percent) who complained had new carpeting. From the way questions were answered in this section of the survey, some respondents had no knowledge of the potential relationship between new carpeting and the odor complaints (i.e. they had no idea to ask complaining customers if they had recently installed new carpeting). Some wrote in "unknown," while others left all questions pertaining to new carpeting blank. Another respondent wrote "no way of knowing" and put "?" throughout the section as if he was puzzled by the questions.

STATISTICAL TESTS

Chi-square analyses were conducted to determine if the odors were related to the type of distribution system residual. Analysis of the final disinfectants chlorine and chloramine were weakened because only four of the companies that responded to the survey used chloramine as a final disinfectant. In general, a bias is established in the chi-square analysis if any cell in the contingency table has a

response of zero (Zar, 1984). Also, as a rule of thumb, no more than 20 percent of the cells should be less than five. In this case, most of the cells were less than five, and at least one cell in the chloramine row was always zero (Previous Section Table 12). The conclusion drawn from these data was that the type of final disinfectant (chlorine or chloramine) was not significantly related to the appearance of cat-urine-like, chlorinous, and kerosene-like tastes-and-odors. Ammoniation may form chloramines, thus removing the pathway for chlorine dioxide regeneration by reaction of chlorite and chlorine (Hoehn, et al., 1990). More studies need to be conducted to substantiate this potential amelioration technique.

The Wilcoxon paired-sample test was used to determine differences in responses to intensity of tastes-and-odors when chlorine dioxide was on compared to when it was off. In order to have paired data, the data submitted by the eleven companies that applied chlorine dioxide all of the time were not included in the analysis. The test indicated that several odors were problems only when chlorine dioxide was being added at the plant, but the intensity of tastes was not changed in the presence or absence of chlorine dioxide. The lowest tabled critical value was for numerical ranks from six or more respondents (Zar, 1984). Potentially significant odors were found not significant because the sample size was too small, one example of this occurrence was the hydrocarbon odor which

had a sample size of five (Appendix D Table 14).

The cluster analysis was used to determine directly from the data, groups of tastes-and-odors that were associated. Seven clusters of odors were formed when chlorine dioxide was being added compared to none formed when the chemical was not being added. The formation of a cluster indicated that the odors were reported at the same level by many of the utilities, for instance most utilities indicated that their water never smelled like floral, fragrant, pig pen, or wet paper. Cat urine was considered a "stand alone" smell to the research team, but clusters generated by similar responses to the survey grouped this odor with hydrocarbon and lighter fluid odors. These data support reports of other hydrocarbon-type smells (diesel fuel, gasoline, kerosene, and natural gas) observed at sites experiencing the odors (Hoehn et al., 1990). The hydrocarbon smells were also found to be statistically associated with one another through the cluster analysis.

Interestingly, many of the computerized odor clusters resemble the classes of tastes-and-odors generated by the research team (Table 27). If the final cluster generated by the statistical analysis was not exactly as the class established by the research team, then the prior cluster was often times very similar. For example, the hydrocarbon class (Previous Section Table 9) generated by the research team was very close to the cluster (Previous Section Figure 15) that lead to computerized clusters number two and six (Previous

Table 27. Resemblance of Computer Generated Clusters to the Research Team's Imposed Classes for Odors.

CLASSES	CLUSTER
Cat Urine	Cat Urine, Hydrocarbon, Lighter Fluid
Antiseptic, Bleach, Chlorinous, Chlorox, Medicinal, Phenolic, Purex, Swimming Pool	Bleach, Chlorinous, Chlorox, Purex, Swimming Pool
Diesel Fuel, Gasoline, Hydrocarbon, kerosene, Lighter Fluid, Natural Gas, Organic Solvent, Plastic, Plastic Pipe, Rubber, Varnish	Diesel Fuel, Gasoline, Kerosene, Natural Gas
Earthy, Moldy, Potato, Potato Bin, Varnish, Wet Paper, Woody	Organic Solvent, Phenolic, Plastic, Plastic Pipe, Rubber, Varnish
Floral, Fragrant, Sweet	Floral, Fragrant, Pig Pen, Wet Paper
Decayed Vegetation, Fishy, Marshy, Pig Pen, Septic, Sewage, Swampy	Decayed Vegetation, Earthy, Grassy, Haylike, Marshy, Moldy, Septic, Sewage, Swampy, Woody
Cucumber, Grassy, Haylike	Antiseptic, Cucumber, Fishy, Medicinal, Potato, Potato Bin, Sweet

Section Table 14).

The Wilcoxon test indicated that the intensity of several odors increased when chlorine dioxide was turned on at the water treatment plant. The cluster analysis indicated that responses to several of the odors recognized in the Wilcoxon test were similar. For instance, diesel fuel, gasoline, kerosene, and natural gas odors were intensified in the presence of chlorine dioxide according to the Wilcoxon test and were grouped together in the computerized cluster analysis. The combination of these two tests demonstrates that the use of chlorine dioxide seemed to enhance the intensity and number of odors in the tap water of customers.

FIELD STUDIES

Because of the transient nature of tastes-and-odors, the mechanisms by which they are generated often remains a mystery for years. In the case of this research, the presence of chlorine dioxide at the tap of customers homes was a clue that the oxidant itself may have been involved somehow with the offensive odors. The new technology of flow injection analysis, which made possible the quantification of chlorine dioxide at low-levels, made possible the confirmation of these findings. Recently, the VPI&SU team that conducted this research proposed two mechanisms (Equations 1 and 2) by which the reformation of chlorine dioxide may occur in the

distribution systems of utilities that experience odor events (Hoehn et al., 1990). The generation of the odors by the volatilization of chlorine dioxide in a newly carpeted room further supported the correlation of new carpeting and chlorine dioxide with odor events.

LABORATORY STUDIES

FATE OF CHLORITE IN PAC-TREATED WATER

The removal of chlorite from water containing activated carbon (PAC) was found to occur by oxidation-reduction reactions. Contact of chlorite for 15 minutes with several concentrations of activated carbon brought about the complete reduction of chlorite to chloride. When the contact period was 30 minutes or seven days, not only was chlorite reduced, it also was oxidized to chlorate. In these reactions, the chlorite ion disproportionated and chlorite was simultaneously oxidized and reduced. This type of reaction is common when chlorine gas is added to water:

$$Cl_{2(g)} + H_2O \rightarrow HOCl_{(aq)} + Cl^-_{(aq)} + H^+ \qquad [25]$$

Interestingly, after seven days of contact, the sample containing no carbon had significant levels of chlorate (approximately 5.74 mg/L) present. This may have occurred because at acidic conditions (the pH of this solution ranged

from 5.5 to 6.0) chlorite will react with the hydrogen ions present in the water and produce some chlorine dioxide which in turn can oxidize some of the chlorite to chlorate (Masschelein and Rice, 1979). This mechanism may account for the high levels of chlorate in the control after seven days of contact. Since no chlorate was detected after 15-minute of PAC contact, the reaction likely exhibited a lag phase, although any proposed mechanism is uncertain. The lag phase may exist because of changes that occur at the carbon surface. For instance, a catalyst may be released from the surface when chlorite is reduced to chloride, and the catalyst may then cause the oxidation of chlorite to chlorate.

Because chlorate was formed, higher levels of chlorite than are normally observed during water treatment were used in the laboratory studies to facilitate accurate analyses of the reaction products (chlorate is usually difficult to analyze in low concentrations). In all cases, removal of chlorite was proportional to contact time and PAC dose. Hence, increased PAC dose and contact time caused removal efficiencies to increase. The reaction sites at the carbon surfaces eventually became exhausted and chlorite removal ceased. The exhaustion of sites may have occurred by the loss of functional groups that interact with chlorite on the carbon surface or a build of interferents at the carbon surface.

Chlorite was contacted with PAC in Milli-Q water in one experiment so that the reaction kinetics could be determined.

In that ideal case, the decay of chlorite in the presence of PAC closely resembled second order kinetics. Since the data followed second order kinetics ($r^2 = 0.98$), the explanation of the decay of chlorite did not seem to require an adsorption term. One may assume, if adsorption occurred at all, that the step was instantaneous and did not substantially change the kinetics of the reaction.

KINETIC STUDIES WITH PAC IN LABORATORY-CONSTITUTED WATER

The removal of chlorite in laboratory-constituted water was most effective when the combination of alum and PAC (50 mg/L) was used. Originally, it was thought that alum floc would entrap the carbon particles and block the active sites from reactions with chlorite. The observed enhancement of chlorite removal by floc-enmeshed PAC suggests that diffusion through the liquid layer surrounding the PAC particle was the main barrier to mass transport instead of "floc particle diffusion". These results are similar to those reported by Lettinga et al., 1978. The concentration of PAC (50 mg/L) required to effectively reduce residual chlorite to low levels in drinking water would not be cost effective in plant-scale operations, however. An economically feasible dose of 10 mg/L PAC was also examined, but the chlorite removal was only 17.2 percent after four hours of contact.

KINETIC STUDIES WITH PAC IN PO RIVER WATER

As was observed in studies of chlorite removal by PAC in laboratory-constituted water, the removal of chlorite in Po

River water that had been pretreated with 7.58 mg/L chlorine dioxide was most effective when alum and PAC (50 mg/L) were added together. Chlorite removal occurred when chlorine dioxide was depleted from the water. The PAC effectively removed residual chlorine dioxide within 15 minutes, and the removal of chlorite by PAC followed. The rate of chlorite removal in Po River water (0.047 hours*L/min) treated with alum and PAC was similar to that observed in the Milli-Q water (0.039 hours*L/min). These results indicate that the sites at the carbon surface used to remove chlorite were not significantly blocked or changed by the high level of TOC. The concentration of PAC required to remove residual chlorite in this system exceeds the cost that most treatment facilities would be willing to pay.

SIMULATION OF A FLOC-BLANKET CLARIFIER

The integrity of the floc in the simulated clarifier was lost due to extended shear forces on the particles over the 24 hours of slow mixing. The loss of floc in the effluent could have been averted by the addition of polymer. The high TOC in Mattaponi River water did not change or block the sites on the carbon surface that are used to remove chlorite. The application of PAC in the simulated floc-blanket clarifier demonstrated that high concentrations of chlorite could be removed for long periods of time by this process. While the process proved effective, few treatment plants are equipped with these units, therefore, this application would only apply

to a few installations. These results suggest that chlorine dioxide could be applied at very high levels (> 5 mg/L) during the preoxidation step in water treatment.

CHAPTER 6

SUMMARY AND CONCLUSIONS

The objectives of this research were: (1) to determine the cause of odors that occurred in drinking water systems when chlorine dioxide was added during treatment and then (2) to investigate potential amelioration techniques. To gather information leading to the cause of odors, a survey was sent to companies using chlorine dioxide and the water at two plants was sampled during odor events. Once the cause of odors was determined and confirmed, the removal of residual chlorite from drinking water became the objective of the laboratory phase of the project.

SUMMARY OF SURVEY RESULTS

A good response to the survey was obtained, and the significant conclusions derived from that phase of the project are:

1. The major purpose for applying chlorine dioxide was to reduce precursors of THM's.
2. Chlorine dioxide was applied during most months of the year by the utilities surveyed.
3. Most chlorine dioxide generators have been installed since 1980. Utilities generally do not calibrate their generators very often.

4. The number of complaints increased when chlorine dioxide was in use. Odors were commonly detected in both the air and water of the kitchen and bathroom.
5. Customers that had recently installed new carpeting complained more frequently than those who had not.
6. None of the classes of tastes-and-odors correlated with any of the raw- or finished-water characteristics.
7. The point of chlorine dioxide application at the plant did not affect the frequency of complaints of cat urine, chlorinous, or kerosene tastes-and-odors.
8. The cat-urine-like, chlorinous, and kerosene-like odors were reported by systems that used both chlorine and chloramine for distribution system residuals. Since only a few (4) of the respondents used chloramines the Chi-Square analysis was weakened. The analysis indicated that the final disinfectants chlorine and chloramine did not cause significant differences in responses to cat urine, chlorinous, and kerosene tastes-and-odors. The significance of this finding needs to be confirmed.

9. Some odors were reported more frequently and were more intense when chlorine dioxide was being applied at the treatment plant. Of significance to this project, cat urine and kerosene odor responses were different in the presence versus the absence of chlorine dioxide.
10. Seven, computer-generated clusters were obtained for the odor descriptions when chlorine dioxide was in use. Diesel fuel, gasoline, kerosene, and natural gas were found to be associated with one another in a cluster. Cat urine, hydrocarbon, and lighter fluid were also associated with one another in a cluster. No clusters were obtained when the chlorine dioxide was not in use.
11. Five computer generated clusters were obtained for the taste descriptions when chlorine dioxide was in use. Two clusters were obtained when the chemical was not in use.

SUMMARY OF FIELD RESULTS

The field studies provided a means by which the mechanism of odor generation could be determined and then substantiated. The significant conclusions from this phase of the project are:

1. Low levels of chlorine dioxide were discovered in the distribution systems of two water treatment plants.
2. The research team described odor homes as smelling cat-urine-like or kerosene-like.
3. The volatilization of chlorine dioxide in a room with new carpeting produced the offensive cat-urine-like and kerosene-like odors.

SUMMARY OF LABORATORY RESULTS

Methods for removing residual chlorite from water were evaluated to provide a means by which the reformation of chlorine dioxide could be prevented. The significant conclusions from this phase of the project are:

1. Decay of chlorite in the presence of PAC occurred by a disproportionation reaction in which chloride and chlorate were formed.
2. The reduction of chlorite by PAC in Milli-Q water followed second-order kinetics.
3. The combination of alum and PAC enhanced chlorite removal in laboratory-constituted water, when compared to either treatment alone. The concentration of PAC required to achieve satisfactory chlorite removal was not cost-effective.

4. The combination of alum and PAC enhanced chlorite removal in Po River water, when compared to either treatment alone. The concentration of PAC required to achieve satisfactory chlorite removal was not cost-effective.
5. The removal of high levels of chlorite by simulating a floc-blanket clarifier was very successful. This method provides a means to reduce high levels of chlorite, thus increasing the amount of chlorine dioxide that can be applied to drinking water.

CONCLUSIONS

1. Chlorine dioxide reforms in distribution systems, most likely from reactions involving chlorite. The exact mechanism has not been elucidated.
2. The offensive tastes-and-odors associated with chlorine dioxide application at water treatment plants result from the formation of compounds, yet unidentified, that occur when chlorine dioxide in the tap-water escapes and reacts with organic compounds in the air of customers' homes or businesses.
3. Complaints of odors other than the offensive cat-urine-like and kerosene-like increased when

chlorine dioxide is added at water treatment plants.

4. The quality of raw waters being treated with chlorine dioxide was not a factor in intensity or frequency of appearance of the obnoxious odors. Neither were the applied dose or the point of application in the treatment plant.

5. Conventional PAC application can be effectively used for chlorite-control only if high doses are applied ($\geq$ 50 mg/L). Ten mg/L was not a high enough dose to reduce chlorite concentration by more than 17 percent; the 50 mg/L dose reduced it by 64 percent. Alum and PAC applied together removed 22 percent of the chlorite at the 10 mg/L dose, and 78 percent at the 50 mg/L dose. The removal of chlorite in an ideal system occurred by second-order reaction kinetics. Concentrations of PAC that could be achieved in an upflow, sludge-blanket clarifier would be high enough to remove significant levels of chlorite (9.58 mg/L) from drinking water.

RECOMMENDATIONS FOR FUTURE RESEARCH

1. The efficiency of chlorine dioxide generators at water treatment plants needs to be monitored more closely to prevent the unnecessary formation of

chlorite and chlorate.

2. The mechanism by which chlorine dioxide reforms in distribution systems needs to be verified.
3. The disproportionation of chlorite in the presence of activated carbon needs to be studied at concentrations more representative of drinking water treatment to determine if chlorate is formed.
4. The potential of chlorate formation when PAC is used needs further verification and evaluation in plant-scale or large pilot scale operation.
5. Further research with chlorite-reducing agents (sulfur dioxide and ferrous iron) should be conducted under conditions similar to those encountered in water treatment plants.
6. Studies should be conducted to determine the extent of chlorine dioxide reformation from chlorite when the final oxidant is chloramine.
7. More accurate and precise methods for qunatitatively detecting chlorite, chlorate, chloride, and chlorine dioxide should be developed.

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APPENDIX A

SURVEY AS SENT TO UTILITIES THAT APPLY CHLORINE DIOXIDE

CHLORINE DIOXIDE USE IN DRINKING WATER TREATMENT

A SURVEY

Conducted For
The American Water Works Association Research Foundation
by
Virginia Polytechnic Institute and State University (VPI&SU)
and the American Water Works Service Company

Robert C. Hoehn and Andrea M. Dietrich, VPI&SU
Ramon G. Lee, American Water Works Service Company
Jeff Oxenford, American Water Works Association Research Foundation

This survey is being conducted as part of an AWWA Research Foundation project entitled "Cause and Control of Taste-and-Odor Problems Associated with the Use of Chlorine Dioxide as a Primary Disinfectant and Oxidant." Your facility has been identified as one that uses chlorine dioxide, and you are being contacted to determine if you have experienced any unusual problems, particularly an increased incidence of taste-and-odor complaints, while you were adding that oxidant. Your answers will help us determine the causes of these problems -- and, hopefully the solutions -- so that chlorine dioxide may be used to better advantage by the industry.

The survey is in four parts dealing with the following:

1) your water source
2) the treatment you provide
3) your use of chlorine dioxide
4) taste-and-odor problems you may have experienced

Please fill out and return the questionnaire as soon as possible. A self-addressed, stamped envelope has been provided for your convenience. If you have questions or comments, please telephone either Robert Hoehn at (703)231-6133 or Andrea Dietrich at (703)231-5773. Thank you for your cooperation!

SOURCE DESCRIPTION

1. **Indicate the type of raw water source(s). Check all that apply.**

_____ groundwater
_____ lake
_____ impounded stream
_____ off-stream impoundment
_____ river; stream
_____ other (describe) _____

If multiple sources are used, give percentages:

% Surface Water:_____ % Groundwater:_____

2. **Source size:**

Surface Waters:

a. Lake or Reservoir: surface acres:_____ avg. depth (ft):_____ volume (acre-ft):_____

b. Streamflow: avg. cfs or mgd (specify which):_____

Groundwater Sources:

a. Wells: number:_____ Flow: gpm or mgd (specify):_____

3. **Population Served: Check the appropriate population.**

_____ < 10,000

_____ 10,000-50,000

_____ 50,000 - 75,000

_____ 75,000 - 100,000

_____ 100,000 - 500,000

_____ 500,000 - 1,000,000

_____ > 1,000,000

4. **Indicate Raw Water And Distributed Water Quality for the Following (N/A if not monitored):**

a. Raw Water Quality

Parameter	Annual Average	Annual Range
Color units, number		
Total Organic Carbon, mg/L		
Fe, mg/L		
Mn, mg/L		
Turbidity, NTU		
pH		
Ammonia-N, mg/L		
Odor, Threshold Odor No.		
Total Dissolved Solids, mg/L		
Bromide, mg/L		
Chloride, mg/L		
Coliforms, number/100 mL		
Total Kjeldahl Nitrogen, mg/L		

b. Distributed Water Quality

Parameter	Annual Average	Annual Range
Color units, no.		
Total Organic Carbon, mg/L		
Fe, mg/L		
Mn, mg/L		
Turbidity, NTU		
pH		
Ammonia-N, mg/L		
Odor, Threshold Odor No.		
Total Dissolved Solids, mg/L		
Free Chlorine, mg/L		
Combined Chlorine, mg/L		
Chlorine Dioxide, mg/L		
Chlorite ion, mg/L		
Other:		

5. **What algae have been identified with specific odors in your source water?**

Algal Type	Associated Odor
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____

TREATMENT

6. **Describe treatment processes**

a. Pretreatment:

coagulants: Check all that apply.

_____ alum
_____ iron salts
_____ polymer
_____ others (list): _____
_____ none

oxidants: Check all that apply.

_____ chlorine
_____ chlorine dioxide
_____ chloramines
_____ permanganate
_____ ozone
_____ others (list): _____
_____ none

b. Clarification: Check the appropriate description.

_____ conventional flocculation, settling
_____ sludge-blanket clarifier
_____ others (list): _____
_____ none

c. Filtration: Check the appropriate filtration method.

_____ rapid sand
_____ slow sand
_____ dual media (anthracite and sand)
_____ trimedia (anthracite, sand, garnet)
_____ others (list): _____
_____ none

d. Other Pretreatment (Please describe in the space below.)

7. **Do you use granular activated carbon either as sand replacement or as post-filter absorbers? Circle yes or no.**

yes no

8. **If your answer to 7. was yes, in which mode, sand replacement or post-filter adsorbers? Circle one.**

sand replacement post filter adsorbers

CHLORINE DIOXIDE USE

9. **What is the *MAJOR* purpose for adding chlorine dioxide? Check only one.**

_____ odor control
_____ THM-precursor control
_____ preoxidant for manganese and/or iron control
_____ predisinfection
_____ Other (list):_____

10. **What, if any, is the *SECONDARY* purpose for adding chlorine dioxide? Check only one.**

_____ odor control
_____ THM-precursor control
_____ preoxidant for manganese and/or iron control
_____ predisinfection
_____ Other (list):_____

11. **During what months of the year do you normally add chlorine dioxide? (Please circle months.)**

Jan. Feb. Mar. Apr. May June July Aug. Sept. Oct. Nov. Dec

12. **Is any other oxidant added to raw water at the same time ClO_2 is added? Circle yes or no below.**

yes no

If you answered yes, which oxidant(s)? Check all that apply.

_____chlorine
_____permanganate
_____other: Specify which: _____

13. **Equipment For Chlorine Dioxide Generation:**

a. Name of manufacturer ? _____

b. Date of installation ? _____

c. Type chlorite feed? Circle one below.

liquid dry

d. If liquid, what percentage chlorite? _____

e. Is acid added as part of the chlorine dioxide generation procedure? Circle yes or no.

yes no

14. **Operations:**

a. Generator efficiency:_____%; Frequency determined:_____

b. Chlorine dioxide application point? (Check all that apply.):

_____intake
_____flash mixer
_____after settling but before filtration
_____after filtration before clear well
_____in or after clear well before distribution
_____other; List:_____

c. Target dosage if applied at single point: _____ mg/l.

d. At what point in the flow train, if any, do you measure chlorine dioxide to control the dosage? That is, where is your chlorine dioxide control point, if one is used?

_____

e. Target residual concentration desired at control point: _____ mg/L

f. Type of oxidant residual measured at the control point? (check all that apply):

total oxidants _____ chlorine dioxide _____

chlorites _____ chlorates _____

g. Analytical Method For Chlorine Dioxide and Chlorite Detection: Check those that apply.

_____DPD
_____Leucocrystal violet
_____Other (list): _____

QUESTIONNAIRE CONTINUED NEXT PAGE

TASTES AND ODORS

16. **Taste-and-Odor Complaints:**

a. *ODORS*. Check terms **used by customers** to describe the odors and circle one number to indicate the frequency of occurrence, ranging from never (1) to most frequent (5).

Description	ClO_2 In Use Never				Frequent	ClO_2 Not In Use Never				Frequent
antiseptic	1	2	3	4	5	1	2	3	4	5
bleach	1	2	3	4	5	1	2	3	4	5
cat urine	1	2	3	4	5	1	2	3	4	5
chlorinous	1	2	3	4	5	1	2	3	4	5
Chlorox	1	2	3	4	5	1	2	3	4	5
cucumber	1	2	3	4	5	1	2	3	4	5
decayed vegetation	1	2	3	4	5	1	2	3	4	5
diesel fuel	1	2	3	4	5	1	2	3	4	5
earthy	1	2	3	4	5	1	2	3	4	5
fishy	1	2	3	4	5	1	2	3	4	5
floral	1	2	3	4	5	1	2	3	4	5
fragrant	1	2	3	4	5	1	2	3	4	5
gasoline	1	2	3	4	5	1	2	3	4	5
grassy	1	2	3	4	5	1	2	3	4	5
haylike	1	2	3	4	5	1	2	3	4	5
hydrocarbon	1	2	3	4	5	1	2	3	4	5
kerosene	1	2	3	4	5	1	2	3	4	5
lighter fluid	1	2	3	4	5	1	2	3	4	5
marshy	1	2	3	4	5	1	2	3	4	5
medicinal	1	2	3	4	5	1	2	3	4	5
moldy	1	2	3	4	5	1	2	3	4	5
natural gas	1	2	3	4	5	1	2	3	4	5
organic solvent	1	2	3	4	5	1	2	3	4	5
phenolic	1	2	3	4	5	1	2	3	4	5
pig pen	1	2	3	4	5	1	2	3	4	5
plastic	1	2	3	4	5	1	2	3	4	5
plastic pipe	1	2	3	4	5	1	2	3	4	5
potato	1	2	3	4	5	1	2	3	4	5
potato bin	1	2	3	4	5	1	2	3	4	5
Purex	1	2	3	4	5	1	2	3	4	5
rubber	1	2	3	4	5	1	2	3	4	5
septic	1	2	3	4	5	1	2	3	4	5
sewage	1	2	3	4	5	1	2	3	4	5
swampy	1	2	3	4	5	1	2	3	4	5
sweet	1	2	3	4	5	1	2	3	4	5
swimming pool	1	2	3	4	5	1	2	3	4	5
varnish	1	2	3	4	5	1	2	3	4	5
wet paper	1	2	3	4	5	1	2	3	4	5
woody	1	2	3	4	5	1	2	3	4	5

Other odor descriptions (Please list.): _____

---

b. Are the odors in the air, or can they be detected also in a water sample? Please circle.

in air only in water only in both water and air

c. *TASTES.* Check terms used by customers to describe the tastes and circle one number to the frequency of occurrence, ranging from never (1) to most frequent (5).

Description	ClO_2 In Use Never				Frequent	ClO_2 Not In Use Never				Frequent
antiseptic	1	2	3	4	5	1	2	3	4	5
bleach	1	2	3	4	5	1	2	3	4	5
cat urine	1	2	3	4	5	1	2	3	4	5
chlorinous	1	2	3	4	5	1	2	3	4	5
Chlorox	1	2	3	4	5	1	2	3	4	5
cucumber	1	2	3	4	5	1	2	3	4	5
decayed vegetation	1	2	3	4	5	1	2	3	4	5
diesel fuel	1	2	3	4	5	1	2	3	4	5
earthy	1	2	3	4	5	1	2	3	4	5
fishy	1	2	3	4	5	1	2	3	4	5
floral	1	2	3	4	5	1	2	3	4	5
fragrant	1	2	3	4	5	1	2	3	4	5
gasoline	1	2	3	4	5	1	2	3	4	5
grassy	1	2	3	4	5	1	2	3	4	5
haylike	1	2	3	4	5	1	2	3	4	5
hydrocarbon	1	2	3	4	5	1	2	3	4	5
kerosene	1	2	3	4	5	1	2	3	4	5
lighter fluid	1	2	3	4	5	1	2	3	4	5
marshy	1	2	3	4	5	1	2	3	4	5
medicinal	1	2	3	4	5	1	2	3	4	5
moldy	1	2	3	4	5	1	2	3	4	5
natural gas	1	2	3	4	5	1	2	3	4	5
organic solvent	1	2	3	4	5	1	2	3	4	5
phenolic	1	2	3	4	5	1	2	3	4	5
pig pen	1	2	3	4	5	1	2	3	4	5
plastic	1	2	3	4	5	1	2	3	4	5
plastic pipe	1	2	3	4	5	1	2	3	4	5
potato	1	2	3	4	5	1	2	3	4	5
potato bin	1	2	3	4	5	1	2	3	4	5
Purex	1	2	3	4	5	1	2	3	4	5
rubber	1	2	3	4	5	1	2	3	4	5
septic	1	2	3	4	5	1	2	3	4	5
sewage	1	2	3	4	5	1	2	3	4	5
swampy	1	2	3	4	5	1	2	3	4	5
sweet	1	2	3	4	5	1	2	3	4	5
swimming pool	1	2	3	4	5	1	2	3	4	5
varnish	1	2	3	4	5	1	2	3	4	5
wet paper	1	2	3	4	5	1	2	3	4	5
woody	1	2	3	4	5	1	2	3	4	5

Others (Please list.): _____

e. Respond to the following questions about detection of odors at your treatment plant.

Are odors detected at the treatment plant?

yes no

If the answer to the above was yes, answer the next two questions to better define where you detect them.

Are odors detected at the plant in the filter effluent? Circle yes or no below.

yes no

Are odors detected at the plant in the clearwell? Circle yes or no below.

yes no

f. Average weekly number of customer complaints about tastes and odors:

At times when ClO_2 is being added: _____

At times when ClO_2 is not being added: _____

g. Location of complaints in the distribution system: Check all that apply.

_____at points distant from the treatment plant
_____near the treatment plant
_____isolated customers throughout the system
_____near transmission mains
_____in areas near dead ends
_____neighboring homes in one or more areas of the system
_____no consistent pattern

h. What time of days are most complaints received?

_____ Throughout the day _____ Morning

_____ Afternoon _____ Night

i. Do the customer complaints seem to increase when the chlorine dioxide dosage exceeds some particular level? Circle yes or no below.

yes no

If your answer was "yes:", above what dosage do complaints seem to increase? _____

j. Are the T & O worse during periods of high rainfall? Circle yes or no below.

yes no

k. Does the frequency of complaints seem to be related to your plant production level? Circle yes or no below.

yes no

If "yes:", are complaints more numerous with ***increased*** or ***decreased*** production? Circle one.

with increased production with decreased production

l. To your knowledge, had any complaining customers recently installed new carpet? Circle yes or no below.

yes no

m. List the approximate percentage of the total number of complaining customers who had new carpet.

_____

n. To your knowledge, had any complaining customers recently redecorated or painted their homes? Circle yes or no below.

yes no

o. List the approximate percentage of the total number of complaining customers who had redecorated or painted.

_____

p. Are the T & O detected in cold or hot water, or both? Circle one below.

cold hot both hot and cold

q. In what area(s) of the homes are the odors most often reported? Check the ones that apply.

_____in the bathroom
_____in the laundry room
_____in the kitchen
_____other (please list) _____

16. **What analytical techniques do you use to quantify tastes and odors?**

_____threshold odor number (TON)

_____flavor profile analysis (FPA)

_____gas chromatographic identification of odor compounds

_____other (describe) _____

17. **In your opinion, what factors contribute to the development of tastes and odors in your system?**

_____
_____
_____
_____
_____
_____
_____
_____
_____
_____

18. **Name of Respondent:** _____

Name of Treatment Plant: _____

Address: _____

_____

_____

Telephone No. _____

Hours spent filling out this form: _____

PLEASE PROVIDE A SCHEMATIC DIAGRAM OF YOUR PLANT SHOWING POINTS OF CHEMICAL ADDITION IF ONE IS AVAILABLE.

THANK YOU FOR YOUR COOPERATION!

APPENDIX B

LETTERS SENT ALONG WITH THE SURVEY TO UTILITIES THAT APPLY CHLORINE DIOXIDE

COVER LETTER MAILING ONE

Dear Water Treatment Professional:

As a project officer at the American Water Works Association Research Foundation (AWWARF), I am requesting your assistance in a significant research effort. A current AWWARF project is evaluating the possible causes and solutions to the taste-and-odor problems associated with drinking water treatment, particularly with respect to the use of chlorine dioxide. This project is being conducted by a research team at Virginia Polytechnic Institute and State University, directed by Drs. Robert C. Hoehn and Andrea M. Dietrich.

Enclosed you will find a very important questionnaire concerning taste-and-odor problems and the application of chlorine dioxide for disinfection and oxidation. Your prompt response to this questionnaire will be greatly appreciated. As experts who have the practical experience of day-to-day water treatment plant operations, your answers are critical to understanding the taste and odor problems.

I realize your time is valuable, but if we can work together on this problem then a solution my be close at hand. On behalf of the AWWA Research Foundation, I thank you for your cooperation on this research

Sincerely yours,

Jeff Oxenford
Project Officer

JO:kp

Enclosure

POST CARD MAILING TWO

Last week a questionnaire seeking information about your company's use of chlorine dioxide was mailed to you. Your facility was identified as a chlorine dioxide user.

If you already completed and returned it to us please accept our sincere thanks. If not, please do so at your earliest convenience. Because it has been sent to only chlorine dioxide users, it is extremely important that yours also be included in the study if the results are to accurately represent the information available about chlorine dioxide.

If by some chance you did not receive the questionnaire, or it got misplaced, please call me as soon as possible at (703) 231-6133, and I will put one in the mail to you today.

Sincerely,

Robert C. Hoehn
Project Director

COVER LETTER MAILING THREE

Dear Sir:

Recently I mailed you a questionnaire asking for information about your utility's use of chlorine dioxide. That questionnaire is part of a research project funded by the American Water Works Research Foundation. We are trying to gather as much information as possible concerning utilities experiences with chlorine dioxide, especially focusing on taste-and-odor problems that may be associated with its use. Because we haven't received your completed questionnaire, we wondered if perhaps you did not receive it, so we are sending you another one just in case the first one got lost in the mail.

I know that your work load is heavy enough without having to concern yourself with filling out a detailed questionnaire, and doing so is definitely an imposition on your valuable time, but we are hoping nevertheless that you will help us out because the experiences of every utility are important to our survey. We have identified only about thirty-seven utilities that use chlorine dioxide, and we are trying to get information from as many as possible so that the data we finally report will be truly representative of the water industries experiences with it.

I realize that summertime is not an ideal time to take on additional tasks because of vacations, etc., but if you can possibly find the time to fill out the questionnaire , we'd greatly appreciate it. You may have already mailed it, and if so, thank you for your help. If you feel you cannot fill out the questionnaire for some reason or another, or of you would not be able to fill it out right away, I'd appreciate either a note from you or a phone call at (703) 231-6133.

Your efforts on our behalf will be duly acknowledged in the final report, but I want to assure you that your response will remain anonymous. Each utility will be assigned a code, and the data we collect will be expressed only in statistical terms.

Thank you in advance for your help in this project. We deeply appreciate your participation.

Sincerely,

Robert C. Hoehn
Professor

THANK-YOU MAILING FOUR

Dear Sir:

Thank you for your participation in the chlorine dioxide survey this past summer. This questionnaire was part of a larger project sponsored by AWWARF to investigate taste-and-odor problems associated with chlorine dioxide use. Your input as a water treatment professional gave excellent insight to the current use of chlorine dioxide. Your responses were evaluated carefully. As a special thanks to you, we have enclosed a summary of the preliminary data from the survey. A final report will be available in the winter of 1990 from the AWWA Research Foundation, 6666 W. Quincy Ave., Denver, CO 80235.

Enclosed is an announcement you might be interested in concerning an upcoming workshop on the analysis of oxidants by flow injection.

Thank you again for your cooperation with this survey, it was your thoughtful answers that gave the results value.

Sincerely,

Robert C. Hoehn
Andrea M. Dietrich
Margaret P. Orr
VPI&SU
Environmental Engineering
Blacksburg, VA 24061

SHORT SUMMARY OF SURVEY

* 67.6% of the utilities surveyed cited their main use of chlorine dioxide was for THM-precursor control.

* Most utilities used chlorine dioxide every month of the year.

* 85% of the utilities surveyed installed their generator after 1980.

* 88.2% of the utilities surveyed use a liquid chlorite feed.

* 56.3% of the utilities surveyed used the DPD method for chlorine dioxide and chlorite detection while 46.9% used the Amperometric method.

* The cat urine odor was never observed in 59.4% of the utilities surveyed while 37.5% of the utilities surveyed sometimes observed the odor while chlorine dioxide was in use.

* The kerosene odor was never observed in 34.4% of the utilities surveyed while 62.5% of the utilities surveyed sometimes observed the odor while chlorine dioxide was in use.

* The cat urine odor was never observed in all of the utilities surveyed when chlorine dioxide was not in use.

* The kerosene odor was never observed in all of the utilities surveyed when chlorine dioxide was not in use.

* The cat urine taste was never observed in the utilities surveyed when chlorine dioxide was in use or not in use.

* The kerosene taste was never observed in 69% of the utilities surveyed while 24.2% of the utilities surveyed sometimes observed the taste while chlorine dioxide was in use.

* The kerosene taste was never observed in the utilities surveyed when chlorine dioxide was not in use.

* 63.3% of the utilities surveyed indicated that complaining customers had recently installed new carpeting.

* Thirty-four utilities from eighteen states were represented by this survey. 97% of the utilities surveyed responded to the questionnaire.

* The mean time for filling out the survey was 1.82 hours.

APPENDIX C

TABULATED CHLORINE DIOXIDE SURVEY

CHLORINE DIOXIDE USE IN DRINKING WATER TREATMENT

A SURVEY

Conducted For
The American Water Works Association Research Foundation
by
Virginia Polytechnic Institute and State University (VPI&SU)
and the American Water Works Service Company

Robert C. Hoehn and Andrea M. Dietrich, VPI & SU
Ramon G. Lee, American Water Works Service Company
Jeff Oxenford, American Water Works Association Research Foundation

This survey is being conducted as part of an AWWA Research Foundation project entitled "Cause and Control of Taste-and-Odor Problems Associated with the Use of Chlorine Dioxide as a Primary Disinfectant and Oxidant." Your facility has been identified as one that uses chlorine dioxide, and you are being contacted to determine if you have experienced any unusual problems, particularly an increased incidence of taste-and-odor complaints, while you were adding that oxidant. Your answers will help us determine the causes of these problems--and, hopefully the solutions--so that chlorine dioxide may be used to better advantage by the industry.

The survey is in four parts dealing with the following:

1) your water source
2) the treatment you provide
3) your use of chlorine dioxide
4) taste-and-odor problems you may have experienced

Please fill out and return the questionnaire as soon as possible. A self-addressed, stamped envelope has been provided for your convenience. If you have questions or comments, please telephone either Robert Hoehn at (703)231-6133 or Andrea Dietrich at (703)231-5773. Thank you for your cooperation!

SOURCE DESCRIPTION

1. **Indicate the type of raw water source(s). Check all that apply.** (Percent Based on n=32)

Frequency	Percent	
7	21.9	groundwater
8	25.0	lake
8	25.0	impounded stream
2	6.3	off-stream impoundment
18	56.3	river; stream
1	3.1	other (describe) _____

If multiple sources are used, give percentages:

% Surface Water:

Frequency	Mean	SDEV	Minimum Value	Maximum Value
29	86.9	29.0	0.0	100.0

% Groundwater:

Frequency	Mean	SDEV	Minimum Value	Maximum Value
26	11.3	27.3	0.0	100.00

2. **Source size:**

Surface Waters:

a. Lake or Reservoir:

surface acres:

Frequency	Mean	SDEV	Minimum Value	Maximum Value
16	934.25	1078.96	15.00	3600.00

avg. depth (ft):

Frequency	Mean	SDEV	Minimum Value	Maximum Value
15	56.4	147.77	2.00	589.00

volume (acre-ft):

Frequency	Mean	SDEV	Minimum Value	Maximum Value
16	1879269.97	7452783.18	18.41	29827000.00

b. **Streamflow: avg. cfs or mgd (specify which):**

Frequency	Mean	SDEV	Minimum Value	Maximum Value
16	2431.75	8498.87	0.00	34148.76

Groundwater Sources:

a. Wells: number:

Frequency	Mean	SDEV	Minimum Value	Maximum Value
10	11.10	16.82	0.00	50.0

Flow: gpm or mgd (specify):

Frequency	Mean	SDEV	Minimum Value	Maximum Value
8	25.50	51.11	0.00	150.0

3. **Population Served: Check the appropriate population.** (Percent Based on n=32)

Frequency	Percent	
0	0	< 10,000
9	28.1	10,000 - 50,000
5	15.6	50,000 - 75,000
8	25.0	75,000 - 100,000
8	25.0	100,000 - 500,000
2	6.3	500,000 - 1,000,000
0	0	> 1,000,000

4. **Indicate Raw Water and Distributed Water Quality for the Following: (N/A if not monitored)**

a. Raw Water Quality

ANNUAL AVERAGE

PARAMETER	N	Mean	Standard Deviation	Minimum Value	Maximum Value
Color Units, number	17	41.65	45.46	2.5	200.0
Total Organic Carbon, mg/L	7	7.65	7.84	2.0	25.0
Fe, mg/L	24	1.26	2.81	0.019	13.0
Mn, mg/L	21	0.13	0.13	0.004	0.45
Turbidity, NTU	29	20.11	27.82	0.44	138.0
pH	29	7.4	0.7	5.7	8.2
Ammonia-N, mg/L	8	0.25	0.17	0.02	0.49
Odor, Threshold Odor No.	14	5.07	6.13	1.00	24.0
Total Dissolved Solids, mg/L	16	248.94	159.09	26.0	558.0
Bromide, mg/L	5	0.24	0.35	0.0	0.86
Chloride, mg/L	22	43.23	41.57	4.9	200.0
Coliforms, number/100 mL	25	3941.7	8314.7	1.0	37300.0
Total Kjeldahl Nitrogen, mg/L	4	1.09	1.18	0.23	2.80

ANNUAL RANGE

PARAMETER		N	Mean	Standard Deviation	Minimum Value	Maximum Value
Color Units, number	Low	16	22.94	29.08	0.0	120.0
	High	16	159.78	293.96	2.50	1200.0
Total Organic Carbon, mg/L	Low	5	6.70	7.51	1.58	20.0
	High	5	15.1	13.98	6.89	40.0
Fe, mg/L	Low	23	0.22	0.30	0.0	1.0
	High	23	2.02	2.84	0.04	11.0
Mn, mg/L	Low	20	0.07	0.09	0.0	0.40
	High	20	0.63	0.97	0.01	4.23
Turbidity, NTU	Low	26	5.63	8.75	0.08	37.0
	High	26	278.32	521.45	1.00	2390.0
pH	Low	27	7.0	0.6	5.3	7.9
	High	27	8.1	0.8	6.2	9.5
Ammonia-N, mg/L	Low	7	0.11	0.13	0.0	0.37
	High	7	1.14	1.55	0.02	4.56
Odor, Threshold Odor No.	Low	13	3.53	4.55	0.0	17.0
	High	13	14.49	26.50	1.0	100.0
Total Dissolved Solids, mg/L	Low	15	209.20	147.52	31.00	538.0
	High	15	378.84	191.48	43.6	750.0
Bromide, mg/L	Low	4	0.09	0.04	0.05	0.15
	High	4	0.64	0.92	0.06	2.00
Chloride, mg/L	Low	19	24.93	13.44	8.00	60.00
	High	19	79.97	87.31	22.00	365.00
Coliforms, number 100 mL	Low	22	599.13	1704.09	0.00	8000.00
	High	21	14249.0	25107.83	1.00	105650.00
Totla Kjeldahl Nitrogen, mg/L	Low	2	0.52	0.69	0.03	1.00
	High	2	1.15	0.21	1.00	1.30

b. **Distributed Water Quality**

ANNUAL AVERAGE

PARAMETER	N	Mean	Standard Deviation	Minimum Value	Maximum Value
Color Units, number	19	2.02	1.82	0.00	5.00
Total Organic Carbon, mg/L	7	3.88	2.21	1.00	8.00
Fe, mg/L	28	0.05	0.06	0.01	0.30
Mn, mg/L	27	0.03	0.01	0.00	0.09
Turbidity, NTU	30	0.32	0.21	0.10	1.00
pH	30	7.8	0.60	6.8	9.00
Ammonia-N, mg/L	7	0.34	0.36	0.06	1.00
Odor, Threshold Odor No.	18	1.76	1.59	0.00	0.38
Total Dissolved Solids, mg/L	21	273.11	203.46	48.0	1000.00
Free Chlorine, mg/L	29	1.25	0.87	0.00	2.90
Combined Chlorine, mg/L	21	1.29	0.87	0.00	3.00
Chlorine Dioxide, mg/L	20	0.17	0.32	0.00	1.00
Chlorine Ion, mg/L	12	0.32	0.28	0.001	0.80

ANNUAL RANGE

PARAMETER		N	Mean	Standard Deviation	Minimum Value	Maximum Value
Color Units, number	Low	18	0.72	0.84	0.00	2.50
	High	18	5.56	7.09	0.00	1.67
Total Organic Carbon, mg/L	Low	6	2.90	1.74	1.00	6.00
	High	6	5.91	2.97	1.00	10.00
Fe, mg/L	Low	25	0.02	0.02	0.00	0.05
	High	25	0.17	0.24	0.03	1.00
Mn, mg/L	Low	24	0.01	0.02	0.00	0.05
	High	23	0.05	0.05	0.00	0.25
Turbidity, NTU	Low	29	0.13	0.18	0.01	1.00
	High	29	1.03	1.17	0.20	6.50
pH	Low	29	7.4	0.6	6.3	8.6
	High	29	8.3	0.7	7.2	9.8
Ammonia-N, mg/L	Low	6	0.09	0.14	0.00	0.36
	High	6	0.53	0.46	0.08	1.04
Odor, Threshold Odor No.	Low	17	0.92	1.09	0.00	4.00
	High	16	4.47	4.55	0.00	15.00
Total Dissolved Solids, mg/L	Low	19	187.05	120.78	47.00	536.00
	High	19	315.33	132.84	112.30	587.00
Free Chlorine, mg/L	Low	26	0.89	0.72	0.00	2.00
	High	26	1.77	0.98	0.00	3.60
Combined Chlorine, mg/L	Low	20	0.67	0.77	0.01	2.50
	High	20	1.71	1.20	0.10	3.50
Chlorine Dioxide, mg/L	Low	20	0.17	0.32	0.00	1.00
	High	20	0.28	0.38	0.00	1.00
Chlorite Ion, mg/L	Low	10	0.19	0.20	0.00	0.60
	High	10	0.40	0.36	0.01	1.20

5. **What algae have been identified with specific odors in your source water?**

Algal Type	Associated Odor
Asterionella	Weedy, spicy, Geranium, musty, fishy, earthy, vegetable
Synura	None, earthy, musty
Anabaena	Earthy, musty, swampy, cucumber
Aphanizomenon	None, unknown, musty, cucumber
Melosira	None, woody, musty
Synura	Cucumbers, unknown
Gomphosphaeria	Unknown
Oscillatoria	Unknown, fishy, earthy
Fragilaria	Musty, vegetable
Tribonema	Musty
Dinobryon	Fishy, chemical
Volvox	Chemical
Hydrodictyon	Chemical
Ceratium	Earthy, musty
Scenedesmus	Vegetable, grassy
Stephanodiscus	Geranium
Chlamydomonas	Musty/Grassy
Cyclotella	Geranium
Ankistrodesmus	Earthy/musty
Zynedra	Earthy/musty
Nostoc	None Given

TREATMENT

6. **Describe treatment processes**

a. **Pretreatment:**

coagulants: Check all that apply.
(Percentage of each based on n=32)

Frequency	Percent	
22	68.8	alum
7	21.9	iron salts
18	56.3	polymer
2	6.3	others (list): _____
1	3.1	none

oxidants: Check all that apply.
(Percent Based on n=32)

Frequency	Percent	
26	81.3	chlorine
28	87.5	chlorine dioxide
5	15.6	chloramines
9	28.1	permanganate
0	0	ozone
0	0	others (list): _____
1	3.1	none

b. **Clarification: Check the appropriate description.** (Percent based on n=31)

Frequency	Percent	
22	71.0	conventional flocculation, settling
9	27.3	sludge-blanket clarifier
0	0	others (list): _____
0	0	none

c. Filtration: Check the appropriate filtration method.
(Percent Based on n=32)

Frequency	Percent	
10	31.3	rapid sand
2	6.3	slow sand
10	31.3	dual media (anthracite and sand)
7	21.6	trimedia (anthracite, sand, garnet)
3	9.4	others (list): _____
0	0	none

d. Other Pretreatment (Please describe in the space below). (Percent Based on n=32)

Frequency	Percent	
6	18.8	Lime
5	15.6	Activated Carbon
2	6.3	copper sulfate
2	6.3	pH Adjustment
1	3.1	Aeration

7. **Do you use granular activated carbon either as sand replacement or as post-filter absorbers? Circle yes or no.** (Percentage based on n=32)

yes		no	
Frequency	Percent	Frequency	Percent
7	21.9	1	3.1

8. **If you answer to 7 was yes, in which mode, sand replacement or post-filter absorbers? Circle one.** (Percentage based on n=32)

sand replacement		post filter absorbers	
Frequency	Percent	Frequency	Percent
6	18.7	1	3.1

CHLORINE DIOXIDE USE

9. **What is the MAJOR purpose for adding chlorine dioxide? Check only one.** (Percent Based on n=32)

Frequency	Percent	
6	18.8	odor control
21	65.6	THM-precursor control
1	3.1	preoxidant for manganese and/or iron control
3	9.4	predisinfection
1	3.1	Other (list): _____

10. **What, if any, is the SECONDARY purpose for adding chlorine dioxide? Check only one.** (Percent Based on n=25)

Frequency	Percent	
5	20.0	odor control
6	24.0	THM-precursor control
5	20.0	preoxidant for manganese and/or iron control
9	36.0	predisinfection
0	0	Other (list): _____

11. **During what months of the year do you normally add chlorine dioxide? (Please circle months).** (Percentage based on n=30)

Month	Frequency	Percent
January	19	63.3
February	20	66.7
March	19	63.3
April	21	70.0
May	22	73.3
June	23	76.7
July	25	83.3
August	26	86.7
September	25	83.3
October	21	70.0
November	20	66.7
December	20	66.7

12. **Is any other oxidant added to raw water at the same time ClO_2 is added? Circle yes or no below.** (Percent Based on n=32)

yes		no	
Frequency	Percent	Frequency	Percent
14	43.8	18	56.3

If you answered yes, which oxidants(s)? Check all that apply. (Percent Based on n=32)

Frequency	Percent	
10	31.25	chlorine
7	21.9	Permanganate
2	6.3	other: Specify which: _____

13. **Equipment for Chlorine Dioxide Generation:**

a. Name of manufacturer? (Percent Based on n=32)

Frequency	Percent	Name of Manufacturer
3	9.4	Burmah Technical Services
1	3.1	Calgon
1	3.1	Cifec
2	6.3	Drew Chemical
1	3.1	Fisher Porter
2	6.3	Fabricated at Treatment Plant
1	3.1	Modern Process
3	9.4	Olin
1	3.1	Oxychlor
11	34.4	Rio Linda
6	18.8	Wallace & Tiernan

b. Date of installation? (Percent Based on n=31)

Frequency	Percent	Date of Installation
1	3.2	1960
1	3.2	1969
1	3.2	1970
1	3.2	1980
1	3.2	1981
1	3.2	1982
6	19.4	1983
6	19.4	1984
2	6.5	1985
2	6.5	1986
6	19.4	1987
3	9.7	1988

c. Type chlorite feed? Circle one below. (Percent Based on n=32)

liquid		dry	
Frequency	Percent	Frequency	Percent
28	88.2	4	12.5

d. If liquid, what percentage chlorite?

Frequency	Mean	SDEV	Minimum Value	Maximum Value
27	26.20	6.26	10.0	50.0

c. Is acid added as part of the chlorine dioxide generation procedure? Circle yes or no. (Percent based on n=31)

yes		no	
Frequency	Percent	Frequency	Percent
0	0	31	100

14. **Operations:**

a. Generator efficiency

Frequency	Mean	SDEV
26	88.6%	13.1%

Frequency determined: (Percent Based on n=19)

Frequency	Percent	Frequency Determined
2	10.5	Every Four Hours
1	5.3	Every 12 Hours
2	10.5	Twice per week
8	42.1	Weekly
1	5.3	Every two weeks
3	15.8	Monthly
1	5.3	Yearly
1	5.3	Once at Installation

b. Chlorine dioxide application point? (Check all that apply.): (Percent Based on n=32)

Frequency	Percent	
13	40.6	intake
15	46.9	flash mixer
3	9.4	after settling but before filtration
4	12.5	after filtration before clear well
0	0	in or after clear well before distribution
2	6.3	other List: _____

c. Target dosage if applied at single point: (mg/L)

Frequency	Mean	SDEV	Minimum Value	Maximum Value
26	1.24	1.18	0.25	6.0

d. At what point in the flow train, if any, do you measure chlorine dioxide to control the dosage? That is, where is your chlorine dioxide control point, if one is used? (Percent Based on n=26)

Frequency	Percent	Point in Flow Train
2	7.7	Before Filtration
5	19.2	Clarified Water
2	7.7	Clear Well
1	3.8	Distribution
3	11.5	Effluent
2	7.7	Filtered Effluent
4	15.4	Flash Mixer
3	11.5	Floc Basin
2	7.7	Presedimentation

e. Target residual concentration desired at control point: mg/L

Frequency	Mean	SDEV	Minimum Value	Maximum Value
24	0.46	0.55	0.00	2.00

f. Type of oxidant residual measured at the control point? (check all that apply): (Percent Based on n=26)

	Frequency	Percent
total oxidants	12	46.2
chlorites	11	42.3
chlorine dioxide	19	73.1
chlorates	4	15.4

g. Analytical Method For Chlorine Dioxide and Chlorite Detection: Check those that apply. (Percent Based on n=30)

Frequency	Percent	
17	56.7	DPD
0	0	Leucocrystal violet
4	13.3	Other (list): _____
14	46.7	Amperometric

TASTES AND ODORS

16. **Taste-and-Odor Complaints:**

a. **ODORS.** Check term used by customers to describe the odors and circle one number to indicate the frequency of occurrence, ranging from never (1) to most frequent (5).

DESCRIPTION	ClO_2 In Use									
	NEVER								FREQUENT	
	1		2		3		4		5	
	Frequency	Percent	Frequency	Percent	Frequency	Percent	Frequency	Percent	Frequency	Percent
Antiseptic	23	76.7	4	13.3	1	3.3	1	3.3	0	0
Bleach	10	33.3	7	23.3	5	16.7	4	13.3	3	10.0
Cat Urine	17	56.7	1	3.3	4	13.3	4	13.3	3	10.0
Chlorinous	9	30.0	7	23.3	1	3.3	7	23.3	5	16.7
Chlorox	7	23.3	11	36.7	5	16.7	2	6.7	4	13.3
Cucumber	27	90.0	1	3.3	1	3.3	0	0	0	0
Decayed Vegetation	19	63.3	6	20.0	3	10.0	1	3.3	0	0
Diesel Fuel	15	50.0	5	16.7	6	20.0	1	3.3	2	6.7
Earthy	14	46.7	8	26.7	3	10.0	2	6.7	2	6.7
Fishy	19	63.3	6	20.0	4	13.3	0	0	0	0
Floral	29	96.7	0	0	0	0	0	0	0	0
Fragrant	27	90.0	1	3.3	1	3.3	0	0	0	0
Gasoline	13	43.3	6	20.0	7	23.3	1	3.3	2	6.7
Grassy	24	80.0	3	10.0	1	3.3	1	3.3	0	0
Haylike	27	90.0	1	3.3	0	0	1	3.3	0	0
Hydrocarbon	23	76.7	4	13.3	2	6.7	0	0	0	0
Kerosene	11	36.7	7	23.3	3	10.0	3	10.0	5	16.7
Lighter Fluid	23	76.7	4	13.3	1	3.3	1	3.3	0	0
Marshy	22	73.3	4	13.3	1	3.3	2	6.7	0	0
Medicinal	13	43.3	10	33.3	6	20.0	0	0	0	0
Moldy	19	63.3	6	20.0	1	3.3	2	6.7	1	3.3
Natural Gas	18	60.0	4	13.3	4	13.3	2	6.7	1	3.3
Organic Solvent	23	76.7	4	13.3	1	3.3	1	3.3	0	0
Phenolic	25	83.3	2	6.7	2	6.7	0	0	0	0
Pig pen	28	93.3	1	3.3	0	0	0	0	0	0
Plastic	22	73.3	4	13.3	2	6.7	1	3.3	0	0
Plastic pipe	24	80.0	3	10.0	1	3.3	1	3.3	0	0
Potato	27	90.0	2	6.7	0	0	0	0	0	0
Potato Bin	28	93.3	1	3.3	0	0	0	0	0	0
Purex	24	80.0	2	6.7	2	6.7	1	3.3	0	0
Rubber	25	83.3	2	6.7	1	3.3	1	3.3	0	0
Septic	20	66.7	6	20.0	2	6.7	1	3.3	0	0
Sewage	18	60.0	7	23.3	2	6.7	2	6.7	0	0
Swampy	19	63.3	5	16.7	2	6.7	3	10.0	0	0
Sweet	27	90.0	1	3.3	1	3.3	0	0	0	0
Swimming Pool	13	43.3	7	23.3	5	16.7	2	6.7	2	6.7
Varnish	26	86.7	1	3.3	1	3.3	1	3.3	0	0
Wet Paper	28	93.3	1	3.3	0	0	0	0	0	0
Woody	23	76.7	4	13.3	0	0	2	6.7	0	0

* One company stated that this section was not applicable

** Two companies left this section blank

DESCRIPTION	ClO_2 NOT IN USE									
	NEVER									FREQUENT
	1		2		3		4		5	
	Frequency	Percent	Frequency	Percent	Frequency	Percent	Frequency	Percent	Frequency	Percent
Antiseptic	18	60.0	1	3.3	1	3.3	1	3.3	0	0
Bleach	6	20.0	2	6.7	6	20.0	4	13.3	2	6.7
Cat Urine	20	66.7	0	0	0	0	0	0	0	0
Chlorinous	3	10.0	1	3.3	5	16.7	5	16.7	6	20.0
Chlorox	5	16.7	4	13.3	6	20.0	3	10.0	2	6.7
Cucumber	17	56.7	2	6.7	1	3.3	0	0	0	0
Decayed Vegetation	13	43.3	5	16.7	2	6.7	0	0	0	0
Diesel Fuel	18	60.0	2	6.7	0	0	0	0	0	0
Earthy	5	16.7	6	20.0	6	20.0	2	6.7	1	3.3
Fishy	11	36.7	3	10.0	4	13.3	2	6.7	0	0
Floral	18	60.0	1	3.3	1	3.3	0	0	0	0
Fragrant	20	66.7	0	0	0	0	0	0	0	0
Gasoline	18	60.0	2	6.7	0	0	0	0	0	0
Grassy	15	50.0	3	10.0	2	6.7	0	0	0	0
Haylike	19	63.3	1	3.3	0	0	0	0	0	0
Hydrocarbon	20	66.7	0	0	0	0	0	0	0	0
Kerosene	19	63.3	1	3.3	0	0	0	0	0	0
Lighter Fluid	20	66.7	0	0	0	0	0	0	0	0
Marshy	14	46.7	5	16.7	1	3.3	0	0	0	0
Medicinal	10	33.3	6	20.0	4	13.3	0	0	0	0
Moldy	11	36.7	4	13.3	2	6.7	3	10.0	0	0
Natural Gas	20	66.7	0	0	0	0	0	0	0	0
Organic Solvent	20	66.7	0	0	0	0	0	0	0	0
Phenolic	20	66.7	0	0	0	0	0	0	0	0
Pig pen	19	63.3	1	3.3	0	0	0	0	0	0
Plastic	20	66.7	0	0	0	0	0	0	0	0
Plastic pipe	17	56.7	3	10.0	0	0	0	0	0	0
Potato	20	66.7	0	0	0	0	0	0	0	0
Potato Bin	20	66.7	0	0	0	0	0	0	0	0
Purex	16	53.3	2	6.7	1	3.3	1	3.3	0	0
Rubber	20	66.7	0	0	0	0	0	0	0	0
Septic	15	50.0	4	13.3	1	3.3	0	0	0	0
Sewage	11	36.7	6	20.0	3	10.0	0	0	0	0
Swampy	11	36.7	5	16.7	2	6.7	2	6.7	0	0
Sweet	17	56.7	3	10.0	0	0	0	0	0	0
Swimming Pool	6	20.0	4	13.3	7	23.3	2	6.7	1	3.3
Varnish	20	66.7	0	0	0	0	0	0	0	0
Wet Paper	20	66.7	0	0	0	0	0	0	0	0
Woody	18	60.0	1	3.3	1	3.3	0	0	0	0

* Ten companies stated that this section was not applicable

* Two companies left this section blank.

b. Are the odors in the air, or can they be detected also in a water sample? Please circle. (Percent Based on n=28)

in air only		in water only		in both water and air	
Frequency	Percent	Frequency	Percent	Frequency	Percent
8	28.6	4	14.3	18	64.3

c. TASTES. Check terms used by customers to describe the tastes and circle one number to the frequency of occurrence, ranging from never (1) to most frequent (5).

DESCRIPTION	ClO_2 In Use									
	NEVER								FREQUENT	
	1		2		3		4		5	
	Frequency	Percent	Frequency	Percent	Frequency	Percent	Frequency	Percent	Frequency	Percent
Antiseptic	19	70.4	4	14.8	2	7.4	0	0	0	0
Bleach	10	37.0	7	25.9	4	14.8	2	7.4	2	7.4
Cat Urine	22	81.5	2	7.4	0	0	0	0	1	3.7
Chlorinous	12	44.4	5	18.5	3	11.1	3	11.1	2	7.4
Chlorox	12	44.4	5	18.5	6	22.2	0	0	2	7.4
Cucumber	24	88.9	1	3.7	0	0	0	0	0	0
Decayed Vegetation	21	77.8	2	7.4	1	3.7	1	3.7	0	0
Diesel Fuel	23	85.2	1	3.7	0	0	1	3.7	0	0
Earthy	14	51.9	7	25.9	1	3.7	1	3.7	2	7.4
Fishy	18	66.7	6	22.2	1	3.7	0	0	0	0
Floral	25	92.6	0	0	0	0	0	0	0	0
Fragrant	25	92.6	0	0	0	0	0	0	0	0
Gasoline	18	66.7	5	18.5	1	3.7	1	3.7	0	0
Grassy	21	77.8	2	7.4	2	7.4	0	0	0	0
Haylike	24	88.9	1	3.7	0	0	0	0	0	0
Hydrocarbon	25	92.6	0	0	0	0	1	3.4	0	0
Kerosene	19	70.4	4	14.8	1	3.7	1	3.7	0	0
Lighter Fluid	23	85.2	1	3.7	1	3.7	0	0	0	0
Marshy	18	66.7	4	14.8	2	7.4	1	3.7	0	0
Medicinal	15	55.6	5	18.5	4	14.8	1	3.7	0	0
Moldy	18	66.7	4	14.8	0	0	3	11.1	0	0
Natural Gas	21	77.8	4	14.8	0	0	0	0	0	0
Organic Solvent	22	81.5	1	3.7	0	0	2	7.4	0	0
Phenolic	23	85.2	1	3.7	1	3.7	0	0	0	0
Pig pen	25	92.6	0	0	0	0	0	0	0	0
Plastic	19	70.4	4	14.8	2	7.4	0	0	0	0
Plastic pipe	20	74.1	3	11.1	1	3.7	1	3.7	0	0
Potato	24	88.9	1	3.7	0	0	0	0	0	0
Potato Bin	24	88.9	1	3.7	0	0	0	0	0	0
Purex	21	77.8	2	7.4	1	3.7	1	3.7	0	0
Rubber	21	77.8	3	11.1	1	3.7	0	0	0	0
Septic	20	74.1	3	11.1	0	0	2	7.4	0	0
Sewage	21	77.8	1	3.7	2	7.4	1	3.7	0	0
Swampy	18	66.7	4	14.8	1	3.7	2	7.4	0	0
Sweet	22	81.5	2	7.4	1	3.7	0	0	0	0
Swimming Pool	12	44.4	7	25.9	3	11.1	2	7.4	1	3.7
Varnish	24	88.9	1	3.7	0	0	0	0	0	0
Wet Paper	25	92.6	0	0	0	0	0	0	0	0
Woody	21	77.8	2	7.4	1	3.7	0	0	1	3.7

* Two companies stated that this section was not applicable

* Five companies left this section blank.

DESCRIPTION	ClO_2 NOT IN USE									
	NEVER									FREQUENT
	1		2		3		4		5	
	Frequency	Percent	Frequency	Percent	Frequency	Percent	Frequency	Percent	Frequency	Percent
Antiseptic	12	42.9	3	10.7	2	7.1	0	0	0	0
Bleach	7	25.0	1	3.6	5	7.9	2	7.1	2	7.1
Cat Urine	16	57.1	1	3.6	0	0	0	0	0	0
Chlorinous	4	14.3	2	7.1	6	21.4	1	3.6	4	14.3
Chlorox	7	25.0	2	7.1	5	17.9	1	3.6	2	7.1
Cucumber	15	53.6	1	3.6	1	3.6	0	0	0	0
Decayed Vegetation	12	42.9	3	10.7	2	7.1	0	0	0	0
Diesel Fuel	16	57.1	0	0	1	3.6	0	0	0	0
Earthy	6	21.4	8	28.6	2	7.1	0	0	1	3.6
Fishy	9	32.1	5	17.9	3	10.7	0	0	0	0
Floral	16	57.1	1	3.6	0	0	0	0	0	0
Fragrant	17	60.7	0	0	0	0	0	0	0	0
Gasoline	15	53.6	2	7.1	0	0	0	0	0	0
Grassy	12	42.4	4	14.3	1	3.6	0	0	0	0
Haylike	16	57.1	0	0	1	3.6	0	0	0	0
Hydrocarbon	17	60.7	0	0	0	0	0	0	0	0
Kerosene	15	53.6	2	7.1	0	0	0	0	0	0
Lighter Fluid	15	53.6	1	3.6	1	3.6	0	0	0	0
Marshy	11	39.3	5	17.9	1	3.6	0	0	0	0
Medicinal	10	35.7	3	10.7	2	7.1	2	7.1	0	0
Moldy	9	32.1	6	21.4	1	3.6	1	3.6	0	0
Natural Gas	17	60.7	0	0	0	0	0	0	0	0
Organic Solvent	17	60.7	0	0	0	0	0	0	0	0
Phenolic	17	60.7	0	0	0	0	0	0	0	0
Pig pen	17	60.7	0	0	0	0	0	0	0	0
Plastic	16	57.1	1	3.6	0	0	0	0	0	0
Plastic pipe	15	53.6	1	3.6	1	3.6	0	0	0	0
Potato	17	60.7	0	0	0	0	0	0	0	0
Potato Bin	17	60.7	0	0	0	0	0	0	0	0
Purex	13	46.4	1	3.6	3	10.7	0	0	0	0
Rubber	17	60.7	0	0	0	0	0	0	0	0
Septic	13	46.4	4	14.3	0	0	0	0	0	0
Sewage	13	46.4	4	14.3	0	0	0	0	0	0
Swampy	9	32.1	6	21.4	2	7.1	0	0	0	0
Sweet	14	50.0	1	3.6	1	3.6	1	3.6	0	0
Swimming Pool	6	21.4	5	17.9	5	17.9	0	0	1	3.6
Varnish	16	57.1	0	0	1	3.6	0	0	0	0
Wet Paper	17	60.7	0	0	0	0	0	0	0	0
Woody	14	50.0	2	7.1	1	3.6	0	0	0	0

* Eleven companies stated that this section is not applicable

* Four companies left this section blank

e. Respond to the following questions about detection of odors at your treatment plant.

Are odors detected at the treatment plant? (Percent Based on n=32)

yes		no	
Frequency	Percent	Frequency	Percent
13	40.6	19	59.4

If the answer to the above was yes, answer the next two questions to better define where you detect them.

Are odors detected at the plant in the filter effluent? Circle yes or no below. (Percent based on n=18)

yes		no	
Frequency	Percent	Frequency	Percent
9	50.0	9	50.0

Are odors detected at the plant in the clearwell? Circle yes or no below. (Percent Based on n=18)

yes		no	
Frequency	Percent	Frequency	Percent
12	66.7	6	33.3

f. Average weekly number of customer complaints about tastes and odors:

At times when ClO_2 is being added:

Frequency	MEAN	SDEV	Minimum Value	Maximum Value
28	5.34	7.87	0	35

At times when ClO_2 is not being added:

Frequency	MEAN	SDEV	Minimum Value	Maximum Value
20	2.95	6.61	0	30

g. Location of complaints in the distribution system: Check all that apply. (Percent Based on n=30)

Frequency	Percent	
13	43.3	at points distant from the treatment plant
8	26.7	near the treatment plant
22	73.3	isolated customers throughout the system
4	13.3	near transmission mains
13	43.3	in areas near dead ends
6	20.0	neighboring homes in one or more areas of the system
18	60.0	no consistent pattern

h. What time of days are most complaints received? (Percent Based on n=32)

Frequency	Percent	
27	90.0	Throughout the day
4	13.3	Morning
3	10.0	Afternoon
2	6.7	Night

i. Do the customer complaints seem to increase when the chlorine dioxide dosage exceeds some particular level? Circle yes or no below. (Percent Based on n=29)

yes		no	
Frequency	Percent	Frequency	Percent
10	34.5	19	65.5

If your answer was "yes", above what dosage do complaints seem to increase?

Frequency	MEAN	SDEV	Minimum Value	Maximum Value
10	1.5	0.95	0.10	3.0

j. Are the T & O worse during periods of high rainfall? Circle yes or no below. (Percent based on n=28)

yes		no	
Frequency	Percent	Frequency	Percent
10	35.7	18	64.3

k. Does the frequency of complaints seem to be related to your plant production level? Circle yes or no below. (Percent Based on n=30)

yes		no	
Frequency	Percent	Frequency	Percent
3	10.3	26	89.7

If "yes:", are complaints more numerous with increased or decreased production? Circle one. (Percent Based on n=3)

with increased production		with decreased production	
Frequency	Percent	Frequency	Percent
3	100	0	0

l. To your knowledge, had any complaining customers recently installed new carpet? Circle yes or no below. (Percent Based on n=30)

yes		no	
Frequency	Percent	Frequency	Percent
17	60.7	11	39.3

m. List the approximate percentage of the total number of complaining customers who had new carpet.

Frequency	MEAN	SDEV	Minimum Value	Maximum Value
15	46.0	36.2	1.0	100.0

n. To your knowledge, had any complaining customers recently redecorated or painted their homes? Circle yes or no below. (Percent Based on n=29)

yes		no	
Frequency	Percent	Frequency	Percent
10	37.0	17	63.0

o. List the approximate percentage of the total number of complaining customers who had redecorated or painted.

Frequency	MEAN	SDEV	Minimum Value	Maximum Value
8	40.6	30.3	5.0	100.0

p. **Are the T & O detected in cold or hot water, or both? Circle one below. (Percent Based on n=30)**

	Frequency	Percent
cold	8	26.7
hot	0	0
both hot and cold	23	76.7

q. In what area(s) of the homes are the odors most often reported? Check the ones that apply. (Percent Based on n=32)

Frequency	Percent	
22	73.3	in the bathroom
7	23.3	in the laundry room
26	86.7	in the kitchen
2	6.7	other (please list) _____

16. **What analytical techniques do you use to quantify tastes and odors? (Percent Based on n=31)**

Frequency	Percent	
22	75.9	threshold odor number (TON)
0	0	flavor profile analysis (EPA)
2	6.9	gas chromatographic identification of odor compounds
4	13.8	other (describe) _____

17. **In your opinion, what factors contribute to the development of tastes and odors in your system?**

_____

_____

_____

18. **Name of Respondent:** _____

Name of Treatment Plant: _____

Address of Treatment Plant: _____

States of Treatment Plants Represented in This Survey:

Frequency	Percent	STATE
1	3.1	AL
1	3.1	CT
1	3.1	DE
2	6.3	IL
3	9.4	IN
1	3.1	KS
1	3.1	KY
2	6.3	NJ
1	3.1	NV
2	6.3	NY
5	15.6	OH
4	12.5	PA
1	3.1	RI
2	6.3	SC
1	3.1	TN
2	6.3	TX
1	3.1	VA
1	3.1	WV

Telephone No. _____

Hours spent filling out this form:

Frequency	Mean	SDEV	Minimum Value	Maximum Value
27	1.82	1.20	0.25	5.5

PLEASE PROVIDE A SCHEMATIC DIAGRAM OF YOUR PLANT SHOWING POINTS OF CHEMICAL ADDITION IF ONE IS AVAILABLE.

THANK YOU FOR YOUR COOPERATION

APPENDIX D

SURVEY STATISTICS

Appendix D Table 1. Correlations of Classes of Odors with Raw Water Quality Parameters when Chlorine Dioxide was In Use. Pearson's r Values are Listed Followed by P-values in Parentheses below the Correlation.

CLASSES	COLOR UNITS	TURBIDITY	pH	ODOR
Disinfectant	0.52159 (0.0053)	-0.00899 (0.9638)	-0.42432 (0.0244)	0.23851 (0.2406)
Hydrocarbon	0.24830 (0.2117)	0.05411 (0.7854)	-0.18550 (0.3446)	0.06604 (0.7486)
Vegetation	0.23154 (0.2452)	0.16578 (0.3992)	-0.18844 (0.3364)	-0.00425 (0.9836)
Musty	0.34773 (0.0755)	0.07590 (0.7011)	-0.27454 (0.1574)	0.14177 (0.4897)
Rotten	0.43515 (0.0233)	0.07546 (0.7027)	-0.37237 (0.0510)	0.03612 (0.8609)
Pleasant	0.09767 (0.6279)	0.02690 (0.8919)	-0.08898 (0.6525)	-0.03027 (0.8833)
Cat Urine	-0.01434 (0.9434)	0.00470 (0.9811)	-0.06083 (0.7585)	0.11404 (0.5791)

Appendix D Table 2. Correlations of Classes of Odors with Raw Water Quality Parameters when Chlorine Dioxide was Not In Use. Pearson's r Values are Listed Followed by P-values in Parentheses below the Correlation.

CLASSES	COLOR UNITS	TURBIDITY	pH	ODOR
Disinfectant	0.03176 (0.8750)	0.03266 (0.8690)	0.11256 (0.5685)	0.28899 (0.1522)
Hydrocarbon	0.04931 (0.8070)	-0.01070 (0.9569)	-0.02116 (0.9149)	0.31783 (0.1136)
Vegetation	0.04750 (0.8140)	-0.04818 (0.8077)	0.02111 (0.9151)	0.34194 (0.0873)
Musty	0.21386 (0.2841)	-0.11162 (0.5717)	-0.14281 (0.4685)	0.22991 (0.2585)
Rotten	0.22712 (0.2546)	-0.04729 (0.8111)	-0.16370 (0.4070)	0.22358 (0.2722)
Pleasant	0.06000 (0.7662)	-0.05659 (0.7749)	-0.00332 (0.9866)	0.34245 (0.0868)
Cat Urine	0.06836 (0.7348)	-0.03988 (0.8403)	-0.04446 (0.8223)	0.30135 (0.1346)

Appendix D Table 3. Correlations of Classes of Tastes with Raw Water Quality Parameters when Chlorine Dioxide was In Use. Pearson's r Values are Listed Followed by P-values in Parentheses below the Correlation.

CLASSES	COLOR UNITS	TURBIDITY	pH	ODOR
Disinfectant	0.13925 (0.5164)	-0.26741 (0.1963)	-0.00869 (0.9671)	-0.09422 (0.6689)
Hydrocarbon	0.18984 (0.3743)	-0.31277 (0.1279)	-0.17472 (0.4035)	-0.07088 (0.7479)
Vegetation	0.17794 (0.4055)	-0.46659 (0.0187)	-0.11462 (0.5854)	-0.14764 (0.5014)
Musty	0.06452 (0.7646)	-0.23073 (0.2672)	-0.00001 (1.0000)	-0.05291 (0.8105)
Rotten	0.23192 (0.2755)	-0.26514 (0.2002)	-0.15482 (0.4599)	-0.19854 (0.3638)
Pleasant	0.18890 (0.3767)	-0.50709 (0.0097)	-0.17404 (0.4054)	-0.16679 (0.4469)
Cat Urine	0.00894 (0.9669)	-0.35187 (0.0845)	-0.00116 (0.9956)	0.13315 (0.5447)

Appendix D Table 4. Correlations of Classes of Tastes with Raw Water Quality Parameters when Chlorine Dioxide was Not In Use. Pearson's r Values are Listed Followed by P-values in Parentheses below the Correlation.

CLASSES	COLOR UNITS	TURBIDITY	pH	ODOR
Disinfectant	0.02411 (0.9089)	-0.23299 (0.2520)	0.07214 (0.7262)	0.32102 (0.1261)
Hydrocarbon	0.19003 (0.3629)	-0.35475 (0.0754)	-0.18135 (0.3753)	0.14982 (0.4847)
Vegetation	0.25850 (0.2122)	-0.35328 (0.0767)	-0.19175 (0.3480)	0.14584 (0.4965)
Musty	0.28701 (0.1642)	-0.33952 (0.0897)	-0.24148 (0.2347)	0.17885 (0.4030)
Rotten	0.27426 (0.1846)	-0.31430 (0.1179)	-0.22852 (0.2615)	0.17363 (0.4171)
Pleasant	0.37317 (0.0662)	-0.36372 (0.0678)	-0.33205 (0.0975)	0.11094 (0.6058)
Cat Urine	0.17094 (0.4140)	-0.36632 (0.0657)	-0.11961 (0.5606)	0.15797 (0.4610)

Appendix D Table 5A. Correlations of Classes of Odors with Finished Water Quality Parameters when Chlorine Dioxide was In Use. Pearson's r Values are Listed Followed by P-values in Parentheses below the Correlation.

CLASSES	pH	Odor	Free Chlorine	Combined Chlorine
Disinfectant	-0.46957 (0.0117)	0.02062 (0.9203)	-0.10973 (0.5783)	-0.22364 (0.2526)
Hydrocarbon	-0.24251 (0.2137)	-0.14288 (0.4862)	0.08154 (0.6800)	-0.28755 (0.1379)
Vegetation	-0.08921 (0.6517)	0.07994 (0.6979)	-0.33910 (0.0775)	0.06367 (0.7476)
Musty	-0.29733 (0.1244)	0.10066 (0.6247)	-0.16128 (0.4123)	-0.00734 (0.9704)
Rotten	-0.28439 (0.1424)	0.00515 (0.9801)	-0.24548 (0.2080)	-0.02662 (0.8930)
Pleasant	-0.01141 (0.9541)	0.02681 (0.8965)	-0.01763 (0.9290)	-0.07224 (0.7149)
Cat Urine	-0.00557 (0.9776)	-0.03810 (0.8534)	0.35468 (0.0640)	-0.04995 (0.8007)

Appendix D Table 5B. Correlations of Classes of Odors with Finished Water Quality Parameters when Chlorine Dioxide was In Use. Pearson's r Values are Listed Followed by P-values in Parentheses below the Correlation.

CLASSES	Chlorine Dioxide	Chlorite
Disinfectant	0.04186 (0.8358)	-0.07733 (0.6957)
Hydrocarbon	0.00046 (0.9982)	-0.03261 (0.8691)
Vegetation	-0.04585 (0.8203)	0.26247 (0.1772)
Musty	-0.02303 (0.9092)	0.19140 (0.3292)
Rotten	-0.04488 (0.8241)	0.19725 (0.3144)
Pleasant	-0.24338 (0.2212)	-0.03165 (0.8730)
Cat Urine	0.07779 (0.6998)	0.06791 (0.7313)

Appendix D Table 6. Correlations of Classes of Odors with Finished Water Quality Parameters when Chlorine Dioxide was Not In Use. Pearson's r Values are Listed Followed by P-values in Parentheses below the Correlation.

CLASSES	pH	Odor	Free Chlorine	Combined Chlorine
Disinfectant	-0.36448 (0.0565)	0.17826 (0.3836)	0.24902 (0.2013)	-0.16651 (0.3971)
Hydrocarbon	-0.26288 (0.1765)	0.20273 (0.3206)	0.29235 (0.1311)	-0.04306 (0.8277)
Vegetation	-0.27488 (0.1569)	0.26054 (0.1986)	0.18575 (0.3440)	-0.03971 (0.8410)
Musty	-0.34821 (0.0694)	0.19607 (0.3371)	0.31050 (0.1078)	-0.11201 (0.5704)
Rotten	-0.33695 (0.0795)	0.10118 (0.6228)	0.13356 (0.4980)	-0.09560 (0.6285)
Pleasant	-0.27123 (0.1627)	0.21695 (0.2871)	0.20593 (0.2931)	-0.03177 (0.8725)
Cat Urine	-0.25720 (0.1864)	0.22584 (0.2673)	0.29521 (0.1272)	-0.03473 (0.8607)

Appendix D Table 7A. Correlations of Classes of Tastes with Finished Water Quality Parameters when Chlorine Dioxide was In Use. Pearson's r Values are Listed Followed by P-values in Parentheses below the Correlation.

CLASSES	pH	Odor	Free Chlorine	Combined Chlorine
Disinfectant	-0.21952 (0.2917)	0.07235 (0.7429)	-0.05867 (0.7806)	-0.25458 (0.2194)
Hydrocarbon	-0.20701 (0.3208)	0.12746 (0.5622)	0.01130 (0.9573)	-0.17227 (0.4103)
Vegetation	-0.11097 (0.5975)	0.23951 (0.2710)	-0.13088 (0.5329)	-0.26726 (0.1965)
Musty	-0.09667 (0.6457)	0.28583 (0.1861)	-0.13118 (0.5319)	-0.01367 (0.9483)
Rotten	-0.19776 (0.3433)	0.15005 (0.4944)	-0.15842 (0.4495)	-0.06547 (0.7559)
Pleasant	-0.10726 (0.6098)	0.17258 (0.4310)	-0.15575 (0.4572)	-0.13614 (0.5164)
Cat Urine	-0.00617 (0.9766)	0.31181 (0.1475)	0.17291 (0.4085)	-0.09035 (0.6676)

Appendix D Table 7B. Correlations of Classes of Tastes with Finished Water Quality Parameters when Chlorine Dioxide was In Use. Pearson's r Values are Listed Followed by P-values in Parentheses below the Correlation.

CLASSES	Chlorine Dioxide	Chlorite
Disinfectant	0.11614 (0.5889)	0.11349 (0.5891)
Hydrocarbon	-0.18722 (0.3810)	-0.00270 (0.9898)
Vegetation	0.01073 (0.9603)	0.19100 (0.3604)
Musty	0.06045 (0.7790)	0.29201 (0.1567)
Rotten	-0.04136 (0.8478)	0.10464 (0.6186)
Pleasant	0.03939 (0.8550)	0.10342 (0.6228)
Cat Urine	0.18855 (0.3776)	0.41585 (0.0387)

Appendix D Table 8. Correlations of Classes of Tastes with Finished Water Quality Parameters when Chlorine Dioxide was Not In Use. Pearson's r Values are Listed Followed by P-values in Parentheses below the Correlation.

CLASSES	pH	Odor	Free Chlorine	Combined Chlorine
Disinfectant	-0.35677 (0.0736)	0.26655 (0.2080)	0.24767 (0.2225)	-0.13031 (0.5258)
Hydrocarbon	-0.28128 (0.1639)	0.25150 (0.2358)	0.23424 (0.2494)	-0.14875 (0.4683)
Vegetation	-0.33975 (0.0895)	0.26314 (0.2141)	0.13839 (0.5002)	-0.18468 (0.3664)
Musty	-0.36524 (0.0665)	0.23892 (0.2609)	0.22736 (0.2640)	-0.17769 (0.3852)
Rotten	-0.41291 (0.0360)	0.12947 (0.5465)	0.24051 (0.2366)	-0.16671 (0.4157)
Pleasant	-0.39413 (0.0463)	0.15892 (0.4582)	0.12178 (0.5534)	-0.17006 (0.4062)
Cat Urine	-0.31453 (0.1176)	0.29083 (0.1680)	0.26906 (0.1838)	-0.15000 (0.4646)

Appendix D Table 9. Correlations of Classes of Tastes-and-Odors with the Target Dose of Chlorine Dioxide. Pearson's r Values are Listed Followed by P-values in Parentheses below the Correlations.

CLASSES	ODORS	TASTES
Disinfectant	-0.02130 (0.8782)	-0.02646 (0.9069)
Hydrocarbon	-0.07792 (0.7112)	0.04879 (0.8293)
Vegetation	0.01318 (0.9502)	-0.04703 (0.8354)
Musty	0.23056 (0.2675)	-0.03251 (0.8858)
Rotten	0.36491 (0.0729)	0.23888 (0.2843)
Pleasant	-0.08349 (0.6915)	0.01827 (0.9357)
Cat Urine	-0.21063 (0.3122)	-0.14191 (0.5287)

Appendix D Table 10. Correlations of Cat Urine, Chlorinous, and Kerosene Odors with the Point of Application in the Water Treatment Plant. Pearson's r Values are Listed Followed by P-Values in Parentheses Below the Correlation.

POINT OF APPLICATION	CAT URINE	CHLORINOUS	KEROSENE
Intake	-0.27922 (0.1351)	-0.00827 (0.9654)	-0.17025 (0.3684)
Flash Mixer	0.10853 (0.5681)	-0.09747 (0.6084)	0.09752 (0.6082)
After Settling but befor Filtration	-0.07837 (0.6806)	0.14858 (0.4333)	-0.13901 (0.4638)
After Filtration but before Clearwell	-0.07126 (0.7083)	-0.08344 (0.6611)	0.10223 (0.5909)
In or After Clearwell but before Distribution	0.00000 (1.0000)	0.00000 (1.0000)	0.00000 (1.0000)
Other	0.33703 (0.0686)	0.30865 (0.0970)	-0.05573 (0.7699)

Appendix D Table 11. Correlations of Cat Urine, Chlorinous, and Kerosene Tastes with the Point of Application in the Water Treatment Plant. Pearson's r Values are Listed Followed by P-Values in Parentheses Below the Correlation.

POINT OF APPLICATION	CAT URINE	CHLORINOUS	KEROSENE
Intake	-0.13980 (0.4868)	-0.03848 (0.8489)	-0.00296 (0.9883)
Flash Mixer	0.07856 (0.6969)	-0.02703 (0.8935)	0.28202 (0.1541)
After Settling but befor Filtration	-0.26764 (0.1771)	-0.20628 (0.3019)	-0.31895 (0.1049)
After Filtration but before Clearwell	-0.02676 (0.8946)	0.18050 (0.3676)	-0.06934 (0.7311)
In or After Clearwell but before Distribution	0.00000 (1.0000)	0.00000 (1.0000)	0.00000 (1.0000)
Other	0.55670 (0.0026)	0.48477 (0.0104)	-0.05547 (0.7835)

Appendix D Table 12. Chi Square Comparison to Determine if the Final Disinfectant (chlorine versus chloramine) was independent of Kerosene, Chlorinous, and Cat Urine Tastes-and-Odors when Chlorine Dioxide was In Use. Chi Square Values are Listed Followed by P-Values in Parentheses.

DESCRIPTION	ODORS	TASTES
Kerosene	1.059 (0.901)	0.489 (0.783)
Chlorinous	2.709 (0.608)	2.200 (0.699)
Cat Urine	1.791 (0.774)	0.220 (0.896)

Appendix D Table 13. Chi Square Comparison to Determine if the Final Disinfectant (chlorine versus chloramine) was independent of Kerosene, Chlorinous, and Cat Urine Tastes-and-Odors when Chlorine Dioxide was Not In Use. Chi Square Values are Listed Followed by P-Values in Parentheses.

DESCRIPTION	ODORS	TASTES
Kerosene	0.247 (0.619)	0.327 (0.568)
Chlorinous	4.169 (0.384)	2.068 (0.723)
Cat Urine	0.000 (1.000)	0.152 (0.696)

Appendix D Table 14. Sum of the Ranks for the Wilcoxon Paired-Test of the Odors. The value of N was the Number of Ranked Differences.

Odor	N	T_-	T_+	Odor	N	T_-	T_+
Antiseptic	4	5	5	Moldy	6	18	2
Bleach	13	37.5	44	Natural Gas	7	0	28
Cat Urine	11	0	66	Organic Solvent	5	0	15
Chlorinous	10	36.5	18.5	Phenolic	3	0	6
Chlorox	11	34	32	Pig Pen		*	*
Cucumber	4	6.5	3.5	Plastic	3	0	6
Decayed Vegetation	5	7.5	7.5	Plastic Pipe	3	3	3
Diesel Fuel	9	0	45	Potato	1	0	1
Earthy	9	38	7	Potato Bin		*	*
Fishy	6	21	0	Purex	5	8	9
Floral	2	3	0	Rubber	3	0	6
Fragrant	1	0	1	Septic	4	4	6
Gasoline	11	0	66	Sewage	9	27	18
Grassy	4	4	0	Swampy	8	29	7
Haylike	1	1	0	Sweet	4	7.5	2.5
Hydrocarbon	5	0	15	Swimming Pool	10	41	14
Kerosene	11	0	66	Varnish	3	0	6
Lighter Fluid	5	0	15	Wet Paper	1	0	1
Marshy	6	18	3	Woody	3	0	6
Medicinal	4	2	8				

* The level of intensity reported by the companies was the same when chlorine dioxide was on or off at the water treatment plant, therefore, no significant differences were observed.

Appendix D Table 15. Sum of the Ranks for the Wilcoxon Paired-Test of the Tastes. The Value of N was the Number of Ranked Differences.

Odor	N	T_-	T_+	Odor	N	T_-	T_+
Antiseptic	4	6	4	Moldy	4	0	10
Bleach	5	15	0	Natural Gas	3	0	6
Cat Urine	4	2	8	Organic Solvent	2	0	3
Chlorinous	8	29	7	Phenolic	1	0	1
Chlorox	7	19	9	Pig Pen		*	*
Cucumber	2	3	0	Plastic	2	0	3
Decayed Vegetation	3	6	0	Plastic Pipe	3	2	4
Diesel Fuel	3	2	4	Potato		*	*
Earthy	8	25	11	Potato Bin		*	*
Fishy	7	24.5	3.5	Purex	3	4.5	1.5
Floral	1	1	0	Rubber	3	0	6
Fragrant		*	*	Septic	2	1	2
Gasoline	5	0	15	Sewage	3	4	2
Grassy	2	3	0	Swampy	4	10	0
Haylike	1	1	0	Sweet	4	8	2
Hydrocarbon		*	*	Swimming Pool	5	12	3
Kerosene	3	0	6	Varnish	2	1.5	1.5
Lighter Fluid	3	3	3	Wet Paper		*	*
Marshy	5	8.5	6.5	Woody	2	2	1
Medicinal	6	17	4				

* The level of intensity reported by the companies was the same when chlorine dioxide was on or off at the water treatment plant, therefore, no significant differences were observed.

APPENDIX E

LABORATORY DATA

Appendix E Table 1. Concentration of Chloride Determined by Ion Chromatography at two PAC-Contact Times. Chlorite was Contacted with Different Concentrations of PAC for 15 minutes and 30 minutes in Milli-Q Water. Chlorite and Chlorate Concentrations are Listed in the Text as Tables 20 and 21 Respectively.

PAC (mg/L)	Chloride Concentration, mg/L, at Two PAC-Contact Times	
	15 minutes	30 minutes
0	0.00	0.00
5	0.00	1.03
10	0.32	0.89
20	0.80	1.29
30	1.04	1.12
40	1.25	1.60
50	1.68	2.73
100	3.28	3.45

Appendix E Table 2. Concentration of Chlorite Determined by Amperometric Titration and Chloride and Chlorate Determined by Ion Chromatography after Seven Days of Contact with Various PAC Concentrations in Distilled Water. The concentration of Chlorate is approximate.

PAC (mg/L)	Concentration, mg/L		
	Chlorite	Chlorate	Chloride
0	12.82	5.74	5.90
5	8.31	6.90	7.53
10	8.54	5.72	7.48
20	3.46	7.09	10.15
25	1.89	7.75	10.44
30	1.11	7.77	11.41
35	0.39	7.94	11.76

Appendix E Table 3. Concentration of Chloride Determined by Ion Chromatography. Chlorite was Contacted with PAC (50 mg/L) in Milli-Q water for 48 Hours in a Batch Reactor. Chlorite and Chlorate COncentrations are Listed in the Text as Tables 22 and 23 Resepectively.

Time (Hours)	Chloride Concentration, mg/L
0	0.016
0.25	1.68
0.50	2.29
0.75	2.85
1	2.87
1.5	3.38
2	3.73
3	4.39
4	4.87
8	5.76
16	6.57
24	6.98
36	7.18
48	7.52

Appendix E Table 4. Chlorite Removal in Laboratory-Constituted Water for the Control Experiments. Three Different Runs were Conducted, and Chlorite (mg/L) was Monitored by Amperometric Titration.

Time (Hours)	Run 1	Run 2	Run 3
0	1.61	1.60	1.60
0.25	1.55	1.60	1.59
0.50	1.56	1.56	1.58
1	1.55	1.60	1.59
2	1.50	1.60	1.58
3	1.56	1.58	1.58
4	1.54	1.57	1.58

Appendix E Table 5. Chlorite Removal in Laboratory-Constituted Water by Alum. Three Different Runs were Conducted, and Chlorite (mg/L) was Monitored by Amperometric Titration.

Time (Hours)	Run 1	Run 2	Run 3
0	1.60	1.60	1.58
0.25	1.56	1.56	1.53
0.50	1.50	1.51	1.53
1	1.52	1.56	1.54
2	1.53	1.52	1.55
3	1.52	1.52	1.52
4	1.55	1.54	1.52

Appendix E Table 6. Chlorite Removal in Laboratory-Constituted Water by PAC (10 mg/L). Three Different Runs were Conducted, and Chlorite (mg/L) was Monitored by Amperometric Titration.

Time (Hours)	Run 1	Run 2	Run 3
0	1.70	1.70	1.68
0.25	1.56	1.58	1.61
0.50	1.54	1.52	1.57
1	1.51	1.53	1.53
2	1.44	1.42	1.44
3	1.42	1.47	1.44
4	1.38	1.43	1.40

Appendix E Table 7. Chlorite Removal in Laboratory-Constituted Water by PAC (50 mg/L). Three Different Runs were Conducted, and Chlorite (mg/L) was Monitored by Amperometric Titration.

Time (Hours)	Run 1	Run 2	Run 3
0	1.70	1.70	1.70
0.25	1.35	1.25	1.29
0.50	1.24	1.19	1.14
1	1.00	0.93	0.98
2	0.82	0.80	0.76
3	0.73	0.62	0.66
4	0.66	0.56	0.62

Appendix E Table 8. Chlorite Removal in Laboratory-Constituted Water by Alum and PAC (10 mg/L). Three Different Runs were Conducted, and Chlorite (mg/L) was Monitored by Amperometric Titration.

Time (Hours)	Run 1	Run 2	Run 3
0	1.67	1.68	1.66
0.25	1.49	1.48	1.51
0.50	1.44	1.45	1.44
1	1.38	1.41	1.37
2	1.30	1.35	1.29
3	1.32	1.36	1.28
4	1.25	1.36	1.28

Appendix E Table 9. Chlorite Removal in Laboratory-Constituted Water by Alum and PAC (50 mg/L). Three Different Runs were Conducted, and Chlorite (mg/L) was Monitored by Amperometric Titration.

Time (Hours)	Run 1	Run 2	Run 3
0	1.60	1.58	1.60
0.25	0.92	0.97	0.89
0.50	0.75	0.78	0.70
1	0.74	0.63	0.62
2	0.42	0.45	0.34
3	0.36	0.37	0.30
4	0.32	0.45	0.28

Appendix E Table 10. Chlorite Removal in Po River Water Preoxidized by Chlorine Dioxide in the Control Experiment. Three Different Runs were Conducted; Chlorite (mg/L) and Chlorine Dioxide (mg/L) were Monitored by Amperometric Titration.

Contact Time (Hours)	Run 1		Run 2		Run 3	
	ClO_2^-	ClO_2	ClO_2^-	ClO_2	ClO_2^-	ClO_2
Demand Free Distilled Water 30 Seconds Contact	0.12	8.30	0.08	7.91	0.21	7.77
Po River Immediate Dose 30 Seconds Contact	2.43	4.93	2.18	5.63	2.08	4.04
Po River After 30 Minutes Contact, Also Time Zero of Floc Period	3.32	3.28	3.07	3.03	3.33	2.25
0.25	3.62	2.13	3.47	2.01	3.57	1.55
0.50	4.04	1.29	3.78	1.31	3.83	1.26
1	4.26	0.53	4.10	0.68	3.89	0.26
2	4.59	0.00	4.27	0.17	4.66	0.00
3	4.29	0.04	4.16	0.07	4.21	0.00
4	4.59	0.00	4.33	0.10	4.21	0.13

Appendix E Table 11. Chlorite Removal in Po River Water Preoxidized by Chlorine Dioxide by Alum. Three Different Runs were Conducted; Chlorite (mg/L) and Chlorine Dioxide (mg/L) were Monitored by Amperometric Titration.

Contact Time (Hours)	Run 1		Run 2		Run 3	
	ClO_2^-	ClO_2	ClO_2^-	ClO_2	ClO_2^-	ClO_2
Demand Free Distilled Water 30 Seconds Contact	0.28	6.57	0.11	6.14	0.09	7.22
Po River Immediate Dose 30 Seconds Contact	2.13	4.47	2.45	3.27	2.66	4.34
Po River After 30 Minutes Contact, Also Time Zero of Floc Period	3.05	2.39	3.10	1.65	3.03	1.87
0.25	2.78	0.51	2.80	0.68	2.70	0.29
0.50	3.06	0.33	2.82	0.51	2.68	0.34
1	3.40	0.00	3.12	0.00	2.96	0.03
2	3.23	0.05	3.11	0.00	2.86	0.15
3	2.98	0.03	2.97	0.03	2.89	0.00
4	3.14	0.11	2.89	0.02	2.90	0.00

Appendix E Table 12. Chlorite Removal in Po River Water Preoxidized by Chlorine Dioxide by PAC (50 mg/L). Three Different Runs were Conducted; Chlorite (mg/L) and Chlorine Dioxide (mg/L) were Monitored by Amperometric Titration.

Contact Time (Hours)	Run 1		Run 2		Run 3	
	ClO_2^-	ClO_2	ClO_2^-	ClO_2	ClO_2^-	ClO_2
Demand Free Distilled Water 30 Seconds Contact	0.10	8.91	0.12	7.74	0.10	6.86
Po River Immediate Dose 30 Seconds Contact	1.68	6.79	2.15	4.76	1.81	4.79
Po River After 30 Minutes Contact, Also Time Zero of Floc Period	2.91	2.50	2.82	2.58	2.57	1.50
0.25	†	†	3.00	†	3.15	0.12
0.50	3.19	0.50	2.70	0.19	3.64	0.00
1	3.65	0.01	†	†	3.04	0.00
2	3.36	0.00	2.71	0.00	2.84	0.05
3	3.16	0.15	2.49	0.08	2.76	0.16
4	3.69	0.06	2.35	0.21	2.62	0.01

† Sample Lost Due to Error

Appendix E Table 13. Chlorite Removal in Po River Water Preoxidized by Chlorine Dioxide by Alum and PAC (50 mg/L). Three Different Runs were Conducted; Chlorite (mg/L) and Chlorine Dioxide (mg/L) were Monitored by Amperometric Titration.

Contact Time (Hours)	Run 1		Run 2		Run 3	
	ClO_2^-	ClO_2	ClO_2^-	ClO_2	ClO_2^-	ClO_2
Demand Free Distilled Water 30 Seconds Contact	0.10	6.80	0.17	6.07	0.13	6.62
Po River Immediate Dose 30 Seconds Contact	2.51	4.17	2.22	4.61	2.04	5.59
Po River After 30 Minutes Contact, Also Time Zero of Floc Period	3.10	1.52	2.84	1.72	3.09	3.38
0.25	2.86	0.00	†	†	2.53	0.10
0.50	2.18	0.01	2.13	0.00	2.67	0.00
1	2.00	0.00	1.93	0.00	2.53	0.00
2	1.81	0.00	1.85	0.00	2.15	0.22
3	1.71	0.00	1.83	0.005	2.29	0.03
4	1.67	0.00	1.77	0.00	2.10	0.02

† Sample Lost Due to Error

Appendix E Table 14. Effluent Concentration of Chlorite for Both Laboratory-Constituted Water and Mattaponi River Water from a Simulated Floc-Blanket Clarifier. Mean Chlorite Feed Concentration was 9.58 mg/L.

Effluent Chlorite Concentration, mg/L, from a Simulated Floc-Blanket Clarifier		
Time (Hours)	Laboratory Constituted Water	Mattaponi River Water
0	0.12	0.00
1	0.08	0.08
2	0.08	0.08
3	0.08	0.11
4	0.08	*
5	0.11	0.13
6	0.10	0.10
7	0.11	0.11
8	0.09	0.12
9	0.07	0.12
10	0.08	0.17
11	0.26	0.26
12	0.08	0.26
13	0.08	0.35
14	0.08	0.59
15	0.09	0.28
16	0.08	0.38
17	0.10	0.40
18	0.33	0.78
19	0.10	1.17
20	0.10	1.93
21	0.21	1.28
22	0.26	1.14
23	0.15	0.98
24	0.27	2.47

* Sample Lost Due to Error

VITA

Margaret Prehn Orr was born on May 14, 1962 in Joliet, Illinois. She received her primary and secondary education in the Romeoville, Illinois, Public School System and graduated from Romeoville High School in May, 1980. In August, 1980, she entered Illinois Benedictine College. She graduated from that college in May, 1984, with a Bachelor of Science degree in biology. In June, 1984, she entered the Tennessee Technological University Graduate School. She graduated from that college in June, 1986, with a Master of Science degree in biology. At that time, she decided to acquire an engineering degree and spent the next two years taking courses in the undergraduate civil engineering program. In August, 1988, she entered the VPI&SU Graduate School. She is a member of Tau Beta Pi, Phi Kappa Phi, and Sigma Xi. After receiving her Master of Science degree in Environmental Engineering she will work for Dow Chemical U.S.A. in Midland, Michigan, as an Environmental Engineer.

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