# WATER QUALITY IMPACTS OF

# PURE CHLORINE DIOXIDE PRETREATMENT

# AT

# THE ROANOKE COUNTY (VIRGINIA) WATER TREATMENT PLANT

by

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# WATER QUALITY IMPACTS OF PURE CHLORINE DIOXIDE PRETREATMENT AT THE ROANOKE COUNTY (VIRGINIA) WATER TREATMENT PLANT

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(ABSTRACT)

Chlorine dioxide ($ClO_2$) was included in the Spring Hollow Water Treatment Plant (Roanoke County, Virginia) to oxidize manganese and iron, prevent tastes and odors, and avoid the formation of excessive halogenated disinfection by-products. A state-of-the-art, gas:solid $ClO_2$ generation system manufactured by CDG Technology, Inc. was installed at the plant and is the first full-scale use of this technology in the world. The $ClO_2$ generator produces a feed stream free of chlorine, chlorite ion ($ClO_2^-$), and chlorate ion ($ClO_3^-$), resulting in lower by-product concentrations in the treatment system

The objectives of this project were to study $ClO_2$ persistence and by-product concentrations throughout the treatment plant and distribution system and to evaluate granular activated carbon (GAC) columns for removing $ClO_2^-$ from the finished water.

The $ClO_2$ dosages applied during this study were relatively low (<0.75 mg/L), and, as a result, $ClO_2^-$ concentrations never approached the maximum contaminant level (MCL) (1.0 mg/L). Likewise, the plant effluent $ClO_2$ concentration never approached the maximum residual disinfectant level (MRDL) (0.80 mg/L), but concentrations as high as 0.15 mg/L reformed in the distribution system by $ClO_2^-$ reaction with chlorine.

Chlorate ion was monitored despite the fact that no $ClO_3^-$ MCL has been proposed, and concentrations were quite low (never greater than 0.10 mg/L) throughout the treatment plant and in the distribution system. The reasons for the low concentrations are that $ClO_3^-$ is

not produced by the gas-solid generator used at the facility and $ClO_2^-$ concentrations in the clearwell prior to chlorination were uniformly low.

The average $ClO_2^-$ reduction upon passage of treated water through the GAC contactor was approximately 64 percent, but the GAC effectiveness was declining over the six-month study period. Apparently, GAC effectiveness, as shown by others, is short-lived, and if higher $ClO_2$ dosages are ever applied at the Roanoke County facility, the $ClO_2^-$ concentrations will have to be reduced by either ferrous coagulants or reduced-sulfur compounds.

Regenerated $ClO_2$ concentrations in the distribution system were below 0.2 mg/L, but concentrations as low as 0.03 mg/L were found at homes of customers who complained of odors. During this study, twelve complaints were received from eight customers, and each complainant had recently installed new carpeting, which has been shown to contribute volatile organics that react with $ClO_2$ to produce odors similar to kerosene and cat urine. While meeting the $ClO_2^-$ MCL likely will be no problem if the $ClO_2$ dose at the plant remains below 1.0 mg/L, the problem of offensive odors in the distribution system will likely continue as long as any $ClO_2^-$ is in the finished water when chlorine is present.

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# CHAPTER I
# INTRODUCTION

Roanoke County, Virginia's Utility Department began using chlorine dioxide ($ClO_2$) as a preoxidant at its Spring Hollow Water Treatment Plant (WTP) in August, 1997, approximately nineteen months after the plant became operational. The plant's raw water source is the Spring Hollow Reservoir, which is a pump-storage reservoir that impounds water from the Roanoke River. The plant is a Trident® process plant comprised of upflow adsorption clarifiers followed by trimedia filters and deep bed, post-filter granular activated carbon (GAC) filters. Chlorine dioxide is generated at the WTP by passing humidified chlorine gas through solid sodium chlorite ($NaClO_2$), a method that is unique in the water treatment industry. Other commercial generators produce $ClO_2$ from 25 percent $NaClO_2$ solutions with either aqueous or gaseous chlorine. Production of $ClO_2$ by the gas/solid system is easily regulated, even at low levels, and the generator effluent contains no chlorite ($ClO_2^-$), chlorate ($ClO_3^-$), or chlorine. The Spring Hollow WTP installation of this system was the first full-scale installation in the United States and provided a unique opportunity for a study of $ClO_2$ persistence and by-product concentrations throughout the treatment plant and distribution system, and evaluation of the GAC columns for removing $ClO_2^-$ from the finished water.

Chlorine dioxide was included in the Spring Hollow WTP to oxidize manganese and iron, prevent tastes and odors, and avoid the formation of excessive halogenated disinfection by-products (DPBs). Chlorine dioxide is the favored oxidant for plants that desire preoxidation and DBP control. Unlike chlorine, $ClO_2$ oxidizes but does not chlorinate natural organic matter except under special circumstances not commonly found in drinking water

treatment plants. Inorganic disinfection by-products, however, are formed, and one of these, the chlorite ion ($ClO_2^-$), is currently regulated by a maximum contaminant level (MCL) of 1.0 mg/L. The other inorganic by-product, chlorate ion ($ClO_3^-$), is not currently regulated, but an MCL will be promulgated some time in the future.

The $ClO_2^-$ MCL is not the only concern associated with $ClO_2$ use. Utilities that apply $ClO_2$ as a preoxidant and add free chlorine to finished water prior to distribution often receive complaints of offensive odors in homes and businesses. Past studies have shown that these odors are caused by unidentified chemicals produced during air-phase reactions between $ClO_2$ released from water when the customer opens a tap and volatile organic compounds originating from a variety of sources, primarily new carpeting. Often, the problems have been sufficient cause for utilities to abandon $ClO_2$ addition at their treatment facilities. The problem does not occur in systems that convert free chlorine to monochloramine prior to distribution or remove $ClO_2^-$ prior to chlorine addition. The $ClO_2$ MCL (0.80 mg/L), which is measured at the entrance to the distribution system, is relatively high compared to concentrations that reform in the distribution system and cause customer complaints. A relatively new $ClO_2$ analysis method can be used to quantify low $ClO_2$ concentrations (0.01 mg/L), and the availability of this method provided an opportunity for the author to study the association between odor complaints and $ClO_2$ levels in the distribution system.

Specific objectives of the study were to: (1) document changes in $ClO_2$, $ClO_2^-$ and $ClO_3^-$ concentrations throughout the Spring Hollow WTP and the distribution system following $ClO_2$ pretreatment of raw water, (2) evaluate the effectiveness of GAC in post-

filter contactors for $ClO_2^-$ removal, and (3) determine the extent of $ClO_2$ reformation in the distribution system and the concentrations associated with customer complaints of odors.

The research presented in this thesis was the basis of a technical presentation at the 1998 Annual American Water Works Association Conference and Exposition in Dallas, Texas. It appears in the proceedings of that conference (Ellenberger et al., 1998).

# CHAPTER II
# LITERATURE REVIEW

## Chlorine Dioxide and By-product Chemistry

Chlorine dioxide ($ClO_2$) exists as a volatile, energetic free radical and is quite reactive. It is explosive at 5.8 psi (40 kPa), or above atmospheric pressure at 6 psig (41 kPa). As a result, $ClO_2$ cannot be compressed or stored and must be generated on-site and solutions with concentrations greater than 10 g/L may present an explosive hazard (Aieta and Berg, 1986). Chlorine dioxide concentrations are generally in the range of 0.1 mg/L to 5.0 mg/L for water treatment.

Chlorine dioxide does not hydrolyze in water but remains a highly soluble gas above 11°C over a broad range of pH (2 to 10). Solutions are greenish-yellow and smell strongly chlorinous (Gordon and Rosenblatt, 1996). Aqueous solutions must be protected from light, as chlorine dioxide is subject to photolysis by ultraviolet light (Zika, 1985), and even fluorescent lights (Griese et al., 1992).

The most common methods for the generation of $ClO_2$ for drinking water treatment involve sodium chlorite ($NaClO_2$), either as a solid or in solution (Aieta and Berg, 1986). Sodium chlorite is reacted with either chlorine gas ($Cl_2$), hypochlorous acid (HOCl), or hydrochloric acid (HCl) in the following reactions (Aieta and Berg, 1986; Gordon et al., 1972):

$$2NaClO_2 + Cl_{2(g)} \rightarrow 2ClO_{2(g)} + 2NaCl \quad [1]$$

$$2NaClO_2 + HOCl \rightarrow NaCl + NaOH + 2ClO_2 \quad [2]$$

$$5NaClO_2 + 4HCl \rightarrow 4ClO_{2(g)} + 2H_2O + 5NaCl \quad [3]$$

During the first two reactions, an unstable intermediate, $Cl_2O_2$, is formed if the reactants are in high concentrations. When chlorite ion ($ClO_2^-$) concentrations are low, the intermediate decays to chlorate ion ($ClO_3^-$). Chlorate ion production can also occur when initial reactant concentrations are low or when chlorine (or hypochlorous acid) is in excess. When initial reactant concentrations are high or when $ClO_2^-$ concentrations are in excess, the intermediate decays to $ClO_2$ (Gordon and Rosenblatt, 1996).

During the generation of $ClO_2$, it is desirable to minimize or eliminate unwanted by-products such as $ClO_2^-$ and $ClO_3^-$ as well as excess chlorine. The production of unwanted by-products can occur when there is feedstock contamination, improper generator control, or excess chlorine (Long et al., 1996; Gates, 1998). In Reaction 3, only an 80 percent conversion of $NaClO_2$ to $ClO_2$ is possible (Aieta and Berg, 1986), and, therefore, this method is not popular.

Recently, a method for generating high-purity $ClO_2$ by reaction of solid $NaClO_2$ with chlorine gas has become available (Gordon and Rosenblatt, 1996***)***. The chlorine gas is first mixed with humidified air and then passed through a series of drums containing solid $NaClO_2$. No unreacted $NaClO_2$ enters the system because the generated $ClO_2$ is in the gas phase, and $ClO_3^-$ is not produced.

The main reaction product of $ClO_2$ in water is the chlorite ion. Its reduction occurs by an one electron transfer, forming $ClO_2^-$ as shown in this half-reaction (White, 1972; Gordon et al., 1972):

$$ClO_2 + e^- \rightarrow ClO_2^- \qquad [4]$$

Masschelein (1979) reported, “In aqueous solution, chlorination by chlorine dioxide is not a direct reaction. However, indirect chlorination by dioxide having undergone a previous

reaction may not necessary be excluded." He attributed reports of chlorinated organic by-products produced to the presence of chlorine in the $ClO_2$ solution that was used. Chlorine, on the other hand, reacts with organic compounds to form chlorinated organic by-products (Rook, 1974; Bellar et al., 1974).

Chlorite ion, which also is an oxidant, reacts at a much slower rate than $ClO_2$ under conditions generally encountered in water treatment. Chlorite ion is reduced to chloride ion ($Cl^-$) by the following reaction (Aieta and Berg, 1986; Gordon et al., 1972; Masschelein, 1979):

$$ClO_2^- + 4H^+ + 4e^- \rightarrow Cl^- + 2H_2O \quad [5]$$

This reaction does not occur, however, unless reduced compounds such as ferrous iron ($Fe^{2+}$), phenol, or humic materials are present. Typically, from 50 to 70 percent of the reacted $ClO_2$ appears as $ClO_2^-$ with the balance forming either $Cl^-$ or $ClO_3^-$ (Aieta and Berg, 1986; Limoni et al., 1984; Rav-Acha et al., 1984; Werdehoff and Singer, 1987; Singer and O'Neil, 1987).

In basic solutions, $ClO_2$ disproportionates to form $ClO_2^-$ and $ClO_3^-$ (Aieta and Berg, 1986):

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O \quad [6]$$

Under certain conditions chlorine and $ClO_2$ can react to form $ClO_3^-$ (Aieta and Berg, 1986):

$$2ClO_2 + HOCl + H_2O \rightarrow 2ClO_3^- + 2H^+ + HCl \quad [7]$$

Chlorine dioxide is subject to photochemical decomposition through a series of reactions to $Cl^-$ and $ClO_3^-$ (Zika, 1985). Griese et al. (1992) reported significant formation of $ClO_3^-$ (0.36 to 0.97 mg/L) when water containing from 3.56 mg/L to 3.99 mg/L $ClO_2$ was

exposed to fluorescent light. In control experiments, water treated with $ClO_2$ and kept in the dark did not contain $ClO_3^-$.

Chlorite ion reacts with chlorine in treated water to reform $ClO_2$, in the same manner that $ClO_2$ is generated (Reaction 2 presented previously). This reaction, however, depends heavily on pH and relative reactant concentrations. In basic solutions when the hypochlorite ion ($OCl^-$) is present, greater amounts of $ClO_3^-$ are formed by the following reaction (Gordon et al., 1990; Werdehoff and Singer, 1987):

$$ClO_2^- + HOCl + OH^- \rightarrow H_2O + Cl^- + ClO_3^- \quad [8]$$

In acidic solutions when $ClO_2^-$ is in excess, more $ClO_2$ than $ClO_3^-$ is formed (Gordon et al., 1972; Gordon et al., 1990; Werdehoff and Singer, 1987):

$$2ClO_2^- + HOCl \rightarrow 2ClO_2 + Cl^- + OH^- \quad [9]$$

In neutral solutions chlorine and $ClO_2$ react to form $ClO_3^-$ and $Cl^-$ (Gordon et al., 1972):

$$2ClO_2 + HOCl + H_2O \rightarrow 2ClO_3^- + Cl^- + 3H^+ \quad [10]$$

## Chlorine Dioxide Applications in Water Treatment

Chlorine dioxide is commonly used as a preoxidant and primary disinfectant during drinking water treatment. As a preoxidant, it is used mainly as an alternative to chlorine, for trihalomethane (THM) control (Dietrich et al., 1992b). It is also used for taste-and-odor control, manganese and iron oxidation, and color removal. In the United States, over 500 water treatment plants use $ClO_2$ full time and as many as 900 use it either part time or seasonally (Hoehn, 1993). In some European countries, $ClO_2$ is also used to maintain a distribution system residual. In the United States, $ClO_2$ application is generally followed by

free chlorine or chloramines to maintain the distribution system residual (Aieta and Berg, 1986).

**Trihalomethane Control**

In the early 1970s, two separate investigators found that chlorination of natural waters containing humic substances caused THM formation (Rook, 1974; Bellar et al., 1974). Since then, additional substances have been identified as precursors to THMs, including fulvic acids, algal materials, and various aromatic substances (Cooper et al., 1985). In 1976, chloroform was reported to cause an increased incidence of tumor formation (Gallagher et al., 1994 citing National Cancer Institute, 1976). Under the newly promulgated Stage 1 Disinfectant/Disinfection By-Product (D/DBP) Rule, total trihalomethanes (TTHMs) and haloacetic acids (HAAs) are regulated at 0.080 mg/L and 0.060 mg/L, respectively (Federal Register, 1998). The search for alternatives to chlorine for disinfection and oxidation has been one of the primary research objectives in water treatment. Chlorine dioxide has been recommended both as an alternative preoxidant and supplemental disinfectant with chlorine (AWWA, 1982).

Chow and Roberts (1981) compared the application of chlorine and $ClO_2$ to two wastewater effluents. They reported no significant amounts of THMs were produced in either wastewater when $ClO_2$ was used. Only marginally significant amounts of total organic halogens (TOX) were produced with $ClO_2$. When chlorine was used, significant amounts of both THMs and TOX were formed. Approximately one percent of the applied chlorine dose was converted to organic halogens.

A study was undertaken in Evansville, Indiana, to evaluate $ClO_2$ as an alternative to chlorine for pretreatment in order to reduce THMs (Lykins and Griese, 1986). The authors reported annual average total trihalomethane (TTHM) concentrations between 50 µg/L to 80 µg/L when using $ClO_2$ for predisinfection. During the year-long pilot study, the authors reported a reduction in finished water THMs of almost 60 percent when $ClO_2$ was used for predisinfection. The authors noted that the $ClO_2$ generator effluent contributed approximately 0.2 mg $Cl_2$/L when the $ClO_2$ dose was 1.6 mg/L. The investigation also included an evaluation of total organic carbon (TOC) removal when both chlorine or $ClO_2$ were used for predisinfection, but no differences in average TOC concentrations were observed following treatment with both predisinfectants. The authors also noted that $ClO_2$ increased disinfection costs and cited another study (USEPA, 1983) in which the increased cost to customers of a utility in South Carolina was $1.77 per residence per year.

Werdehoff and Singer (1987) conducted experiments with waters from various sources in Virginia to determine whether $ClO_2$ pretreatment reduced THM and TOX formation. The authors reported that $ClO_2$ treatment reduced THM and TOX precursor concentrations, but the extent to which they were reduced was dependent on the ratio of $ClO_2$:TOC. A ratio of 0.4 or greater was necessary to obtain a reduction of greater than 10 percent. The authors also observed $ClO_2^-$ was the major end product of the reaction between $ClO_2$ and fulvic acid, indicating that $ClO_2$ reacts primarily by a one-electron transfer.

In a study conducted by the Indianapolis Water Company (Long et al., 1996), raw water was dosed with high-purity $ClO_2$ (1 mg/L to 6 mg/L) and alum. The authors reported $ClO_2$ residuals ranging from 0 mg/L to 3.85 mg/L and TTHM levels from 1.4 µg/L to 10.4 µg/L compared to 69 µg/L and 69.9 µg/L in the chlorine-treated controls. The authors also

noted that the TTHM levels in the treated samples were due almost entirely to the TTHM content of the finished tap water used in preparing the $ClO_2$ solutions, and about 1.5 μg/L to 2.0 μg/L of TTHM were contributed per mg/L $ClO_2$ dose.

**Taste and Odor Control**

Chlorine dioxide was first employed in potable water treatment in 1944 at the Niagara River Plant in Niagara, New York (Synan et al., 1944). It was used successfully to control phenolic/chlorophenolic tastes and odors and seasonal algal tastes and odors at considerable cost savings over those associated with previously employed control methods, chlorine and activated carbon.

A water utility in Alberta, Canada, removed chlorophenolic and other tastes and odors from its water supply with $ClO_2$ treatment for tastes and odors, primarily caused by chlorophenols (Walker et al., 1986). The results indicated $ClO_2$ effectively removed the chlorophenolic tastes and odors. The investigators also found that algal and bacterial metabolites, presumed to be the cause of musty and fishy tastes and odors, were effectively eliminated with $ClO_2$ treatment. Chlorine dioxide treatment also eliminated algal and aquatic weed growths in outdoor basins.

Although $ClO_2$ can effectively oxidize some taste-and-odor compounds, certain ones are resistant. Lalezary et al. (1986) reported that $ClO_2$ reduced geosmin and 2-methylisoborneol (MIB) concentrations by only 30 percent at dosages and contact times considerably greater than those usually used for water treatment. Glaze et al. (1990), reported similar results for geosmin and MIB oxidation by $ClO_2$ with removal levels of 17

percent and 2 percent, respectively, but found that ozone reduced geosmin and MIB levels by 73 percent and 86 percent, respectively, at a dose of 4.0 mg/L.

**Disinfection**

The disinfection capabilities of $ClO_2$ were recognized in the 1940s not long after its introduction in water treatment (McCarthy, 1944). White (1972) mentioned several early studies in which $ClO_2$ was an effective bactericide over a broad range of pH values (Ridenour and Ingols, 1947) and an effective virucide (Hettche and Ehlbeck, 1953). White (1972) also reported on the work of Bernarde et al. (1965), who found that the disinfection efficiency of $ClO_2$ increases as a function of pH. Lykins et al. (1991) summarized CT (concentration times contact time) data from several more recent disinfection studies (Hoff, 1986; Federal Register, 1989; Korich et al., 1990) that show $ClO_2$ to be a superior disinfectant to free chlorine and chloramines against *Giardia lamblia*, *Giardia muris*, and *Cryptosporidium parvum*. The CT value for *Cryptosporidium* inactivation by $ClO_2$ is three orders of magnitude less than the CT values for inactivation by free chlorine and chloramines at pH 7 and 25°C (CT of 78 for 90 percent inactivation for $ClO_2$, 7200 for 90 percent inactivation for chloramines, and 7200 for 99.9 percent inactivation for free chlorine).

Finch et al. (1995) reported the CT value for 99.9 percent *Cryptosporidium* inactivation with $ClO_2$ was 140 (pH 7 and 25°C) using animal infectivity data. Liyanage et al. (1997) reported a synergistic effect on *Cryptosporidium parvum* inactivation when $ClO_2$ pretreatment was followed by application of free chlorine or monochloramine. They found that $ClO_2$ (1.3 mg/L for 120 minutes) followed by free chlorine (1.6 mg/L for 120 minutes) resulted in a 3 log-unit (99.9 percent) reduction in infectivity. Similarly, they found that

$ClO_2$ (1.5 mg/L for 120 minutes) followed by monochloramine (2.8 mg/L for 180 minutes) resulted in a 2.8 log-unit (99.84 percent) reduction in infectivity. The expected inactivations by $ClO_2$, free chlorine or monochloramine alone were 1.7 (98 percent), 0.0, and 0.0 log-units, respectively. The researchers hypothesized that the synergistic effect demonstrated by sequential disinfection is because "the stronger oxidant conditions the outer membrane of the oocysts so that the secondary oxidant can penetrate the oocyst wall more readily."

**Manganese Oxidation**

Soluble manganese ($Mn^{2+}$), which is commonly found in groundwater sources and reservoirs, can cause staining of laundry and plumbing fixtures, and black water (White, 1972). A secondary maximum contaminant level (MCL) of 0.05 mg Mn/L has been set for manganese to avoid these problems (Federal Register, 1979). During water treatment, $Mn^{2+}$ is typically removed by oxidation and the resulting precipitate, manganese dioxide ($MnO_2$), is then removed by sedimentation and/or filtration (Knocke et al., 1987). Chlorine dioxide has been shown to be an effective manganese oxidant and reacts more rapidly than chlorine (White, 1972).

The oxidation-reduction reaction between $Mn^{2+}$ and $ClO_2$ yields $ClO_2^-$, which involves a one-electron transfer between $ClO_2$ and $ClO_2^-$. Experiments conducted by Knocke et al. (1990) demonstrated that $ClO_2^-$ cannot oxidize Mn(II). The reaction between $ClO_2$ and $Mn^{2+}$ at a neutral pH occurs as follow (Knocke et al., 1990):

$$Mn^{2+} + 2ClO_2 + 2H_2O \rightarrow MnO_2(s) + 2ClO_2^- + 4H^+ \qquad [11]$$

From the stoichiometry, 2.45 mg of chlorine dioxide are required to oxidize 1 mg of soluble manganese (White, 1972). Knocke et al. (1987) reported that a $ClO_2$ dose at least

twice the stoichiometric quantity was required to reduce manganese levels below the secondary MCL (0.05 mg Mn/L). In that study, $ClO_2$ was effective over a pH range of 5 to 8 and at temperatures as low as 50°F (10°C). Chlorine dioxide dosages greater than 3 mg/L were required to reduce manganese concentrations to less than 0.05 mg Mn/L, when the total organic carbon (TOC) concentration was 8 mg/L. In water treatment applications, $ClO_2$ dosages of this magnitude would not be practical unless the resulting $ClO_2^-$ concentration was reduced to below the MCL by the addition of ferrous iron or reduced-sulfur compounds. Knocke et al. (1990) showed that manganese forms a weak complex with organic acids and is capable of being oxidized by $ClO_2$.

**Iron Oxidation**

Iron can also cause staining of laundry and plumbing fixtures and promote the growth of iron bacteria in the distribution system (White, 1972). A secondary MCL of 0.3 mg/L has been set for iron to avoid these problems (Federal Register, 1979). Chlorine dioxide can rapidly oxidize iron to an insoluble, iron hydroxide ($Fe(OH)_3$), which can be removed by sedimentation and filtration. Iron oxidation by $ClO_2$ under water treatment conditions, occurs as follows (Knocke et al., 1990):

$$Fe^{2+} + ClO_2 + 3H_2O \rightarrow Fe(OH)_3(s) + ClO_2^- + 3H^+ \qquad [12]$$

From the stoichiometry, 1.2 mg of chlorine dioxide was required to oxidize 1 mg of soluble iron (White, 1972). Chlorite ion also can oxidize Fe(II); the reaction is summarized as follows (Ondrus and Gordon, 1972):

$$4Fe^{2+} + ClO_2^- + 10H_2O \rightarrow 4Fe(OH)_3(s) + Cl^- + 8H^+ \qquad [13]$$

Chlorine dioxide also can oxidize iron when it is complexed with organic compounds (Masschelein, 1979). Knocke et al. (1990), however, found that Fe(II) complexed with organics was stable in the presence of $ClO_2$, even when the $ClO_2$ dosage was well in excess of the stoichiometric amount.

## Analytical Techniques

Several methods for quantifying $ClO_2$, $ClO_2^-$, and $ClO_3^-$ are available. These include amperometric titration, N, N-diethyl-p-phenylenediamine titration (DPD), iodometric titration, chlorophenol red, and ion chromatography. The amperometric method is approved for compliance monitoring of $ClO_2$, and ion chromatography is approved for $ClO_2^-$ analyses (Federal Register, 1998). The lissamine green B Method for detection of $ClO_2$ at low levels in the presence of chlorine, has been developed, but it is not currently an EPA-approved method. These methods are discussed in the following sections.

### The Amperometric Method

The amperometric method can be used to determine $ClO_2$, $Cl_2$, $ClO_2^-$, and $ClO_3^-$. It involves titrimetric determination of iodine that is formed when iodide is oxidized by the species of interest by titration. The titrant may be either phenylarsine oxide (PAO) or sodium thiosulfate (Aieta et al., 1984; APHA, 1995). During the procedure, several titration steps are required following various pretreatment and pH adjustments that allow differentiation between the various species. According to Aieta et al. (1984), "calculations are based on the equivalents of reducing titrant required to react with the equivalents of oxidants present." No differentiation is made between free and combined chlorine by this procedure.

The method can be used for measuring $ClO_2$ concentrations in product streams of $ClO_2$ generators (10 mg/L to 1000 mg/L for individual species) and treated drinking water (0.1 to 1 mg/L) (Aieta et al., 1984). The method detection limit for $ClO_2$ was reported to be 0.05 mg/L. Analytical precision during the titration steps is imperative, as errors in one titration step will affect subsequent calculations. This method relies on calculations of the difference between two large numbers, and small differences in titrant volumes could potentially result in large cumulative errors. The method is subject to several interferences (e.g. dissolved oxygen, manganese, copper, and nitrate) at the low pH conditions required for the $ClO_2^-$ and $ClO_3^-$ analyses (Aieta et al., 1984). Chloramines are also potential interferences in $ClO_2$ measurements since they interfere with the amperometric method for free available chlorine (Jensen and Johnson, 1990).

During the study reported in this thesis, the amperometric method was used only to verify $ClO_2$ stock solution concentrations on a few occasions. It was not used for monitoring $ClO_2$ in either the treatment plant or distribution system.

**Lissamine Green B Method**

The lissamine green B (LGB) method for $ClO_2$ determination was recently developed by Chiswell and O'Halloran (1991). This colorimetric method is not subject to interferences common to other methods such as DPD, chlorophenol red, and amperometric titration. Lissamine green B has a greater redox potential (+1.0V) than combined chlorine, $ClO_2^-$, and $ClO_3^-$, and therefore, is not subject to interferences from those species. The authors raised the solution pH to ensure free chlorine would exist almost entirely as hypochlorite, thereby reducing the interference by free chlorine, as hypochlorous acid, which has a greater redox

potential than LGB. However, $ClO_2$ has been documented to disproportionate in basic solutions. The researchers determined that a solution of LGB in the presence of an ammonia-ammonium chloride buffer at pH 9.0 resulted in optimal conditions. The basis of the test is the oxidation of the lissamine green B dye, which results in reductions in absorbance.

The method involves the addition of a pH 9.0 ammonia buffer and LGB reagent solution to a sample, and the sample absorbance is analyzed by spectrophotometry at 614 nanometers (nm) typically in a 1 centimeter (cm) quartz cuvette. The pH 9.0 buffer ensures that any free chlorine is in the form of hypochlorite, a weaker oxidant than hypochlorous acid, that is less likely to react with the LGB reagent solution. At higher pH levels, the disproportionation of $ClO_2$ would become significant.

Research conducted recently by Hofmann et al. (1998) confirmed that the LGB method is not subject to interference by free chlorine, $ClO_2^-$, $ClO_3^-$, and permanganate at concentrations up to 5 mg/L. The authors reported the method detection limit to be 0.017 mg/L when the path length was 1 cm. The upper limit of the linear range was reported to be 1.8 mg/L. The authors investigated the effects of temperature and measured higher concentrations as the temperature decreased. A 30 percent positive error occurred when analyzed samples were at 4°C and compared to a calibration curve developed at 20°C. The error was less than 10 percent when the sample temperature was 12°C. The researchers recommended no more than 10°C difference between samples and standards. They also investigated potential interferences by color and noted that if the blank absorbance was attributed to both the LGB reagent and natural color, the change in absorbance following

$ClO_2$ addition would be due not only to oxidation of the LGB but also to color-causing compounds as well. They suggested the following equation:

$$[ClO_2]_{MEASURED} \propto \Delta Color_{REAGENT} + \Delta Color_{WATER\ MATRIX} \quad [14]$$

Five different waters with varying degrees of color were tested and the estimated maximum error was 0.05 mg/L. They found that after 10 minutes, $ClO_2$ did not oxidize the color and reacted only with the LGB reagent. The authors suggested using purged matrix water for preparing the calibration curves and blanks.

**Ion Chromatography**

Ion chromatography (IC) is used for the determination of ion concentrations in drinking water. It is also particularly useful for the determination of certain inorganic disinfection by-products, such as oxyhalides of chlorine and bromate, as it is not subject to interferences common in other methods (Pfaff and Brockhoff, 1990).

The USEPA developed Method 300.0B specifically for analyses of $ClO_2^-$ and $ClO_3^-$ which involves the use of an ion exchange column (Dionex AS9) that is specifically designed to enhance the separation of $ClO_3^-$ and $ClO_2^-$ from other closely eluting anions ($NO_3^-$ and $Cl^-$) (Pfaff et al., 1989). The sample is injected into the mobile phase (eluant), which carries the sample through the stationary phase (column). A guard column, which is a shorter version of the analytical column, is usually placed in front of the analytical column to protect the analytical column from contamination. The anions separate based on their affinity for the stationary phase.

After moving through the column, the separated anions flow through an anion micromembrane suppressor, which suppresses the background conductivity of the eluant.

After each anion passes through the suppressor, a conductimetric detector measures the conductivity. Each anion retention time is characteristic for the particular system configuration. The conductivity of column effluent is plotted over time by an integrator, which determines the area or height for each peak.

The unknown concentrations of each anion can be determined by comparison of peak height or peak area to a calibration curve developed from the analyses of a series of standard solutions. The concentrations are then plotted against either the peak height or peak area**,** and the regression is determined. The regression formula is then used to calculate the concentrations of the unknowns. Novatek (1993) recommends a correlation coefficient of at least 0.999. The reported detection limits for Method 300.0B are 0.01 mg/L and 0.003 mg/L for $ClO_2^-$ and $ClO_3^-$, respectively (Pfaff et al., 1989).

According to Method 300.0B, $ClO_2^-$ samples must be analyzed immediately because $ClO_2^-$ is not stable in the presence of chlorine. Research by Pfaff and Brockhoff (1990) showed that $ClO_2^-$ becomes unstable after one hour when chlorine is present. They reported that $ClO_3^-$ should be stable for at least 30 days. Method 300.0B allows a holding time for $ClO_3^-$ samples up to 28 days. Two studies (Dietrich et al., 1992a; Hautman and Bolyard, 1992) have shown that a preservative, ethylenediamine, can be added to the sample to increase the stability of $ClO_2^-$ to 18 days. These studies also confirmed $ClO_3^-$ is stable for at least 18 days without a preservative.

## Chlorite Ion Concentrations in Distribution Systems

Chlorite ion is the most abundant $ClO_2$ byproduct in the distribution system of utilities that add the oxidant during water treatment. Thompson et al. (1989) reported the use at their utility of 0.75 mg/L $ClO_2$ as a preoxidant and as a chlorine co-disinfectant at a dose of 0.75 mg/L. Residual $ClO_2^-$ concentrations in the distribution system decreased from 0.76 mg/L to 0.67 mg/L with increasing distance from the treatment plant, while the $ClO_3^-$ concentration remained constant throughout the system at an average concentration of 0.21 mg/L.

Other investigations of $ClO_2^-$ concentrations in the distribution system have been reported by Gallagher et al. (1994), Bolyard et al. (1993), Hoehn et al. (1990), USEPA (1997) and Bubnis (1997). Gallagher et al. (1994) found $ClO_2^-$ concentrations ranging from nondetectable to 2.41 mg/L in the distribution systems (including clear wells) of five utilities. Bolyard et al. (1993) found concentrations ranging from 0.052 mg/L to 0.74 mg/L at four sites where $ClO_2$ was being used. The USEPA (1997) summarized occurrence data collected from 65 utilities (885 samples). The mean $ClO_2^-$ concentration was 0.58 mg/L while the range was from 0.01 mg/L to 2.60 mg/L. Bubnis (personal communication) reported a $ClO_2^-$ concentration range of 0.21 mg/L to 0.86 mg/L in the distribution systems of 18 Texas utilities during 1997. A vast majority of the utilities would have met the current $ClO_2^-$ MCL of 1.0 mg/L.

McGuire et al. (1999) presented evidence that residual $ClO_2^-$ in the distribution system suppresses nitrification by killing ammonia-oxidizing bacteria, thus preventing nitrifier biofilm production. Coliforms and heterotrophic plate count bacteria were unaffected.

**Chlorine Dioxide Concentrations in Distribution Systems and Associated Odors**

In the United States, $ClO_2$ is seldom added directly to water entering the distribution system. An exception is the Gulf Coast Water Authority in Galveston, Texas. At that utility, $ClO_2$ has been applied both as a preoxidant (dose 0.75 mg/L) and again following filtration (dose 0.75 mg/L) as water entered the clearwell. Chlorine was also applied at the same time, and ammonia was added to form chloramine as the water entered the distribution system. Residual $ClO_2$ concentrations in the distribution system decreased from 0.31 mg/L as water exited the clearwell to 0.12 mg/L in the distribution system.

Direct addition to finished water is not the only way $ClO_2$ can appear in the distribution system, however. It can be regenerated in small amounts by the same reaction between residual $ClO_2^-$ and free chlorine (Reaction 2) as occurs during $ClO_2$ generation at the treatment plant. Chlorate ion can also form by chlorine reactions with both $ClO_2$ (Reaction 7) and $ClO_2^-$ (Reaction 2). Chlorine dioxide can also react with free chlorine to form both $ClO_3^-$ and $ClO_2^-$. The concentrations of $ClO_2$ and its by-products one observes at any particular point in the distribution system are the results of a complex cyclic series of reactions involving $ClO_2$ formation, reduction to $ClO_2^-$ and/or formation of $ClO_3^-$, and then $ClO_2$ reforms once again when free chlorine oxidizes $ClO_2^-$ (Gallagher et al., 1994).

Chlorine dioxide in the distribution system can react to produce odors variously described as “cat urine,” “chlorine,” “petroleum” and “kerosene” in customers’ homes (Hoehn et al., 1990). Reports of tastes and odors in the distribution system that are related to $ClO_2$ use at the treatment plant date back to the 1940s when McCarthy (1944) reported a kerosene taste in the distribution system of a Massachusetts utility. He attributed the tastes, however, to $ClO_2$ oxidation and subsequent detachment of pipe slimes in the distribution

system, which, he believed, exposed airplane fuel that had entered the treatment plant several years earlier following a crash in the reservoir. Some of the fuel escaped treatment and entered the distribution system where he believed it coated the pipes. In time, according to McCarthy, the deposited airplane fuel must have been coated by a layer of biofilm that prevented further odor problems until he began applying $ClO_2$ at the treatment plant.

Hoehn et al. (1990) discovered the actual cause of the kerosene-like odors during an AWWA Research Foundation research project, namely that they result from reactions between volatile organics in the household air and $ClO_2$ volatilized at the tap. The specific organic compounds that produce the odor have not been determined at this time. New carpeting is the most common source of volatile organic compounds that may be precursors to the odors, but other sources (e.g. paints and hand soaps containing hydrocarbons) are possible. Hoehn et al. (1990) cited many reports linking $ClO_2$-related odor complaints to new carpeting. These odors can be avoided either by substituting monochloramine for chlorine in the distributed water or by removing $ClO_2^-$ at the treatment plant prior to distribution system chlorination.

## Regulation of Chlorine Dioxide and Its By-products

Regulation of $ClO_2$ and its by-products has been one of the foremost concerns with its use. As more research studies are undertaken to address the need for health effects data on $ClO_2$ and its by-products, regulations may be set at scientifically based levels.

In July, 1994, the USEPA proposed a maximum residual disinfectant level (MRDL) of 0.8 mg/L for $ClO_2$, and a maximum contaminant level (MCL) of 1.0 mg/L for $ClO_2^-$ in the Disinfection/Disinfectant By-product (D/DBP) Rule (Federal Register, 1994). The proposed

rule also specified a maximum residual disinfectant level goal (MRDLG) of 0.3 mg/L for $ClO_2$ and a maximum contaminant level goal (MCLG) of 0.08 mg/L for $ClO_2^-$. The Final D/DBP Rule (Federal Register, 1998) retained the proposed $ClO_2^-$ MCL and the $ClO_2$ MRDL but increased both the MCLG for $ClO_2^-$ and the MRDLG for $ClO_2$ to 0.8 mg/L on the basis of "a weight-of-evidence evaluation of all health data on $ClO_2^-$ including a two-generation reproductive rat study sponsored by the Chemical Manufacturers Association (CMA, 1996)." In explaining the reason for increasing the $ClO_2$ MRDLG to 0.8 mg/L, the USEPA stated "that data on chlorite are relevant to assessing the risks of chlorine dioxide because chlorine dioxide is rapidly reduced to chlorite" (Federal Register, 1998). The promulgated limits were based on the "no observable adverse effect levels (NOAEL)" for hemolytic effects. No MCL for $ClO_3^-$ was proposed in the D/DBP Rule because health effects data were not available at the time it was published.

## Chlorite Ion Control

Meeting the MCL for $ClO_2^-$ ion most likely will require control at the treatment plant if $ClO_2$ is applied at concentrations high enough for disinfection, especially if *Cryptosporidium* rather than *Giardia* becomes the target organism. Several removal strategies exist for $ClO_2^-$ that vary in effectiveness and end products. While no MCL yet exists for $ClO_3^-$, once it is introduced into or formed in the distribution system, it cannot be removed.

**Reduction by Ferrous Iron**

Ondrus and Gordon (1972) reported $ClO_2^-$ reduction by ferrous iron, Fe(II), under low pH (< 2.0) and high ionic strength (2.00 M) conditions. The overall reaction was:

$$4Fe(II) + ClO_2^- + 10H_2O \rightarrow 4Fe(OH)_{3(s)} + Cl^- + 8H^+ \quad [15]$$

Investigations of $ClO_2^-$ reduction by ferrous iron were also undertaken by Griese et al. (1991). In this study, they found that $ClO_2^-$ ($ClO_2$ dose 1.5 mg/L to 4.0 mg/L) could be completely removed in less than 30 minutes at pH 6.0 to 7.0. These studies were conducted with ferrous iron dosages well in excess of the stoichiometric requirement. The initial and final oxychlorine compound concentrations (e.g. the sum of $ClO_2$, $ClO_2^-$, and $ClO_3^-$) were compared. The final oxychlorine compound concentration was comprised almost entirely of $ClO_3^-$, with no significant differences in the initial and final $ClO_3^-$ concentrations. This indicated that the $ClO_3^-$ originated as a contaminant in the $ClO_2$ generator effluent and not as a result of the ferrous iron treatment.

Further research conducted by Griese et al (1992), combined $ClO_2^-$ reduction by ferrous iron with alternative $ClO_2$ generation methods. In the study, oxychlorine residuals remaining after water was treated with both liquid-phase and gas-phase $ClO_2$ generation systems were compared. The application of gas-phase $ClO_2$ resulted in minimal $ClO_3^-$ concentrations, and the application of ferrous iron resulted in complete removal of $ClO_2^-$ ($ClO_2$ dose 2.0 mg/L to 5.0 mg/L). Chlorate ion concentrations increased dramatically when water treated with $ClO_2$, but not ferrous iron, was chlorinated, indicating the importance of removing $ClO_2$ and $ClO_2^-$ prior to post chlorination. The researchers also verified that $ClO_2$ photochemically degrades to $ClO_3^-$ when exposed to light, as described earlier.

Iatrou and Knocke (1992) reported that ferrous iron added to water at a ratio of 3.1 mg Fe(II)/mg $ClO_2^-$ effectively eliminated $ClO_2^-$ from finished water. They reported also that $ClO_2^-$ reduction by Fe(II) was complete within 1 to 2 minutes at typical water treatment conditions. No $ClO_3^-$ formation occurred when solutions of $ClO_2^-$ (initial concentration up to 4.0 mg/L) were treated with Fe(II) over a pH range of 5.5 to 8.0.

The possible interference of dissolved oxygen in the Fe(II)-$ClO_2^-$ reaction was also investigated by Iatrou and Knocke (1992). They found that the Fe(II)-$ClO_2^-$ reaction at neutral pH was not significantly affected by dissolved oxygen. Residual Fe(II) remaining when the dosages were in excess of the stoichiometric amount was eliminated by reaction with dissolved oxygen at pH 7.0. At pH 6.3 and below, excess Fe(II) was not removed by reaction with dissolved oxygen. In studies with alum coagulation, addition of Fe(II) did not interfere with dissolved organic carbon (DOC) removal or increase the settled-water turbidity.

Hurst and Knocke (1997) investigated $ClO_2^-$ reduction by Fe(II) under alkaline pH conditions (pH 7 to 10) and found that a dosage slightly in excess of the stoichiometric amount was required to remove $ClO_2^-$ effectively. The excess Fe(II) was necessary to account for some DO interference in the Fe(II)-$ClO_2^-$ reaction. Again, no $ClO_3^-$ formation was detected. A mass balance of the oxychlorine species for the Fe(II)-$ClO_2^-$ reaction revealed that $Cl^-$ was the major product (> 95 percent).

**Reduction by Reduced-Sulfur Compounds**

Gordon et al. (1990) reported $ClO_2^-$ reduction by sulfur dioxide-sulfite ion ($SO_2$-$SO_3^{2-}$), which they said occurred by the following reaction over a pH range of 4.0 to 7.5:

$$2SO_4^{2-} + ClO_2^- \leftrightarrow 2SO_4^{2-} + Cl^- \quad [16]$$

Their research indicated that $ClO_2^-$ removal was more rapid when the pH was acidic. The authors reported complete $ClO_2^-$ reduction in less than one minute when a tenfold weight excess of sulfur dioxide/sulfite ($SO_2$-$SO_3^{2-}$) was reacted with 0.5 to 7.0 mg/L $ClO_2^-$ at pH 5 and below and complete $ClO_2^-$ reduction in less than 15 minutes at pH 6.5. The authors noted that dissolved oxygen may interfere with $SO_2$-$SO_3^{2-}$/$ClO_2^-$ reaction by competing for $SO_2$-$SO_3^{2-}$.

Griese et al. (1991) achieved complete $ClO_2^-$ reduction following the addition of $SO_2$-$SO_3^{2-}$, but significant amounts of $ClO_3^-$ were formed when the pH ranged from 4.0 to 8.5. The authors noted an increase in $ClO_3^-$ concentration when the $SO_2$-$SO_3^{2-}$/$ClO_2^-$ reaction occurred in the presence of dissolved oxygen. These results concur with those of Dixon and Lee (1991), who also noted significant $ClO_3^-$ formation. Griese et al. (1991) concluded that the application of sulfur-based reducing agents was not a viable strategy for $ClO_2^-$ removal during drinking water treatment. Griese et al. (1991) also evaluated sodium thiosulfate for $ClO_2^-$ removal and found that it effectively reduced $ClO_2^-$ over a pH range of 4.5 to 6.5. but the reaction was heavily dependent on pH and contact time. No significant $ClO_3^-$ was formed.

**Reduction by Granular Activated Carbon**

Voudrias et al. (1983) determined that chloride ion ($Cl^-$) was the predominant end product in a study in which a $ClO_2^-$ solution of 11 mg/L at pH 7 was passed through a granular activated carbon (GAC) column. During this study, the $ClO_2^-$ removal rate declined significantly after 80 to 90 mg $ClO_2^-$ per gram of carbon had been removed. They found that only 4 percent of the total Cl was not accounted for by $Cl^-$. In another experiment, the authors found that the GAC capacity for removing $ClO_2^-$ was reduced when a solution of $ClO_2^-$ and vanillic acid was passed through a GAC column. They hypothesized that GAC surface functional groups that otherwise would be available for reducing $ClO_2^-$ become unavailable when organic compounds are adsorbed, thus reducing the $ClO_2^-$ removal efficiency.

As part of a potable-water reuse study conducted by the Denver Water Department (Lohman and Rogers, 1987) $ClO_2^-$ removal by GAC was evaluated. Results from a column experiment indicated that complete $ClO_2^-$ reduction was achieved only when the GAC column loading rate was below 15 mL/min of up to 10 mg/L $ClO_2^-$. The authors concluded that at higher loading rates, the reaction time for complete $ClO_2^-$ removal was exceeded. They reported that 80 percent $ClO_2^-$ reduction was still achieved after 7,440 bed volumes had passed through the column (equivalent to six months full-scale operation). During plant-scale tests, complete $ClO_2^-$ reduction was achieved ($ClO_2$ applied dose 1.5 mg/L) with an empty bed contact time (EBCT) of 30 to 40 minutes (equivalent hydraulic loading rate of 4.7 gpm/sf). No apparent differences in the performance of virgin and reactivated carbon were noted. Lohman and Rogers (1987) cited a study by Lykins and DeMarco (1983) who reported a $ClO_2^-$ reduction of 67 percent with an EBCT of 7.7 (hydraulic loading rate 5.1

gpm/sf). Steinbergs (1986) reported $ClO_2^-$ reduction of approximately 85 percent with an EBCT of 6.4 minutes (hydraulic loading rate of 4.3 gpm/sf).

Dixon and Lee (1991) reported that EBCT significantly influenced $ClO_2^-$ removal by GAC. Longer EBCTs resulted in greater $ClO_2^-$ removal efficiency. The authors suggested that the increased contact time allows greater opportunity for $ClO_2^-$ to be reduced to $Cl^-$ at the GAC surface. The researchers also reported that the $ClO_2^-$ reacts with GAC by a dual mechanism**,** which appears to be an initial adsorption of $ClO_2^-$ onto active sites followed by reduction of $ClO_2^-$ to $Cl^-$ as those sites become unavailable. This theory was also proposed by Lohman and Rogers (1987). In their study $ClO_2^-$ was oxidized to $ClO_3^-$ by GAC when free chlorine was present in the applied water. They indicated that widely varying results regarding $ClO_2^-$ removal efficiency have been reported, and they attributed the variations in part to widely differing analytical techniques and differences in EBCT and loading rates in the various studies. Gallagher et al. (1994) also reported production of $ClO_3^-$ when water containing both $ClO_2^-$ and chlorine passed through a 55-inch GAC column; no $ClO_2^-$ remained in the treated water.

Vel Leitner et al. (1992) found that $ClO_2^-$ removal by GAC decreases as pH increases. They also reported that GAC type and dosage affected $ClO_2^-$ removal efficiency. The production of $ClO_3^-$ as an end-product was affected by influent $ClO_2^-$ concentrations, activated carbon concentrations and type, and pH. When low influent $ClO_2^-$ concentrations (< 50 mg/L) at pH 7, which are similar to water treatment plant conditions, were reacted with a large amount of GAC in a batch reactor, the major end product was $Cl^-$ (> 90 percent). Chlorate ion concentrations were below the detection limit.

The Gulf Coast Water Authority reported that a pilot GAC filter for $ClO_2^-$ removal was effective for only a short time, approximately 20,000 bed volumes. No chlorine was applied prior to the GAC filter, and ,therefore, the $ClO_3^-$ concentration remained unchanged through the filter (Thompson, 1993).

In summary, GAC appears to be only marginally effective for $ClO_2^-$ removal, and, therefore, prohibitively expensive if used only for that purpose. While some have found that $ClO_2^-$ removal by GAC was complete when the GAC influent contained chlorine, $ClO_3^-$ was formed, which is not desirable.

**Reduction by Powdered Activated Carbon**

Orr (1990) demonstrated that powdered activated carbon (PAC) was only marginally effective for $ClO_2^-$ removal. Only 35 to 50 percent of the $ClO_2^-$ in water containing 20 mg/L $ClO_2^-$ was removed during 30-minutes contact with 50 mg/L PAC, which is an extremely high dose for routine use during water treatment. Chlorate ion was present in the water at the end of the contact period, and the final pH was 5.5 to 6.0. The author attributed the $ClO_3^-$ formation to a sequence of reactions in which $ClO_2^-$ under acidic conditions (pH 5.5 to 6.0) forms $ClO_2$ and the $ClO_2$ subsequently oxidizes $ClO_2^-$ to $ClO_3^-$ (Masschelein, 1979). For reasons that could not be explained, $ClO_2^-$ reduction by PAC was slightly more effective when the PAC was enmeshed in alum floc. In a similar experiment, 1 mg/L $ClO_2^-$ was reduced by 78 percent in a solution contacted for four hours with 50 mg/L PAC enmeshed in alum floc. After further studies, the author determined that that $ClO_2^-$ removal by PAC occurred by second-order reaction kinetics.

In another experiment, Orr (1990) devised a bench-scale simulation of a floc-blanket clarifier in which high concentrations of PAC were enmeshed in floc and kept suspended in a constantly flowing stream of water containing 9.5 mg/L. Greater than 90 percent $ClO_2^-$ removal was achieved in this system over a period of 10 to 12 hours.

Grabeel (1992) evaluated the effects of pH on $ClO_2^-$ removal by Ceca 20B PAC. After a four-hour contact period, 20 mg/L PAC removed 67.1 percent of $ClO_2^-$ from a pH 5.5 solution of 5.56 mg/L $ClO_2^-$, while only 13.0 percent $ClO_2^-$ removal occurred in a pH 7.5 solution of 4.81 mg/L $ClO_2^-$. While $ClO_2^-$ removal was greater in the pH 5.5 solution, more $ClO_3^-$ was formed. Chlorate ion concentrations near 1.0 mg/L were observed when the initial $ClO_2^-$ dose was 5.0 mg/L. At pH 6.5 to 7.5, $ClO_3^-$ concentrations were below 0.05 mg/L. The carbon usage rate at pH 5.5 (187 mg $ClO_2^-$ removed/g PAC/4 hours) was much higher than that at pH 7.5 (31 mg $ClO_2^-$ removal/g PAC/4 hours). The author noted that the initial $ClO_2^-$ removal rate was rapid and then decreased significantly after two to four hours contact with PAC. The author believed that oxidation-reduction reactions were responsible for $ClO_2^-$ removal by PAC because in all but one experiment, $Cl^-$ accounted for 86 to 117 percent of the chlorine species at the end of the experiments**.**

Grabeel (1992) also compared $ClO_2^-$ removal by two types of PAC, one a wood-based carbon (Westvaco Nuchar SA PAC) and the other a bituminous coal based carbon (Ceca 20B PAC). After a four-hour contact period at pH 5.5, the wood-based carbon removed 28.3 percent of the $ClO_2^-$ and the bituminous coal carbon removed 67.1 percent. No $ClO_3^-$ was detected in the water treated with the wood-based carbon, but, as summarized above, it was present in water treated with the bituminous coal carbon. The carbon usage rate for the

wood-based carbon was much lower than that of the bituminous coal carbon (77 mg $ClO_2^-$ removed/g PAC/4 hours and 187 mg $ClO_2^-$ removal/g PAC/4 hours, respectively).

Grabeel (1992) also evaluated $ClO_2^-$ removal by PAC in a pilot-scale Superpulsator® (Infilco Degrémont, Richmond, Virginia) floc blanket clarifier that was treating water pretreated with $ClO_2$. Removals were lower than expected, ranging from approximately 27 percent when the PAC dose was 10 mg/L to 59 percent when the dose was 20 mg/L. She attributed the low removals to inconsistent PAC feed rates caused by periodic feed-pump failures that caused PAC concentrations in the floc blanket to vary widely.

Mitchell (1993) further investigated the $ClO_2^-$ -removal efficiency of 12 different PACs both in the presence and absence of chlorine. After a 15-minute reaction period four of the PACs reduced the $ClO_2^-$ concentration by more than 40 percent when chlorine was absent while five others reduced it by more than 40 percent in solutions containing chlorine. After a 60-minute reaction period with no chlorine present, all but one PAC reduced the $ClO_2^-$ concentration by 50 percent, and three PACs reduced it by 70 percent or more. Chlorine influence on $ClO_2^-$ removal was inconclusive in that several PACs removed more $ClO_2^-$when it was present, and several removed more when it was absent. The author found that little additional $ClO_2^-$ removal occurred after four hours contact with PAC. The author reported that "the extent of $ClO_2^-$ removal was not related to:

(a) The acid-extracted metal content (aluminum, boron, iron, magnesium, manganese, or zinc) or the total metal content,

(b) The percentage of PAC passing through a 325 mesh screen,

(c) The raw material from which the PAC was manufactured,

(d) The iodine index of the carbon; which is an indicator of the total surface area of the PAC, including the smallest passages,

(e) The BET surface area, a less accurate surface area measurement,

(f) The density of the powdered activated carbon."

The tests also showed that $ClO_3^-$ was not present at levels detectable by ion chromatography when chlorine was absent but always was present when the test medium contained chlorine. The author commented on the importance of pilot testing PACs for use in water treatment under the actual plant conditions, as various factors can contribute to PAC performance.

# CHAPTER III
# MATERIALS AND METHODS

## Reagents

The following ACS certified reagents were purchased from Fisher Scientific (Pittsburgh, PA): sodium carbonate anhydrous (CAS 497-19-8), potassium iodide (CAS 7681-11-0), phosphorus pentoxide (CAS 1314-56-3), and potassium persulfate (CAS 7727-21-1). Sodium chlorite (80 percent) (CAS 7758-19-2), sodium chlorate (99+ percent) (CAS 7775-09-9), lissamine green B (CAS 3087-16-9), and ethylenediamine (99.5+ percent) (CAS 107-15-3) were purchased from Aldrich (Milwaukee, WI). Ultrapure (99.7 percent) sodium chlorite purchased from Novatek (Oxford, OH) was used in chlorite standards for ion chromatography analysis.

All standard solutions were prepared in distilled, deionized water from either a Milli-Q ion exchange system (Millipore Corp., Milford, MA) or a Nanopure Ultrapure water system (Barnstead/Thermolyne, Dubuque, IA).

## Glassware

All glassware was soaked prior to use in 1:1 nitric acid overnight, then rinsed five times in deionized, distilled water and allowed to air dry. Pipettes were soaked in laboratory detergent, rinsed with nitric acid, then rinsed three times with distilled, deionized water and dried in a laboratory oven at 105°C.

All standard $ClO_2^-$ and $ClO_3^-$ solutions were prepared in volumetric flasks and covered with aluminum foil to prevent light catalyzed reactions.

## Collection of Samples for Ion Chromatography Analysis

Water samples collected for analysis at the Spring Hollow Water Treatment Plant in Roanoke County, Virginia, included raw water, clarifier effluent, filter effluent, effluent from the GAC contactors, and clearwell effluent. The samples were collected in clean, dark amber, 125-mL, Nalgene bottles after the plant was on-line for several hours. Sample lines were flushed for ten minutes, and the bottles were rinsed several times before the samples were collected. Samples were then purged of $ClO_2$ with nitrogen gas for at least ten minutes, then preserved with approximately 50 mg/L ethylenediamine to prevent reactions between chlorine and chlorite. Samples were then refrigerated until they were analyzed by ion chromatography within 18 days (Dietrich et al., 1992a).

## Ion Chromatography Method

Chlorite and chlorate were analyzed by ion chromatography (IC). The IC method was a modification of USEPA Method 300B (Pfaff et al., 1989), which requires $ClO_2^-$ samples to be analyzed immediately with no preservative. Research by Dietrich et al. (1992a) has shown that ethylenediamine can be added to the samples to increase the stability of $ClO_2^-$ to 18 days. A Dionex (Sunnyvale, CA) Ion Chromatograph 2010i module with a CDM3 conductivity detector and analytical gradient pump was used for all analyses. The ion chromatograph was equipped with an Ionpac AS9-HC analytical column and an Ionpac AG9-HC guard column. The operational parameters included:

Eluant - 9.0 mM sodium carbonate

Eluant Flow Rate - 1.0 mL/min

Sample Loop Volume - 100 μL

Suppression - Anion Self-Regenerating Suppressor II in the recycle mode

Detector Output Range - 3 microsiemans (μS)

The eluant was prepared fresh each time the analysis was performed and purged with helium for up to three hours prior to analysis to remove gases that might have obscured peaks of interest. The background conductivity was approximately 27 μS.

The samples were warmed to room temperature and all samples and standards were filtered through an in-line 0.45 μm filter before injection into the column. The retention times for $ClO_2^-$ and $ClO_3^-$ were approximately 5.2 minutes and 12.7 minutes, respectively. The retention times for fluoride, chloride, nitrite, nitrate, and sulfate ions were approximately 3.8, 6.9, 11.7, 13.9, and 20.4 minutes, respectively. The ion concentrations were quantified on the basis of either peak area calculated by an integrator (Hewlett Packard 3395 or 3396 Integrator) or manual peak height measurement.

Four standard solutions containing both $ClO_2^-$ and $ClO_3^-$ and two standard solutions containing only $ClO_2^-$ were analyzed, and a peak area or peak height versus concentration calibration curve was determined by linear regression. A small chloride ion peak occurred because this ion was a contaminant in the sodium chlorite used to prepare the standard. A standard curve was prepared each time an analysis was performed.

## Limits of Detection and Quantitation

The limits of detection (LOD) and quantitation (LOQ) for $ClO_2^-$ and $ClO_3^-$ by ion chromatography (IC) were determined. The LOD is the lowest concentration that can be confidently measured as different from zero, and the LOQ is the lowest concentration that can be measured accurately with confidence. The LODs were determined by EPA Method

600 (USEPA, 1982). Detection limits determined by the EPA method based on the variability of the measured concentrations of replicates of a low level standard.

A standard containing 0.02 mg/L of both $ClO_2^-$ and $ClO_3^-$ was analyzed 10 times, and the standard deviations of the mean ion concentrations were calculated. These standard deviations of the mean associated with each set of ion analyses were then multiplied by the Student's t-value that corresponded to the 99 percent confidence level. The LOQs were calculated by multiplying the LODs by five. The LODs and LOQs are shown below (Table 1) and the individual analyses are presented in Appendix Table A7.

Table 1

Chlorite Ion and Chlorate Ion Limits of Detection and Quantitation by Ion Chromatography

| Analyte | Analytical Method | Limit of Detection mg/L | Limit of Quantitation mg/L |
|---|---|---|---|
| Chlorite Ion | IC | 0.004 | 0.02 |
| Chlorate Ion | IC | 0.01 | 0.05 |

**Analytical Comparison with Independent Laboratory**

One quality assurance (QA) evaluation of the $ClO_2^-$ and $ClO_3^-$ IC analytical methods used at Virginia Tech laboratories was accomplished by splitting samples with an independent laboratory. Several field samples preserved with ethylenediamine were split into two aliquots. One was analyzed at Virginia Tech and the other at Novatek in Oxford, Ohio. Each lab used EPA method 300B, with the Dionex Ionpac AS9-HC analytical column and a Dionex Ionpac AG9-HC guard column. The two sets of analytical data were compared by a paired comparison t-test, and no significant differences were indicated at the 99 percent

confidence level. The individual data are presented in Appendix Table A8 and are shown graphically in Appendix Figures A1 and A2.

## Chlorine Dioxide Generation

Chlorine dioxide was generated by a method developed by Granstrom and Lee (1958). Novatek provided specific directions (Novatek, 1993). Chlorine dioxide generated by this method is highly concentrated and contains no chlorine, $ClO_2^-$, or $ClO_3^-$. The method involves reacting potassium persulfate (2 g dissolved in 50 mL distilled, deionized water) with sodium chlorite (4 g dissolved in 25 mL distilled, deionized water) in a gas train similar to the one shown in *Standard Methods for the Examination of Water and Wastewater,* (1995). The overall equation for the reaction is as follows (Granstrom and Lee, 1958):

$$2ClO_2^- + K_2S_2O_8 \rightarrow 2ClO_{2(g)} + 2K^+ + 2SO_4^{2-}$$

The reaction vessel and two $ClO_2$ traps were 250-mL glass gas-washing bottles. Each vessel was wrapped with aluminum foil to avoid photolytic decomposition of the generated oxidant. The two $ClO_2$ traps contained distilled water and were immersed in an ice bath to improve the trapping efficiency. The generated gas was purged from the reaction vessel with nitrogen gas for approximately 45 minutes and forced through the gas train into the cold traps. The final vessel in the gas train was a 1500-mL Erlenmeyer flask containing aqueous potassium iodide to reduce any $ClO_2$ that escaped the chilled traps. The generated $ClO_2$ solution was a bright yellow-green color and the concentration varied from 300 mg/L to 1000 mg/L.

A working $ClO_2$ solution containing approximately 50 mg/L was prepared from the concentrated stock solution by diluting it with distilled, deionized water. The $ClO_2$ concentration of the working solution was determined by UV spectrophotometry at 360 nanometers (nm). The spectrophotometer was zeroed with deionized water. The concentration was then calculated from Beer-Lambert's Law, as follows:

$$a = \in bc \qquad [1]$$

Where:

a = absorbance

$\in$ = $ClO_2$ extinction coefficient, 1225 $M^{-1}cm^{-1}$

b = cuvette path length

c = $ClO_2$ concentration, M.

The $ClO_2$ concentration was then expressed in mg/L by multiplying the molar concentration by 67,450 mg/L/mole.

## Lissamine Green B Method

Chlorine dioxide concentrations in water samples collected from within the treatment plant and distribution system were determined by the lissamine green B method, which was developed by Chiswell and O'Halloran (1991). Separate standard curves were developed for each water type (raw, clarified, and distribution system) because the background absorbances differed markedly. Approximately 1 L of each water was collected and purged for 25 minutes to remove any $ClO_2$ that may have been present. Lissamine green B (LGB) solution (5 mL) and pH 9 buffer (10 mL) were added to each of seven, 100-mL volumetric flasks. Each flask was filled nearly to the mark with purged sample water, then appropriate amounts

of the working $ClO_2$ standard were pipetted into each flask with the tip of the pipette being placed under the liquid surface to avoid losses of the extremely volatile $ClO_2$. The $ClO_2$ standards were placed in a 1cm quartz cuvette, and the absorbance of each determined spectrophotometrically at 614 nm. Purged samples containing no $ClO_2$ were used to zero the spectrophotometer each time a standard curve was prepared. The goal was to generate standard curves with linear regression correlation coefficients ($R^2$) of at least 0.999.

The standard curve developed with clarifier effluent was used during the analysis of filter effluent. Effluents from the GAC contactors and clearwell were analyzed for $ClO_2$ on several occasions, but none was found. All samples for analysis by LGB were collected head-space free in red glass bottles to prevent light-catalyzed decomposition reactions.

Chlorine dioxide concentrations in the distribution system were also determined by the LGB method. Once the sample water is mixed with the dye and buffer, the absorbance is stable for at least one hour, even in the presence of chlorine (Chiswell and O'Halloran, 1991), and the collection and analysis of samples from six sites in the distribution system could be completed within that time.

Buffer and lissamine green B were added to six 100-mL volumetric flasks in the laboratory and taken to the sampling sites. Six samples were usually collected during each sampling trip, but these were not always at the same locations. On some occasions, customers at previously sampled locations turned off their outside taps in preparation for freezing weather, and, in those instances, samples were collected from another location in the same neighborhood. Water from one of the sites was used in the preparation of the standard curve, and the absorbances of the field samples were determined immediately upon return to the laboratory. The spectrophotometer was zeroed with the distribution system water.

# Water Quality Impacts of Pure Chlorine Dioxide Pretreatment at the Roanoke County (Virginia) Water Treatment Plant

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## Introduction

Interest in chlorine dioxide ($ClO_2$) as an alternative to chlorine for oxidation and disinfection during water treatment has increased in recent years as utilities are required to meet increasingly stringent halogenated disinfection by-product (DBPs) regulations. It was first used in the 1940s by the City of Niagara Falls, New York, to control phenolic and chlorophenolic tastes and odors (Synan et al., 1944; McCarthy, 1944; Aston, 1947), though its value as a disinfectant was also recognized. Since 1970, most utilities apply $ClO_2$ as a

chlorine substitute at some point in their treatment process as part of their overall DBP control strategy (Dietrich et al., 1992b; Bissonette and Allegier, 1997).

Chlorine dioxide does not form halogenated organic by-products under typical water treatment conditions, but two important inorganic by-products, chlorite ion ($ClO_2^-$) and chlorate ion ($ClO_3^-$), are formed when $ClO_2$ is chemically reduced. Both of these by-products pose potential health risks.

Chlorate ion, once formed, cannot be removed by conventional water treatment techniques, but $ClO_2^-$ concentrations can be either reduced or eliminated by treatment with reduced-sulfur compounds, ferrous iron compounds, granular activated carbon (GAC), and powdered activated carbon (PAC).

In July, 1994, the United States Environmental Protection Agency (USEPA) proposed a maximum residual disinfectant level (MRDL) of 0.8 mg/L for $ClO_2$ and a maximum contaminant level (MCL) of 1.0 mg/L for $ClO_2^-$ in the Disinfectant/Disinfection By-Products (D/DBP) Rule (Federal Register, 1994). The Final D/DBP Rule, promulgated in December 1998, retained the proposed $ClO_2$ MRDL and $ClO_2^-$ MCL (Federal Register, 1998). No MCL for $ClO_3^-$ was proposed in the D/DBP Rule because health-effects data were not available at the time it was published.

The project described in this paper was designed to provide much-needed information regarding the fate of $ClO_2$ following its addition at a water treatment plant (WTP) and the development of by-products in the WTP and distribution system. Specific objectives were to: (1) document changes in $ClO_2$, $ClO_2^-$ and $ClO_3^-$ concentrations throughout the Roanoke County WTP and distribution system following $ClO_2$ pretreatment of raw water, (2) evaluate the effectiveness of GAC in post-filter contactors for $ClO_2^-$ removal, and (3) determine the

extent to which $ClO_2$ reforms in the distribution system following post chlorination of the treated water and the levels associated with customer complaints of odors.

**Roanoke County Treatment Plant and Spring Hollow Reservoir**

The Roanoke County, Virginia, Spring Hollow Water Treatment Plant, which was the site for this research, went on-line in January, 1996. The plant is a Trident® process plant, which consists of upflow adsorption clarifiers followed by trimedia filters (Figure 1). The coagulant is hydroxylated ferric sulfate, and the dosage requirements typically are quite low (5-10 mg/L) because the water quality is excellent throughout the year. The coagulant is added at a static mixer ahead of the clarifiers, and the dose is controlled by a streaming current monitor.

Following filtration, the water passes through two GAC contactors arranged in series, each containing approximately 70,000 pounds (31,818 kg) of 8 X 30 mesh GAC (Cetco-Aquatec) to an individual depth of 42 inches. The approximate empty bed contact times (EBCTs) were 26 and 13 minutes at treatment rates of 5 and 10 million gallons per day (mgd), respectively. Chlorine and fluoride are added to the GAC-treated water prior to its storage in a 2 million gallon clearwell.

The plant serves approximately 36,000 customers with 8,850 connections. The daily demand during the period of this study was 2 to 3 mgd. The plant capacity is 15 mgd at the present filtration rate. The plant only operates 8 hours each day in order to fill storage tanks in the distribution system and the clearwell. The operators typically run one unit for the entire eight-hour period and bring a second unit on-line for part of the day. The plant is shut down at the end of the single, eight-hour shift.

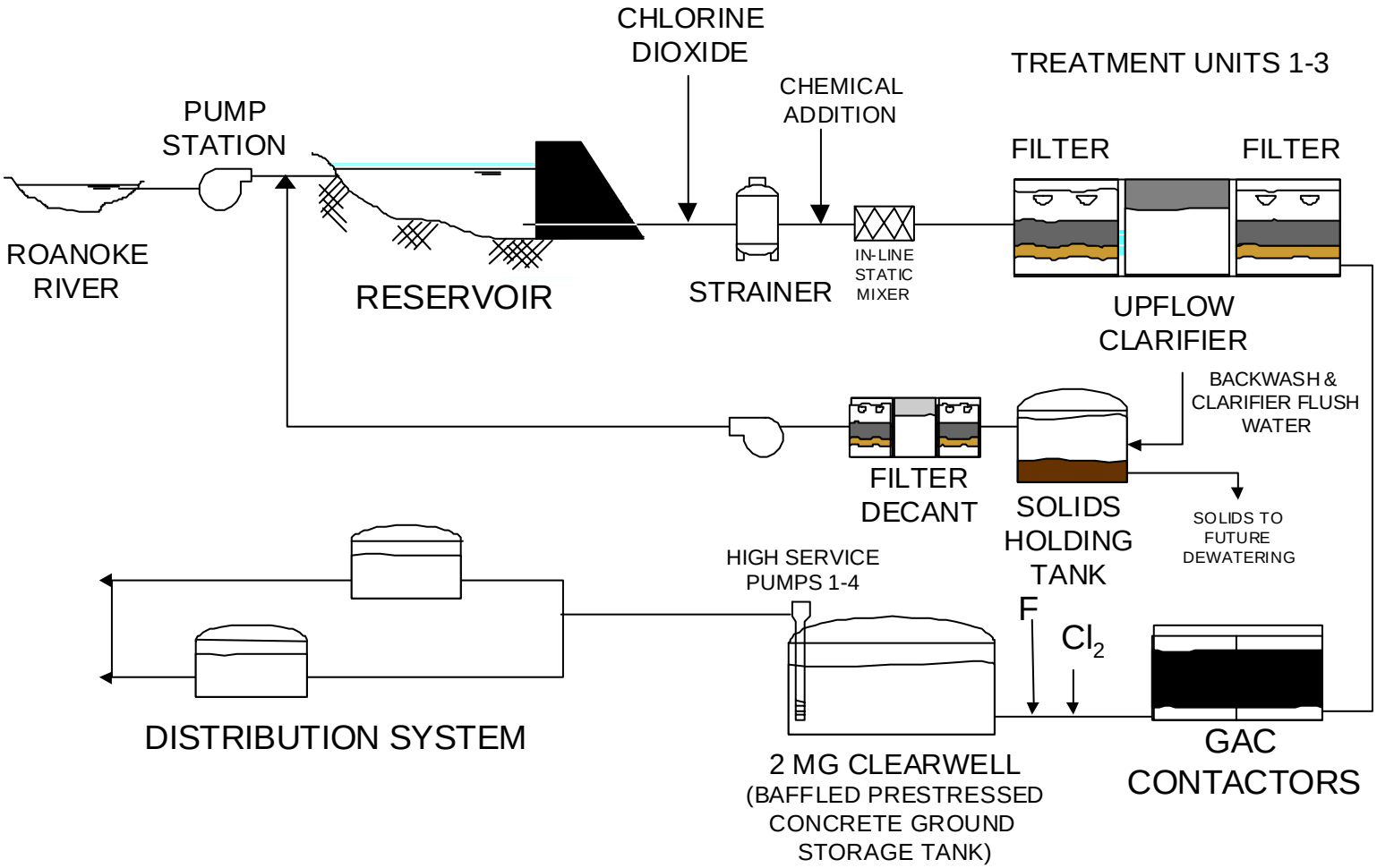


Figure 1. Roanoke County Spring Hollow Water Treatment Plant

The plant's raw water source is the Spring Hollow Reservoir, which is a pump storage reservoir, was completed in 1995 and continued filling throughout 1996. Water is pumped from the Roanoke River to the Reservoir during high-flow periods. The full-pool elevation is 1410 feet (ft) mean sea level (msl), and the maximum depth at the dam is 240 ft. When full, the reservoir impounds 3.2 billion gallons.

Four raw-water intakes are located at elevations 1374 ft, 1344 ft, 1300 ft, and 1220 ft msl, and raw water flows by gravity to the treatment plant through a 36-inch main. The raw water quality is excellent (Table 1). Roanoke County owns a well system and also buys water from the cities of Roanoke and Salem, but the reservoir will eventually be the main drinking water source.

Chlorine dioxide was included in the design of the Spring Hollow Water Treatment Plant as added insurance against problems with manganese, tastes and odors, and disinfection by-products should they ever arise. In the early stages of this project, manganese levels were at times elevated, but they were low during most of the study period because the reservoir thermally destratified in November and became uniformly aerobic from surface to bottom, preventing the release of manganese from the bottom sediments.

**Table 1. Spring Hollow Reservoir Raw Water Characteristics**

| Characteristic | Average | Range |
|---|---|---|
| Turbidity, ntu | 2.9 | 1.6-5.6 |
| Total Organic Carbon, mg/L | 1.9 | 1.7-2.1 |
| Alkalinity, mg $CaCO_3$/L | 132 | 120-143 |
| Hardness, mg $CaCO_3$/L | 150 | 140-166 |
| pH | 7.5 | 7.2-7.8 |

**Chlorine Dioxide Generation**

The $ClO_2$ generator (Figure 2) generates ClO2 by reaction of solid sodium chlorite ($NaClO_2$) with chlorine gas according to equation [1]:

$$2\,NaClO_2 + Cl_{2(g)} \rightarrow 2ClO_{2(g)} + 2NaCl \quad \text{.....[1]}$$

Chlorine gas is first mixed with humidified air and then passed through two drums containing solid $NaClO_2$ in series. The $ClO_2$ production rate is a function solely of the chlorine gas feed rate. Infinite turndown without recalibration is possible, thus making possible the delivery of $ClO_2$ dosages over a wide range. No unreacted $NaClO_2$ enters the system because the generated $ClO_2$ is in the gas phase, and $ClO_3^-$ is not produced. This project was the first full-scale application of the CDG Technology, Inc. process, and the County chose the equipment because it was simple to operate and could reliably provide $ClO_2$ dosages over a wide range.

The generated $ClO_2$ is injected into a raw-water side stream off the 36-inch raw-water main through an ejector, which is a Venturi tube that creates a vacuum in the generator. The side stream then passes through a contactor, which consists of a network of pipes, to ensure thorough mixing, then through an air break to release any air that accumulates in the pipe, and, finally, back to the entrance to the 36-inch main near the Roanoke River approximately 400 ft below the treatment plant.

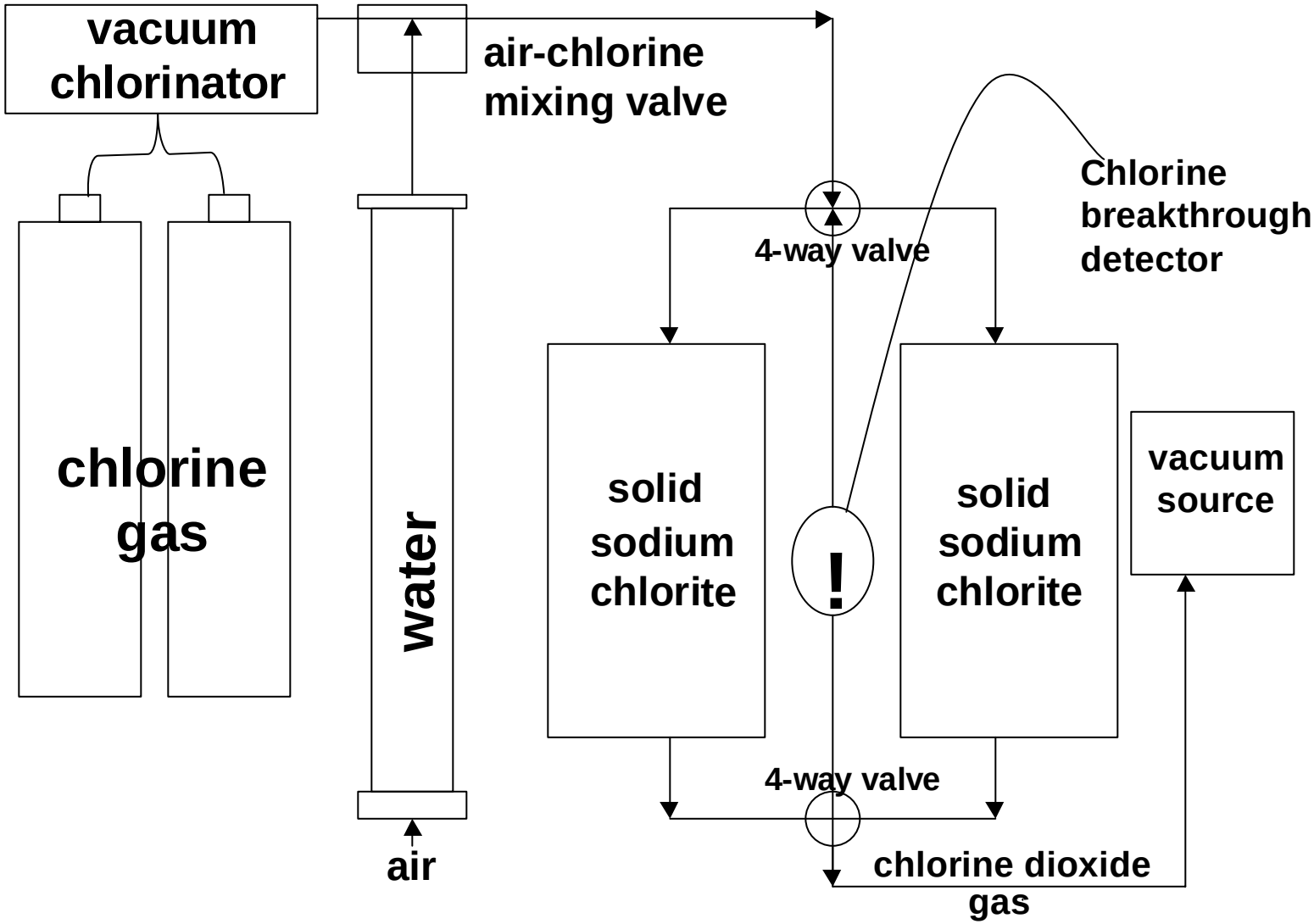


Figure 2. Schematic: full-scale *gas:solid*™ chlorine dioxide generator

## Experimental Methods

### Sample Collection and Preservation Methods

During the study, water samples were collected in acid-washed Nalgene bottles from a variety of locations within the treatment plant and distribution system for analyses of $ClO_2$ and its by-products. Samples were collected within the treatment plant two to four hours after plant startup to ensure that equilibrium had been reached.

Sampling locations included: (1) raw water following $ClO_2$ addition but before coagulant addition, (2) clarifier effluent (filter-applied), (3) filter effluent, (4) post-filter GAC contactor effluent, and (5) clearwell effluent. Sample lines were flushed for approximately ten minutes, and sample bottles were rinsed several times before the samples were collected. The samples were immediately purged with nitrogen gas for at least ten minutes to remove $ClO_2$, then preserved with ethylenediamine (approximately 50 mg/L) to prevent reactions between chlorine and $ClO_2^-$ (Dietrich et al., 1992a). Samples were then refrigerated until they could be analyzed.

### Chlorite and Chlorate Ion Analyses

Chlorite and chlorate were analyzed by ion chromatography (IC). The IC method was a modification of USEPA Method 300B (Pfaff et al., 1989), which requires $ClO_2^-$ samples to be analyzed immediately with no preservative. Research by Dietrich et al. (1992a) has shown that a ethylenediamine can be added to the samples to increase the stability of $ClO_2^-$ to 18 days. A Dionex (Sunnyvale, CA) Ion Chromatograph 2010i module equipped with a CDM3 conductivity detector, analytical gradient pump, Ionpac AS9-HC analytical column, and an Ionpac AG9-HC guard column. The eluant was 9.0 mM sodium carbonate dispensed at a flow rate of 1.0 mL/min and the sample loop volume was 100 mL.

Suppression was achieved with an Anion Self-regenerating Suppressor II in the recycle mode, and the detector output range was 3 microsiemans (μS). Fresh eluant was prepared each day the analyses were performed and purged with helium for up to three hours before use to remove gases that might obscure peaks of interest. The background conductivity was approximately 27 μS.

Samples were warmed to room temperature before analysis and all samples and standards were filtered through an in-line 0.45 μm filter before they were injected into the column. The retention times for $ClO_2^-$ and $ClO_3^-$ were approximately 5.2 minutes and 12.7 minutes, respectively. Concentrations were quantified either by integrated peak areas (Hewlett Packard 3395 or 3396 Integrator) or by manual peak-height measurement. Four standard solutions containing both $ClO_2^-$ and $ClO_3^-$ and two standard solutions containing only $ClO_2^-$ were analyzed. Calibration curves relating either peak area or peak height to analyte concentration by linear regression were developed after each analytical session. The $ClO_2^-$ and $ClO_3^-$ limits of detection (LOD), which were 0.004 mg/L and 0.01 mg/L, respectively; were determined according to EPA Method 600 (USEPA, 1982).

**Laboratory-Scale Chlorine Dioxide Generation and Solution Standardization**

High-purity $ClO_2$ solutions (i.e., no chlorine, $ClO_2^-$, or $ClO_3^-$) for use in developing standard curves were prepared by reacting 50 mL of two percent potassium persulfate with 25 mL of 16 percent $NaClO_2$ (Granstrom and Lee, 1958; Novatek, 1997). The generator consisted of three gas-washing bottles connected in series. The reactant solutions were mixed in the first bottle, and the generated $ClO_2$ was purged from the reaction mixture for approximately 45 minutes by a gentle flow of nitrogen gas through the second vessel, which was empty, and into the third vessel, which contained distilled water immersed in an ice bath.

Undissolved $ClO_2$ from the collection vessel was trapped in a flask containing a strong potassium iodide solution. Generated $ClO_2$ solutions contained from 300 mg/L to 1000 mg/L $ClO_2$, the lower concentrations resulting when the system was purged for too long a period. These solutions were stored in the refrigerator at 4°C when not in use.

Working solutions containing approximately 50 mg/L $ClO_2$ were prepared each day from the concentrated stock solutions and standardized by ultraviolet absorbance at 360 nanometers (nm) in a quartz cuvette. The instrument was zeroed with distilled, deionized water, and the working-standard concentration was determined by the Beer-Lambert Law as follows:

$$a = \in b\, c$$

Where:

a = absorbance

$\in$ = $ClO_2$ extinction coefficient, 1225 $M^{-1}cm^{-1}$;

b = cuvette path length

c = $ClO_2$ concentration, M

**Chlorine Dioxide Analysis by the Lissamine Green B Spectrophotometric Method**

Chlorine dioxide concentrations were determined by the lissamine green B method (Chiswell and O'Halloran, 1991). The value of this test lies in its sensitivity at low $ClO_2$ concentrations and the lack of interference by both chlorine and chloramines. Separate standard curves were prepared for analyses of raw water, clarifier effluent, and distribution-system samples collected in red glass containers (to prevent light catalysis of $ClO_2$) at several points. The distribution-system sampling sites were selected to provide a variety of hydraulic residence times.

The standard curves were prepared daily by adding varying amounts of standardized $ClO_2$ solution to approximately 25-30 mL of nitrogen-purged sample (to remove any $ClO_2$ that might be present) in 100-mL volumetric flasks. Lissamine green B solution (5 mL) and pH 9 buffer (10 mL) were then added to each flask and diluted with the purged sample to a final volume of 100 mL. Reagents were added at the same time to an unpurged sample for determination of the sample $ClO_2$ concentration. The absorbances of samples and standards were determined spectrophotometrically at 614 nm, and the purged sample was used as the instrument zero.

Chlorine dioxide concentrations at multiple points in the distribution system were determined on several occasions. Because the buffered lissamine green solution is stable in samples for at least an hour (Chiswell and O'Halloran, 1991), six samples could be collected, returned to the laboratory, and analyzed within the time limit. To facilitate the analysis, samples collected at the various sites were placed directly in volumetric flasks that already contained LGB and buffer. Samples were left at ambient temperature to avoid having to warm them prior to analysis. Each time system $ClO_2$ concentrations were determined, the standard curve was prepared anew in nitrogen-purged water from one of the sites, and the sample was used as the instrument zero.

## Results

### Treatment Plant $ClO_2$, $ClO_2^-$ and $ClO_3^-$ Profiles

Figure 3 shows the $ClO_2$ concentrations at various points within the treatment plant from November 24, 1997, through February 5, 1998 (total residence time through the filters: approximately 35 minutes at design flow). During this period, dosages were low, ranging from none when the generator was inoperative to 0.42 mg/L, and quite variable. Raw-water

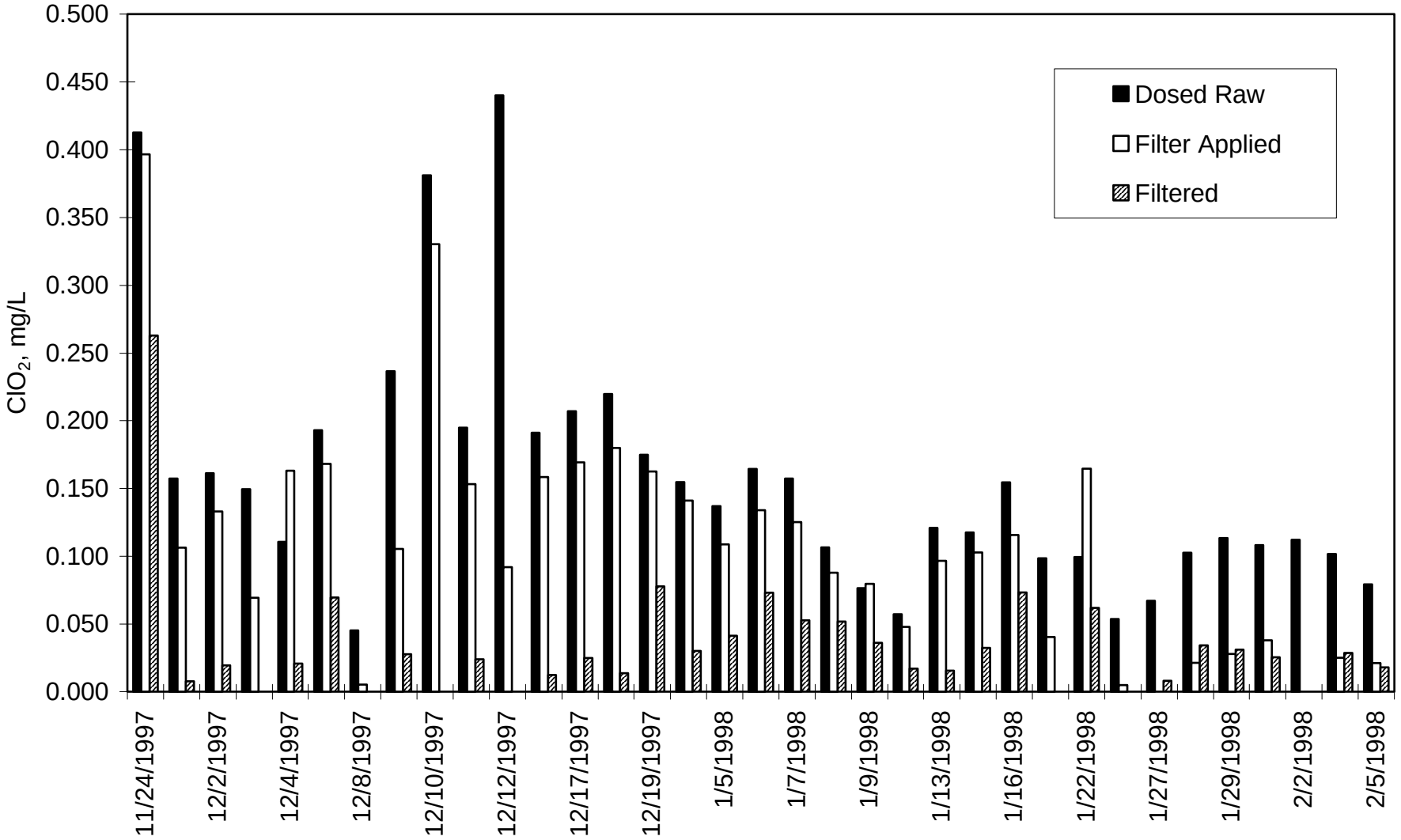


Figure 3. Chlorine dioxide concentrations throughout the treatment plant, November 24, 1997, through February 5, 1998

concentrations were determined less than five minutes after $ClO_2$ was added. In general, the reservoir water $ClO_2$ demand was slowly exerted, and $ClO_2$ persisted through the clarifiers and, on a few occasions, through the filters.

Figures 4 and 5 are box plots that show, respectively, the distributions of $ClO_2^-$ and $ClO_3^-$ concentrations throughout the treatment plant and in the clearwell from September 9, 1997, through February 10, 1998. Figure 6 shows the $ClO_2$ dosages, which ranged from none when the generator was not operating, to 0.96 mg/L (average 0.39 mg/L), throughout the same period.

Box plots were chosen for displaying the data because they provide information regarding the range and variability of the data. The interpretation of these plots, according to Gallagher et al. (1994), is as follows:

> "*Eighty percent of the concentrations fall in the range between the upper and lower tails that appear outside the boxes. Thus, 10 percent of the data fall below the lower tail ($Q_{10}$) and 90 percent fall below the upper tail ($Q_{90}$). The circles below or above each of the tails correspond to individual data points called outliers. The lower and upper lines composing the box are, respectively, the upper limits of the first and third quartiles of the data ($Q_{25}$ and $Q_{75}$,*
>
> *respectively), and the line inside the box shows the upper limit of the second quartile ($Q_{50}$) and denotes the median value."*

Bonferoni corrected paired comparison t-tests ($\alpha$ = 0 .0125) were used to evaluate whether or not the day-to-day $ClO_2^-$ and $ClO_3^-$ concentrations at successive points in the treatment train differed significantly. For the paired comparison t-tests, data was used only

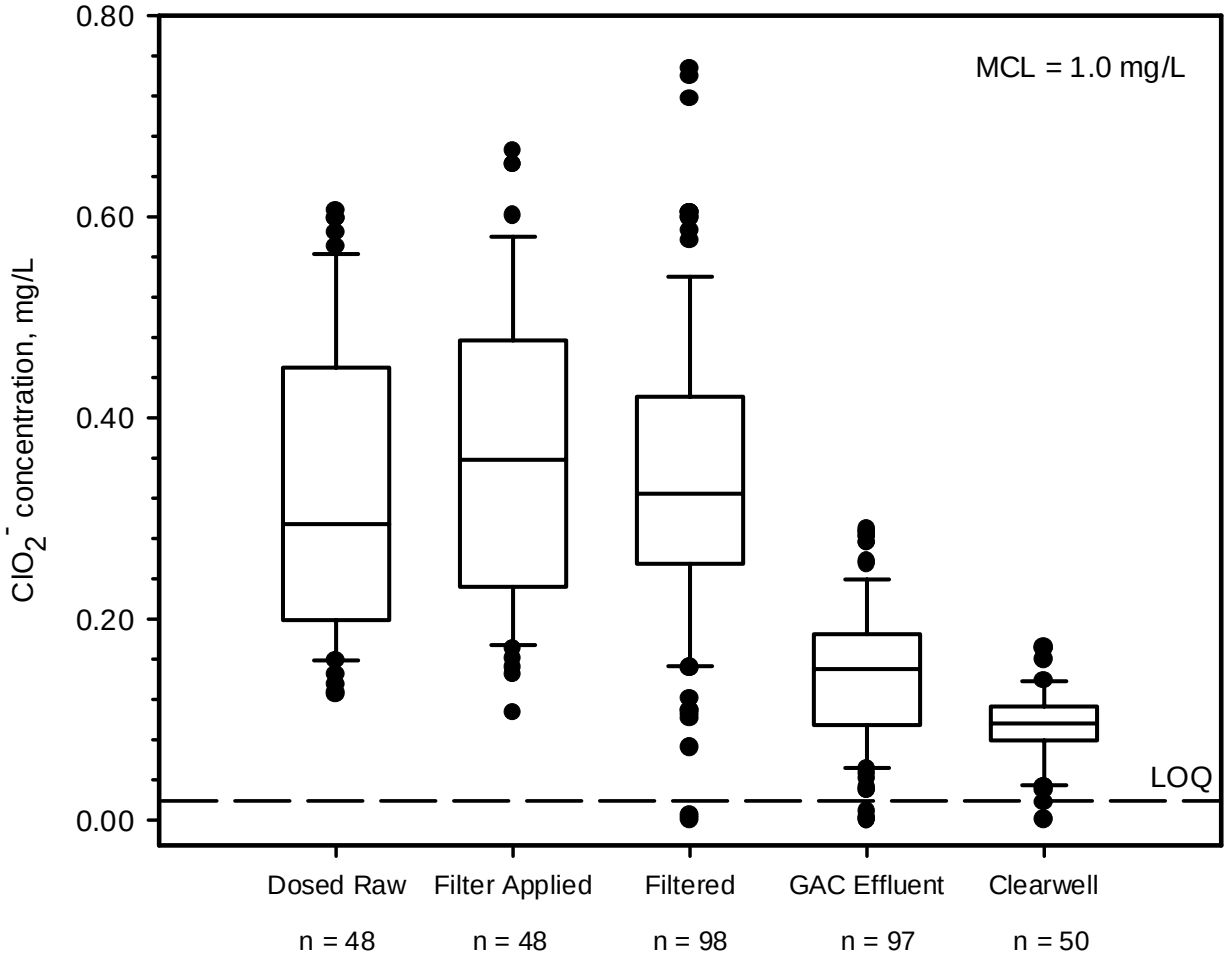


Figure 4. Variations in chlorite ion concentrations through the treatment plant, September 9, 1997, through February 10, 1998: Chlorine dioxide dosage over the period varied from 0 to 0.96 mg/L

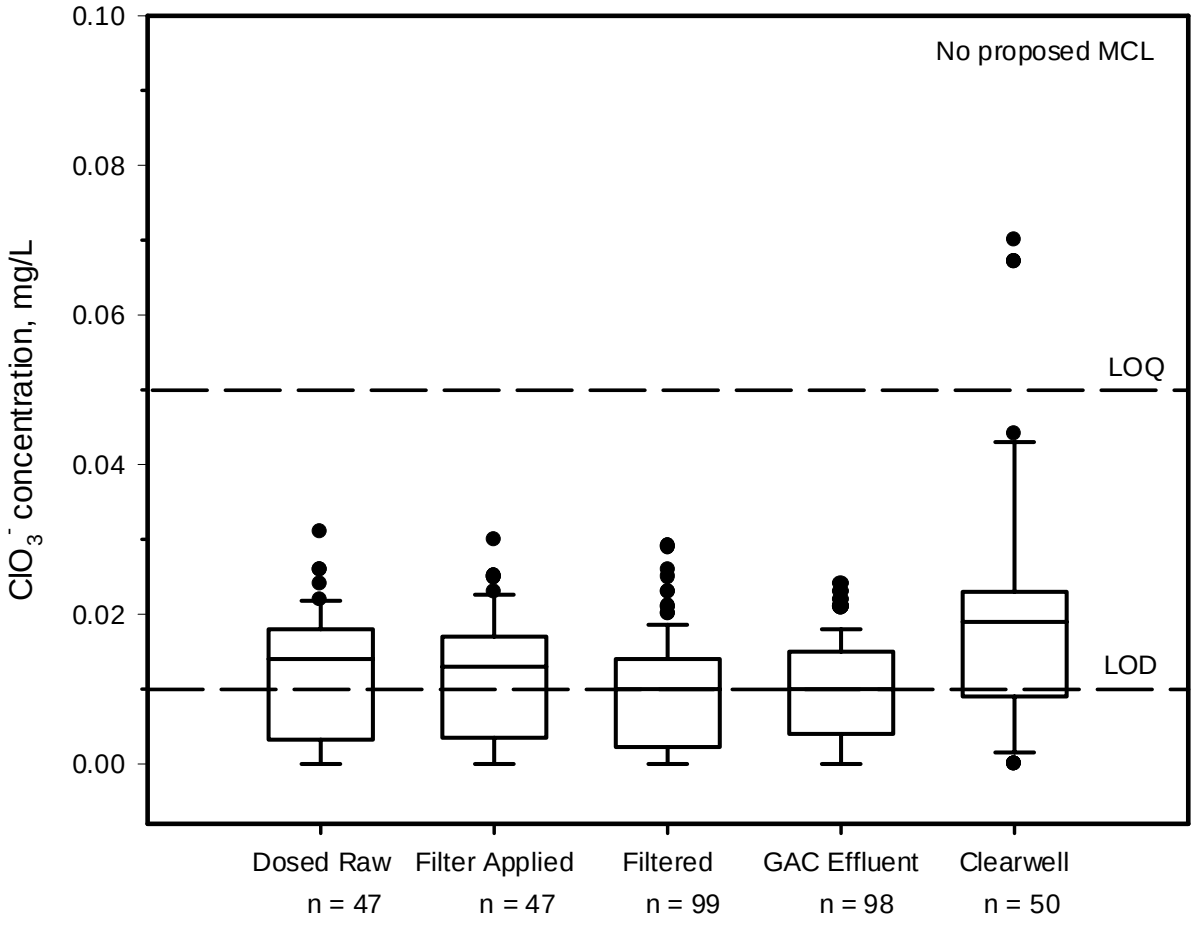


Figure 5. Variations in chlorate ion concentrations through the treatment plant, September 9, 1997, through February 10, 1998: Chlorine dioxide dosage over the period varied from 0 to 0.96 mg/L.

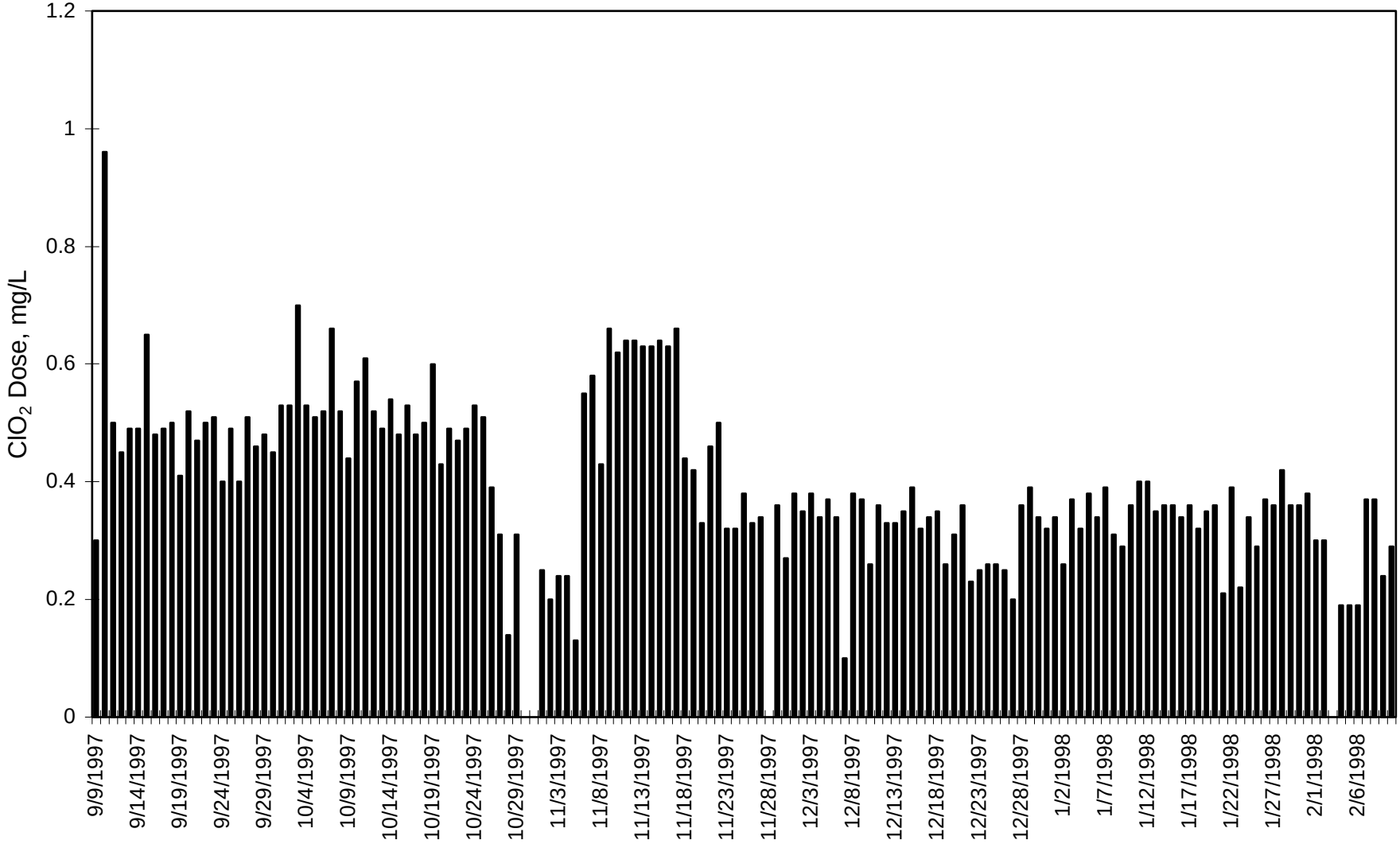


Figure 6. Chlorine dioxide dosages throughout the study period
(Note: 0 mg/L dose indicates that $ClO_2$ generator was off)

from days when there were samples collected at each of the two locations being compared. The box plots present a summary of all the data collected at each successive location in the treatment train. The results showed that $ClO_2^-$ concentrations in $ClO_2$ - treated raw water were significantly less than those in clarifier effluent (filter-applied water)but not significantly less than those in filtered water. Mean concentrations in raw water and clarifier effluent were 0.328 mg/L and 0.367 mg/L, respectively.

Figure 4 also shows a marked $ClO_2^-$ reduction when filtered water passed through the GAC contactors. Concentrations in water exiting the contactors (GAC effluent) were significantly lower than those entering the contactors (shown as "filtered" in Figure 4). Mean concentrations entering and leaving the contactors were 0.337 and 0.146 mg/L, respectively, over the course of the study.

The paired comparison t-test also showed that the GAC effluent $ClO_2^-$ concentrations were significantly greater than the $ClO_2^-$ concentrations in chlorinated water leaving the treatment plant ("clearwell" in Figure 4). The mean $ClO_2^-$ concentration in water leaving the clearwell was 0.092 mg/L, and concentrations ranged from less than the detection limit to 0.172 mg/L.

Chlorate ion concentrations remained quite low throughout the treatment process and were almost always less than quantitation limit (Figure 5). The $ClO_3^-$ concentrations following post chlorination were statistically greater than those in the GAC effluent, even though the mean concentrations (0.02 mg/L and 0.01 mg/L, respectively) were quite low. The $ClO_3^-$ concentrations in the clearwell ranged from less than the detection limit (0.01 mg/L) to 0.07 mg/L.

**Chlorite Ion Removal by GAC Filtration**

Figure 7 shows the relationship between the GAC influent $ClO_2^-$ concentrations and $ClO_2^-$ removal by the GAC contactor over the entire study period. The slope of the regression line (0.63) represents the overall average $ClO_2^-$ removal achieved by the contactor expressed as a fraction of the influent concentration. Removals during the period ranged from 10 percent to 100 percent.

Figure 8 shows in bar-graph form the $ClO_2^-$ concentrations in GAC influent and effluent during the entire study period. The effluent concentrations ranged from less than detection (0.004 mg/L) to 0.300 mg/L (average 0.146 mg/L and median 0.150 mg/L). The applied $ClO_2$ dosages during the study are indicated along the top of the figure, and the individual bar heights correspond to the individual concentrations in the GAC influent and effluent. The bars are not stacked.

The carbon usage rate (g $ClO_2^-$ removed per kg GAC in the two contactors) is shown in Figure 9 as a function of the total water volume treated at various times during the study period. Figure 10 shows the cumulative usage rates over the study period. Both figures indicate that the usage rate was declining steadily.

**Distribution System Levels of $ClO_2$ and Its By-products**

Figure 11 shows locations in the distribution system where samples were collected for analyses of $ClO_2$, $ClO_2^-$, and $ClO_3^-$. The average $ClO_2$ concentrations are listed next to each point. Use of the lissamine green B test made detection of small concentrations possible, even when the samples contained chlorine.

Figure 12 shows the distribution system $ClO_2^-$ concentrations, which ranged from less than the detection limit (0.004 mg/L) to 0.125 mg/L (average and median concentrations:

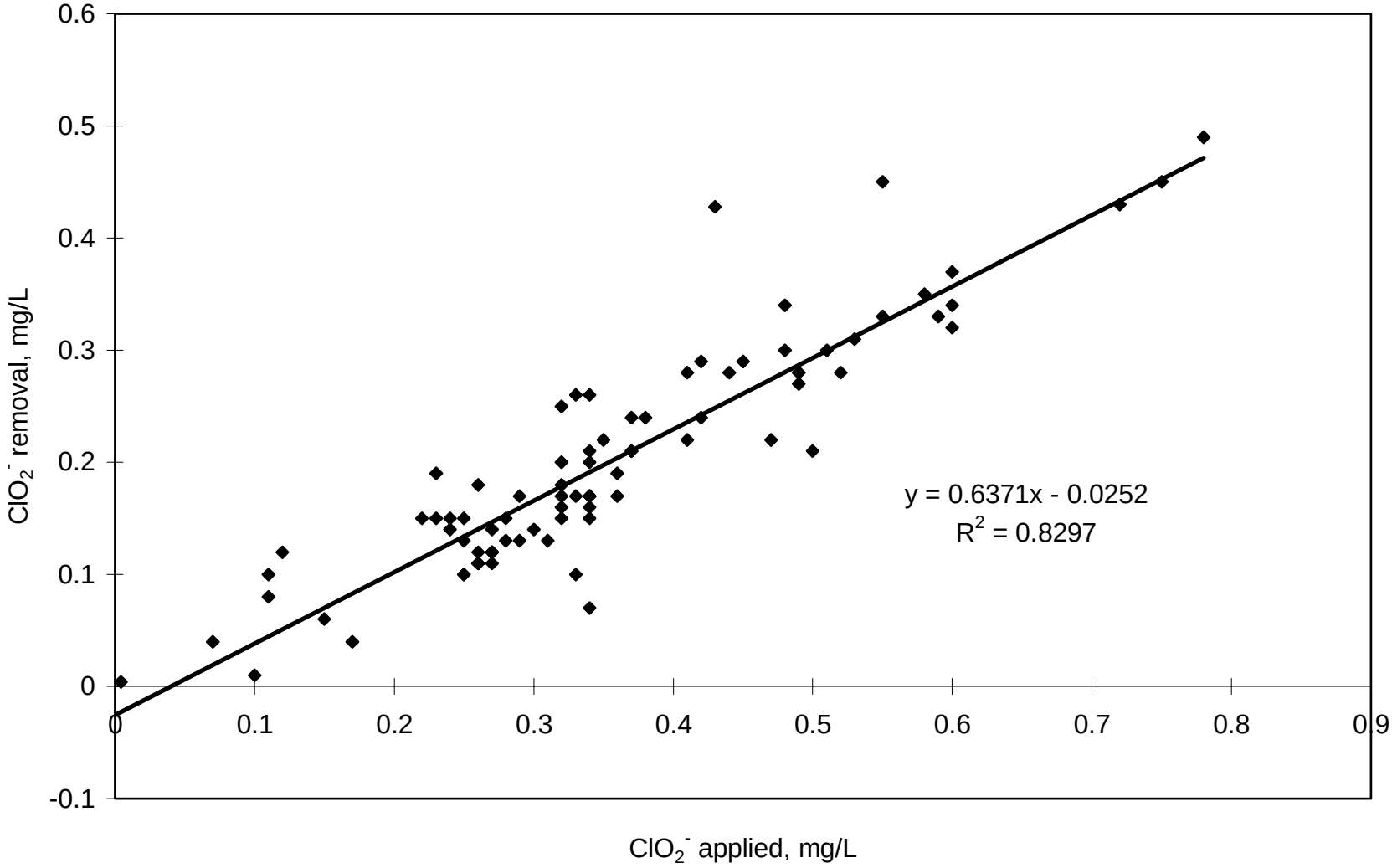


Figure 7. Chlorite ion removal by GAC contactors as a function of the applied concentration.

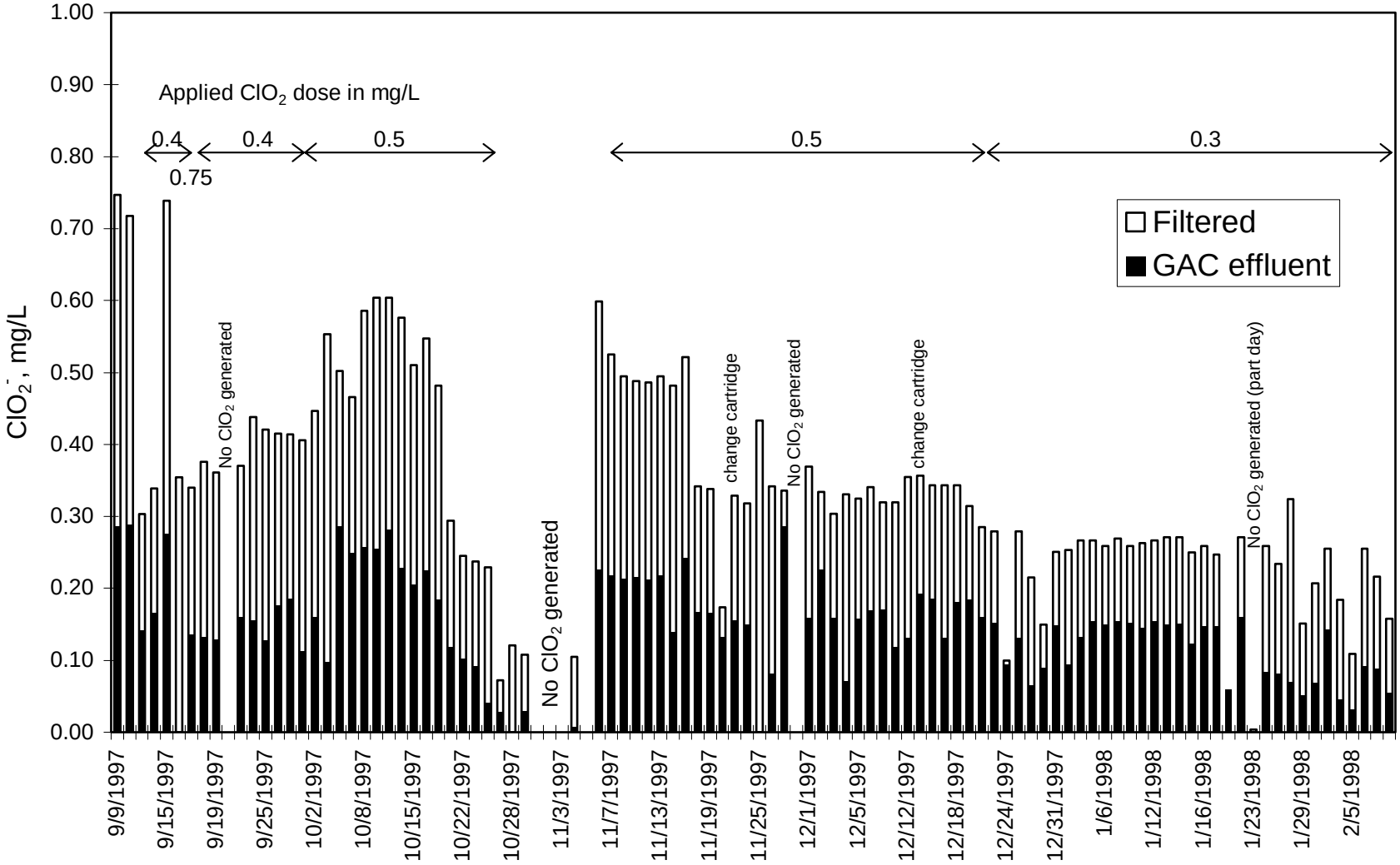


Figure 8. Comparison of GAC influent and effluent chlorite ion concentrations during the period of study.

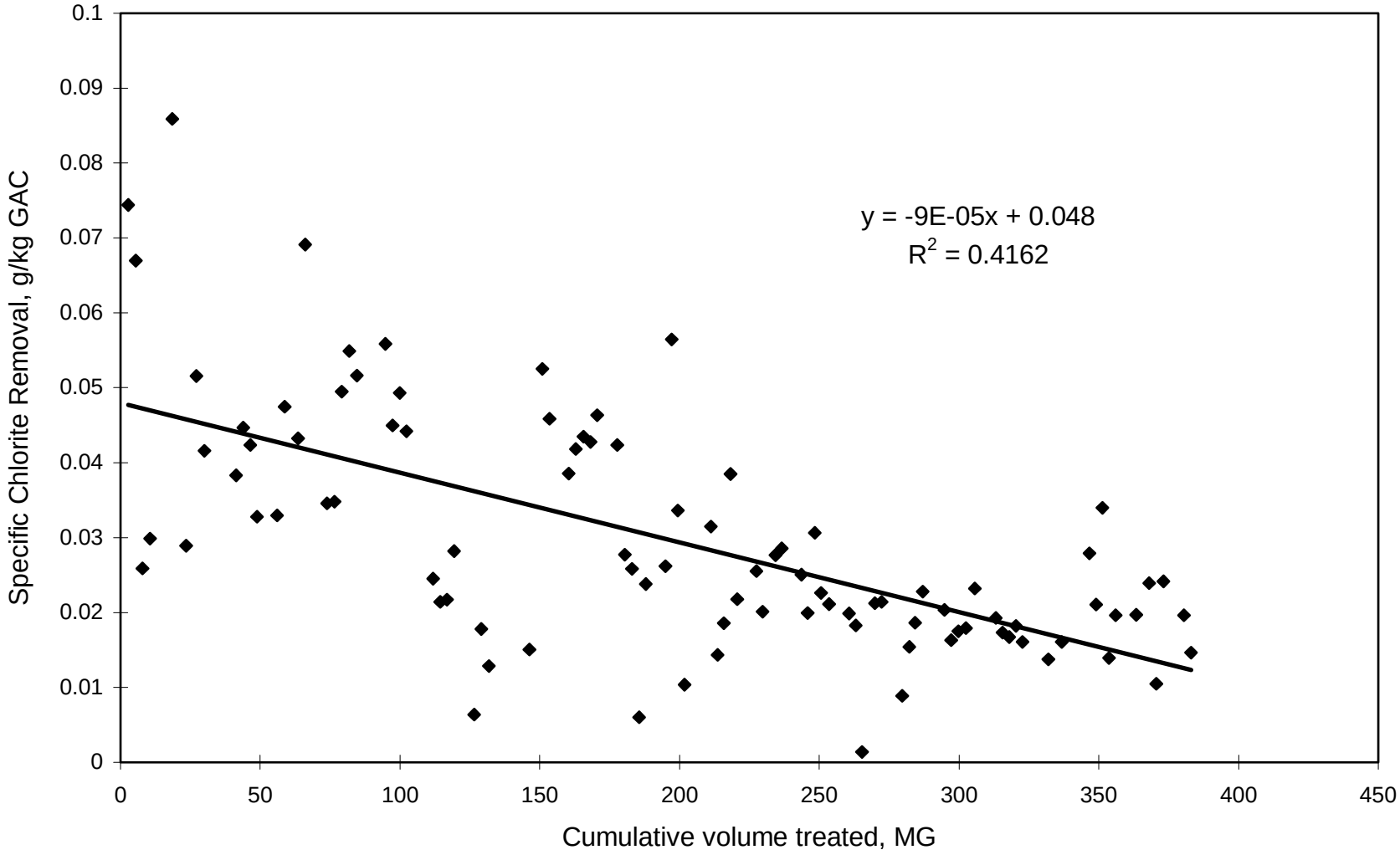


Figure 9. GAC usage rate over period of study (September 9, 1997 - February 10, 1998)

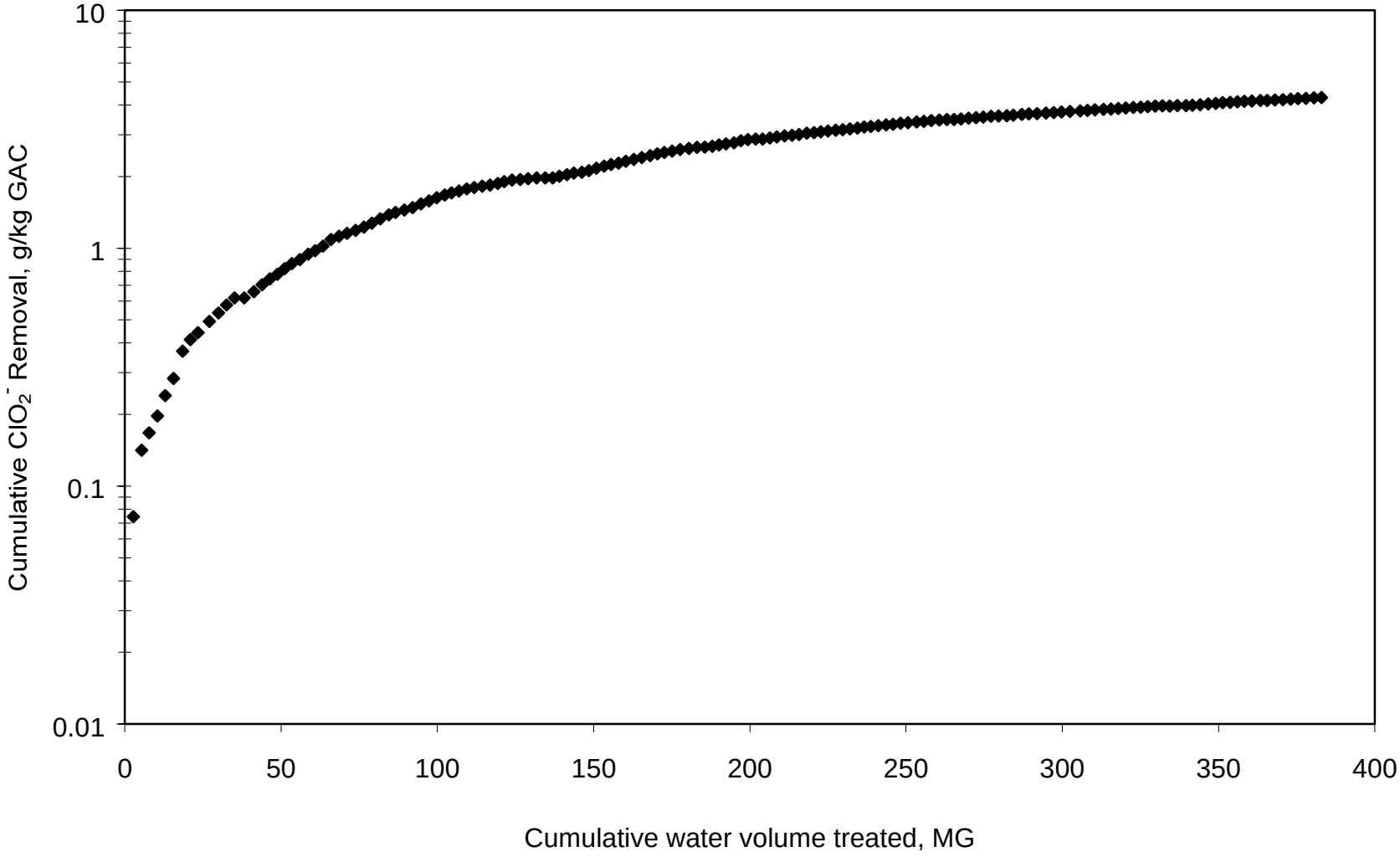


Figure 10. Cumulative chlorite removal over period of the study (September 9, 1997 - February 10, 1998)

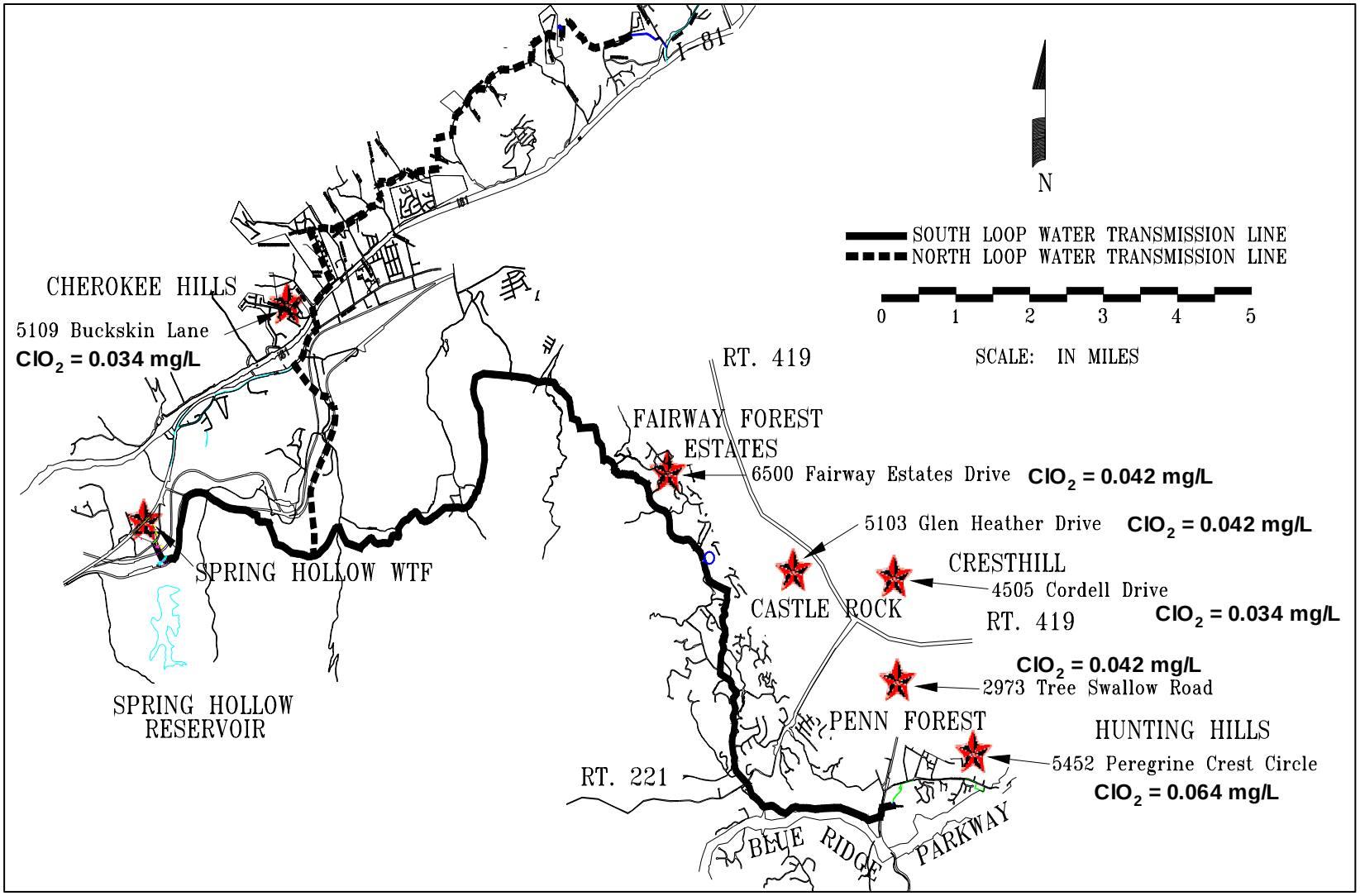


Figure 11. Roanoke County Water Distribution System

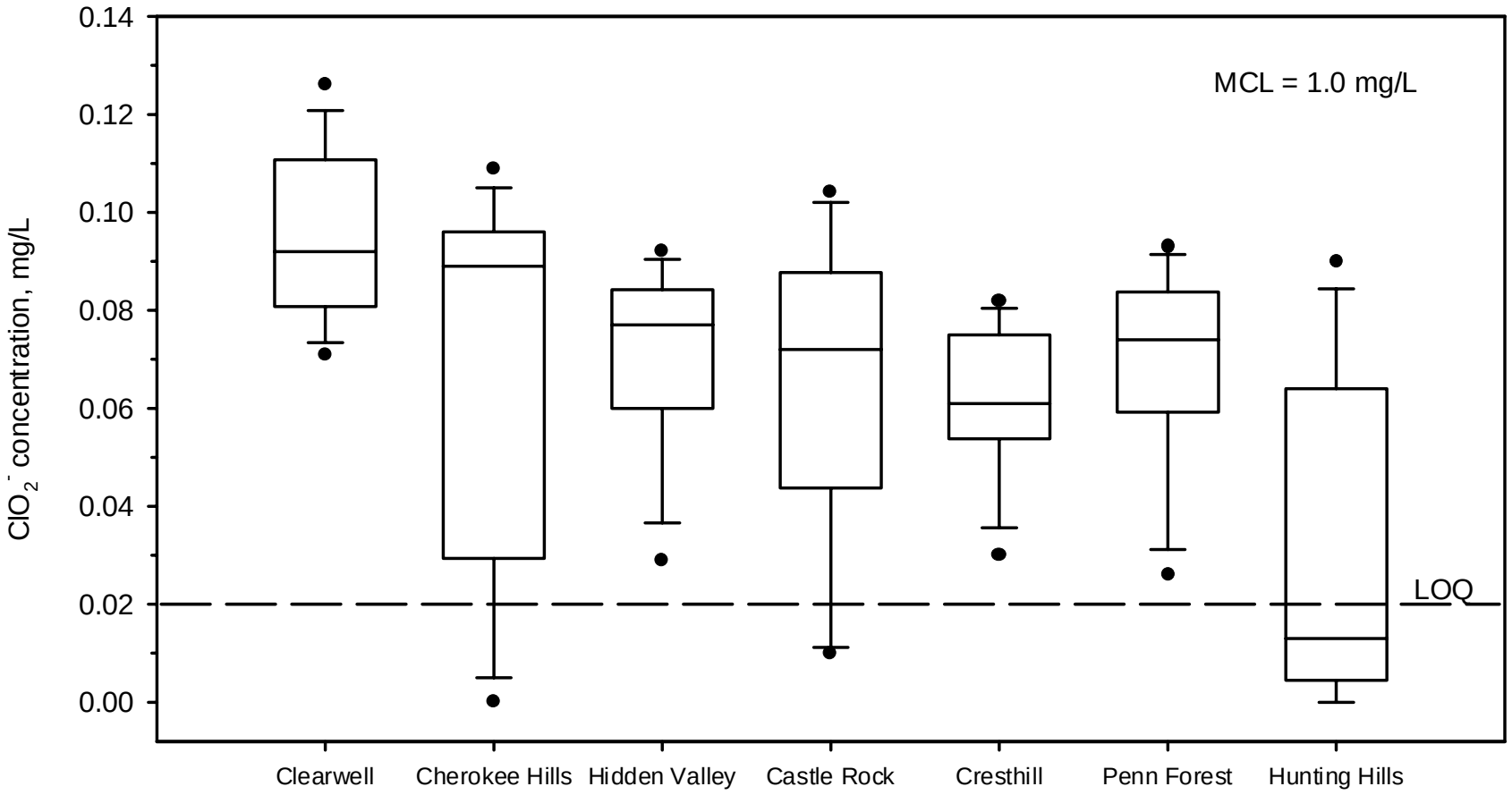


Figure 12. Comparison of chlorite concentrations in the Roanoke County clearwell and distribution system (n = 9). Sites are arranged (left to right) in order of increasing distance from the water treatment plant.

0.060 and 0.066 mg/L, respectively). Clearwell concentrations were compared one-by-one with concentrations at each of the distribution system sites with the paired comparison t-test. While the concentrations at the distribution system sites were significantly lower than the clearwell concentrations at all sites except the one nearest the treatment plant (Cherokee Hills), one cannot conclude that $ClO_2^-$ decreased with increasing distance from the plant because the concentrations at the nearest site (Cherokee Hills) were not significantly greater than those at the farthest site (Hunting Hills). The reason they are not statistically different is probably because the distributions of data collected at the two sites differ markedly, and the median $ClO_2^-$ concentration at the farthest site was well below the medians at the other sites. As can be seen in Figure 12, the data distributions at the other sites were more symmetrically distributed around the median.

Figure 13 shows the distribution system $ClO_3^-$ concentrations, which ranged from 0.01 mg/L to 0.09 mg/L, and averaged 0.03 mg/L (median 0.03 mg/L). The concentrations were uniformly low throughout the distribution system and usually below the quantitation limit (0.05 mg/L). While it is difficult to say with certainty that they increased with increasing distance from the plant, the concentrations at Castle Rock, Cresthill, and Penn Forest were significantly greater than those in the clearwell effluent when tested by the paired comparison t-test, but concentrations at the other three locations were not statistically different than those in the clearwell effluent.

Figure 14 shows the $ClO_2$ concentrations at several distribution system locations on nine occasions. Concentrations at the farthest site (Hunting Hills) were significantly greater than those at the nearest site (Cherokee Hills) when tested by the paired comparison t-test but not at any other site. Concentrations during the nine sampling events ranged from less than

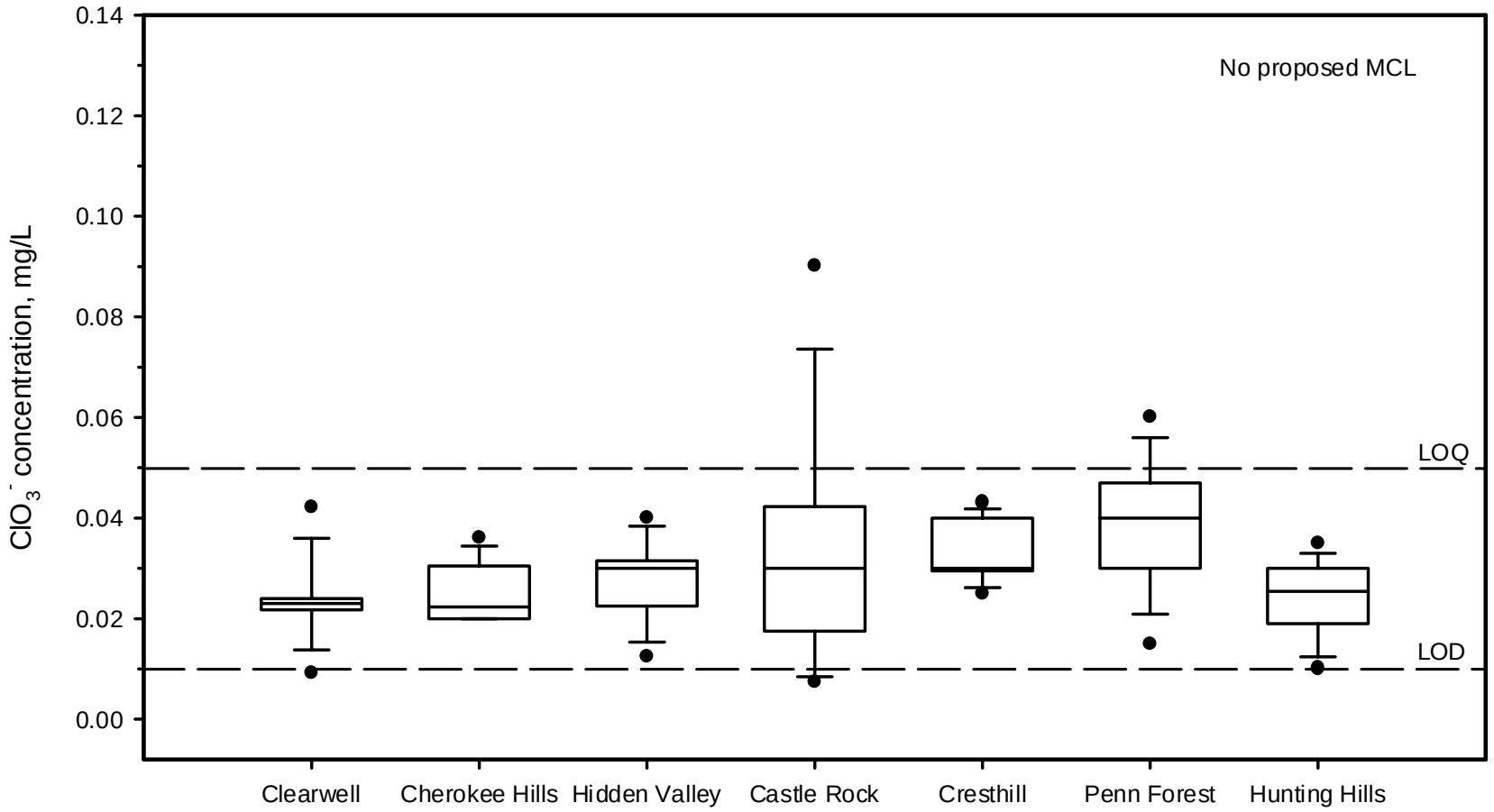


Figure 13. Comparison of chlorate concentrations in the Roanoke County clearwell and distribution system (n = 9). Sites are arranged (left to right) in order of increasing distance from the water treatment plant.

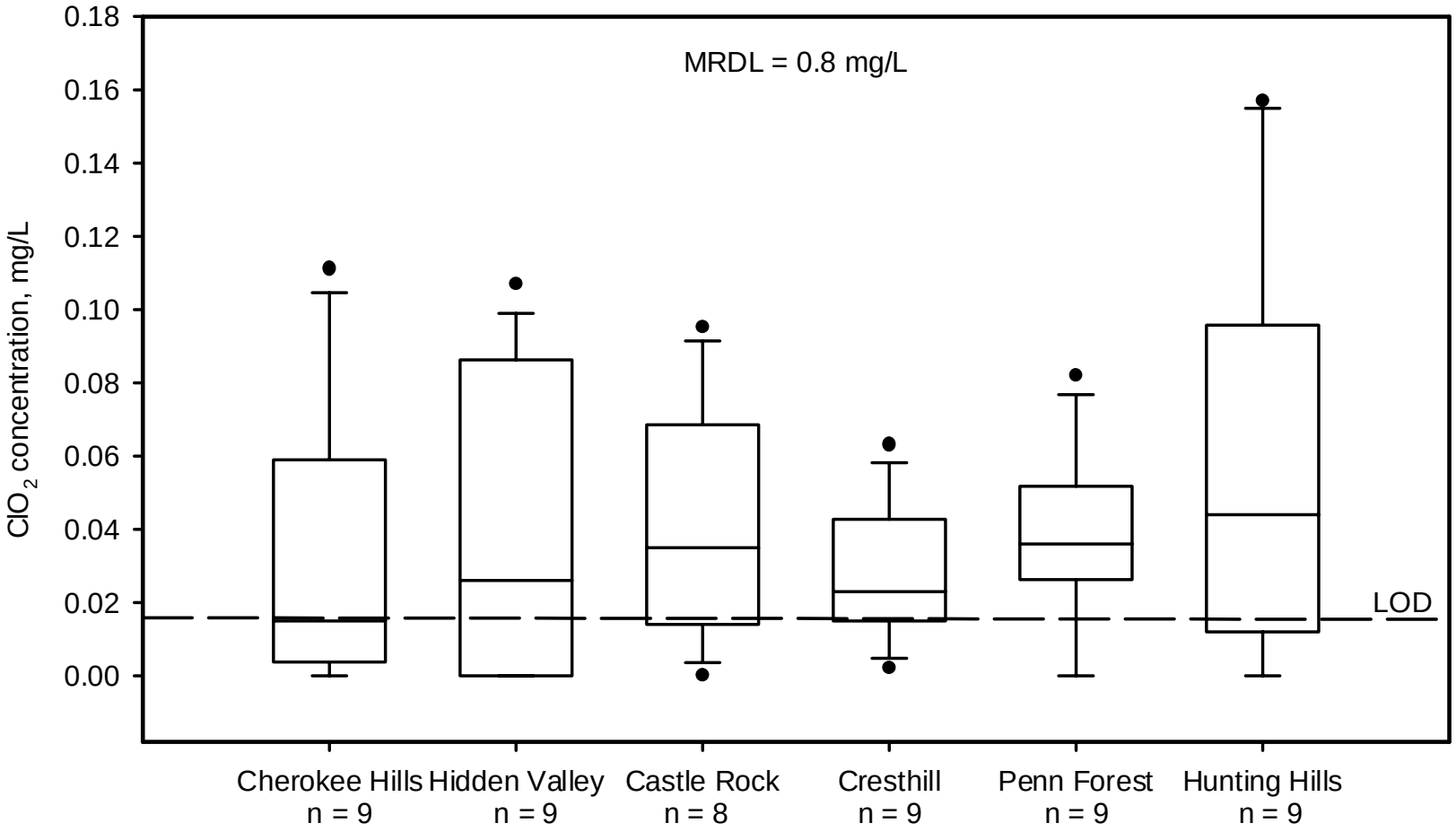


Figure 14. Comparison of chlorine dioxide concentrations in the Roanoke County distribution system. Sites are arranged (left to right) in order of increasing distance from the water treatment plant.

the detection limit (0.017 mg/L) to 0.15 mg/L, and averaged 0.043 mg/L (median 0.03 mg/L). Comparisons between the distribution-system $ClO_2$ concentrations with clearwell concentrations were not possible because concentrations in the clearwell were not routinely determined. On several occasions, no $ClO_2$ was detected in the clearwell.

During the study period, the County received twelve odor complaints that apparently were related to $ClO_2$ use at the treatment plant. Two complaints were received from customers at each of two locations and three complaints were received from another customer. New carpets had been installed at all eight locations within the previous six months. At six locations, new carpet had been installed within the previous week. One customer reported noticing an odor when the carpet was first installed but did not file a complaint for approximately one month after the installation date. Chlorine dioxide concentrations were determined at only two locations at the same time the complaints were being investigated, and they were quite low (0.07 mg/L and 0.03 mg/L).

The first customer to complain stated that the odor had persisted for two weeks after new carpeting was installed. Shortly thereafter, the $ClO_2$ generator was out of service for several days, and she no longer noticed any odors. Complainants described the odors with terms such as “petroleum smell,” “strange pungent odor,” “strong chemical smell,” and “sulfur smell.” At several locations, County employees who investigated the complaints described odors they detected as “kerosene-like,” “cat urine,” “chemical,” and “$ClO_2$.”

Near the end of December, 1997, the treatment plant operators responded to the increasing frequency of complaints (despite the fact that only eight complaints had been received) by reducing the $ClO_2$ dose to approximately 0.3 mg/L, and this action seemed to solve the problem. On March 28, 1998, however, a valve at the treatment plant

malfunctioned and the GAC contactor had to be removed from service so it could be repaired. Shortly after the contactor was taken off line, the County received two additional odor complaints, and in response, the operators reduced the $ClO_2$ dose still further to 0.25 mg/L. Thereafter, odor complaints ceased.

Chlorite ion concentrations in the distribution system following the final $ClO_2$-dose reduction ranged from 0.165 mg/L near the plant to less than the detection limit (0.004 mg/L) at the most distant site. Chlorate ion concentrations ranged from 0.05 mg/L near the plant to less than the detection limit (0.01 mg/L) at the farthest point. Shortly after the final $ClO_2$-dose reduction, $ClO_2$ was not detected in the distribution system.

## Discussion

### $ClO_2$, $ClO_2^-$ and $ClO_3^-$ Distributions Through the Treatment Plant

Chlorine dioxide persistence and the $ClO_2^-$ and $ClO_3^-$ concentrations that one can detect in any particular treatment facility will be dictated by several conditions, including raw-water quality, the $ClO_2$ dose, and the residence time within the treatment plant. The residence time through the Spring Hollow Water Treatment Plant is quite short (approximately 20 minutes to the filters), and the $ClO_2$ demand of the raw water is quite low because the total organic carbon concentrations rarely exceed 2.5 mg/L. These facts explain why $ClO_2$ was detected on most occasions throughout the treatment plant, even when the dosages were low. On many occasions, small but detectable $ClO_2$ concentrations persisted through the filters (Figure 3), which indicates that the filter media were relatively free of organic matter and did not exert a significant oxidant demand.

The $ClO_2$ dose during this study was reduced on several occasions as odor complaints from customers began to be received, and by the end of January, dosages were below 0.4 mg/L. Throughout the study period, therefore, $ClO_2$ residuals in the plant never exceeded the proposed MRDL (0.80 mg/L) because the dosages were well below that level on all but one occasion.

The presence of residual $ClO_2$ in the dosed raw water on most occasions (Figure 3) accounts for the higher $ClO_2^-$ concentrations in the clarifier effluent (Figures 4) because $ClO_2^-$ was formed when the unreacted $ClO_2$ in the raw water continued to react with organic matter. Gordon and Rosenblatt (1996) describe this reaction as:

$$ClO_2 + \text{Organic Matter} \rightarrow ClO_2^- + \text{Products} \quad \text{.....[2]}$$

Chlorite ion concentrations leaving the plant (clearwell sampling site) never exceeded the proposed MCL (1.0 mg/L) because $ClO_2$ dosages were less than 0.80 mg/L during most of the study (Figure 6), and they actually were even lower following chlorination in the clearwell (Figure 4). Chlorine oxidation of $ClO_2^-$ to $ClO_2$ and $ClO_3^-$ is the only plausible explanation for the observed $ClO_2^-$ reductions.

Chlorate ion concentrations were routinely low throughout the treatment plant (Figure 5) and typically were only slightly greater than the limit of detection (0.01 mg/L), even in the clearwell following chlorination of the GAC effluent. Chlorate ion can be formed by photolytic disproportionation of $ClO_2$ (Zika et al., 1985) and by chlorine oxidation of $ClO_2^-$, but the latter reaction no doubt was the major mechanism because the treatment units are not exposed to sunlight.

The low $ClO_3^-$ concentrations in the treatment plant and distribution system reflect one benefit of the gas-solid generator, namely that $ClO_3^-$ is not formed during the generation process. Gallagher et al. (1994) showed that the generators and feedstock solutions accounted for up to 40 percent of the observed distribution system $ClO_3^-$ concentrations. Most of the $ClO_3^-$ in their study was formed by chlorine reaction with $ClO_2^-$ in the clearwell.

**Chlorite Removal by GAC Filtration**

Chlorite-ion removals by the virgin GAC contactors during this study averaged approximately 64 percent (Figure 7) but were declining rapidly as the study progressed (Figure 9). The GAC appeared to be approaching exhaustion for $ClO_2^-$ removal by the end of this project (Figure 10). Activated carbon reduces $ClO_2^-$ to chloride ion, but, in the process, adsorption sites are oxidized. Other studies have also shown that GAC is relatively ineffective for long-term $ClO_2^-$ removal (Dixon and Lee, 1991).

The data from this study clearly show that the GAC contactor at the Spring Hollow Water Treatment Plant may not adequately reduce $ClO_2^-$ concentrations to below the MCL if $ClO_2$ dosages are increased to levels much greater than 1.0 mg/L, and some other technology, such as reduction by reduced iron or sulfur compounds would be required.

**Chlorine Dioxide, Chlorite Ion and Chlorate Ion Occurrences in the Distribution System**

Chlorine dioxide reformed in the distribution system following chlorination of the GAC-filtered water and could be detected throughout the distribution system at levels ranging from less than the detection limit (0.017 mg/L) to 0.15 mg/L. None was detected in the clearwell effluent on several occasions, which may indicate that most, if not all, of the reformation occurred in the distribution system. Gallagher et al. (1994) reported that $ClO_2$

reformed in the clearwell at two locations and was found in the distribution systems as well. At both locations, $ClO_2$ was added as a preoxidant to raw water. No $ClO_2$ was present prior to the clearwell, but the mean concentration was 0.22 mg/L at one distribution system location and 0.03 mg/L at the other. The analyses were by amperometric titration rather than by the LGB method, however.

The reaction accounting for $ClO_2$ reformation is the same as the one that produces $ClO_2$ in the generator (equation 1 shown previously) except that the chlorine is dissolved in water as hypochlorous acid (HOCl) and the $ClO_2^-$ is much less concentrated. The reaction continues throughout the distribution system as long as chlorine and $ClO_2^-$ are present. The concentration at any particular point is the result of a complex cyclic series of reactions involving formation, reduction to $ClO_2^-$ by reaction with organic matter and other chemically reduced substances, and then reformation once again by $ClO_2^-$ oxidation. Chloride ion can be formed as well when $ClO_2$ reacts with organic matter, and one would expect both $ClO_2$ and $ClO_2^-$ concentrations to diminish with increasing residence time in the distribution system. Chlorine dioxide concentrations in the Roanoke County distribution system followed no particular pattern, however, even though $ClO_2^-$ concentrations at distribution system locations nearest and farthest from the treatment plant decreased significantly.

One would expect $ClO_3^-$ concentrations to increase with increasing chlorine contact time in the distribution system, and concentrations at three of the distribution system sites (Castle Rock, Cresthill, and Penn Forest) were statistically greater than clearwell concentrations. Concentrations at all locations, however, were uniformly quite low, and while no $ClO_3^-$ MCL has yet been proposed, the levels detected during this study most likely are not high enough to cause any concern.

**Chlorine Dioxide-Related Odor Complaints**

Only a small number of customers complained about odors in their homes, some repeatedly, and the complaints appeared to coincide with the installation of new carpeting. Previous research (Hoehn et al., 1990; Dietrich et al., 1992b) indicated a similar connection between new carpeting and odors associated with $ClO_2$, and terms such as cat urine and kerosene-like have been used to describe them. Descriptors used by customers in the earlier studies were similar to those used by customers and operators during this study.

Odors could be detected when $ClO_2$ concentrations were quite low, as is evident from the low concentrations (0.03 mg/L and 0.07 mg/L) detected on two occasions at customers' homes on days the complaints were made. Odor complaints did not cease until the $ClO_2$ dosage at the treatment plant was reduced to less than 0.4 mg/L. Even at that low dose, complaints were received during a brief period when the GAC contactor was inoperative, which demonstrates the value of the GAC even though it was not 100 percent effective in eliminating $ClO_2^-$. The lissamine green B method made reliable analysis of low $ClO_2$ levels possible, and this study is the first to document that kerosene and cat-urine odors could be caused by $ClO_2$ concentrations as low as 0.03 mg/L.

Elimination of the odors can be accomplished by only two methods: one, the addition of reduced-iron coagulants or reduced sulfur compounds to remove $ClO_2^-$ at the treatment plant or, two, substitution of chloramines for chlorine in the distribution system. The reducing agents reduce $ClO_2^-$ ultimately to chloride ion (Masschelein, 1979), in which case chlorine can continue to be used. Chloramines do not oxidize $ClO_2^-$ to form $ClO_2$.

## Summary and Conclusions

The chlorine dioxide demand of Spring Hollow Reservoir water was low throughout the study period, and, as a result, only low dosages were applied. As a result, $ClO_2^-$ concentrations never exceeded the MCL (1.0 mg/L). Likewise, the plant effluent $ClO_2$ concentration never approached the MRDL (0.80 mg/L), but concentrations as high as 0.15 mg/L were detected in the distribution system.

Although no $ClO_3^-$ MCL has been proposed, concentrations were quite low (never greater than 0.10 mg/L) throughout the treatment plant and in the distribution system. The reasons for the low concentrations are that $ClO_3^-$ is not produced by the gas-solid generator used at the facility and that $ClO_2^-$ concentrations in the clearwell were uniformly low.

The 7-ft deep GAC contactor reduced $ClO_2^-$ concentrations, on average, by approximately 64 percent, but its effectiveness was declining over the six-month study period. Apparently, GAC effectiveness, as shown by others, is short-lived, and if higher $ClO_2$ dosages are ever applied at the Roanoke County facility, the $ClO_2^-$ concentrations will have to be reduced by either ferrous coagulants or reduce-sulfur compounds.

While meeting the $ClO_2^-$ MCL likely will be no problem if the $ClO_2$ dose at the plant remains below 1.0 mg/L, the problem of offensive odors in the distribution system will likely continue as long as any $ClO_2^-$ is in the finished water when chlorine is present. Concentrations of reformed $ClO_2$ as low as 0.03 mg/L were detected at homes of customers who complained of offensive odors. During this study, twelve complaints were received from eight customers, and each of the customers had recently installed new carpeting.

## References


Aston, R.N. "Chlorine Dioxide Use in Plants on the Niagara Border." *Jour. AWWA* 39:7:687-690 (July 1947).

Bissonette, E. and Allgeier, S. Summary of Disinfection Application Practices, Evaluated Through the Analysis of ICR Plant Schematics and Small Systems CPRE Data. Presented by the authors at the Disinfectant/Disinfection By-Products Rule meeting of FACA, Office of Ground Water and Drinking Water, Technical Support Center, Cincinnati, Ohio, February, 1997.

Dietrich, A.M., Ledder, T.D., Gallagher, D.L., Grabeel, M.N., and Hoehn, R.C. "Determination of Chlorite and Chlorate in Chlorinated and Chloraminated Drinking Water by Flow Injection Analysis and Ion Chromatography." *Anal. Chem.*, 64:5:496-502 (March 1, 1992a).

Dietrich, A.M., Orr, M.P., Gallagher, D.L., and Hoehn, R.C. "Tastes and Odors Associated with Chlorine Dioxide." *Jour. AWWA*, 84:6:82-88 (June 1992b).

Dixon, K.L., and Lee, R.G. "The Effect of Sulfur-Based Reducing Agents and GAC Filtration on Chlorine Dioxide By-products." *Jour. AWWA*, 83:5:48-55 (May 1991).

*Federal Register*, National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts; Proposed Rule. Vol. 59 (No. 145): 38668-38829. 40 CFR Parts 141 and 142, July 29, 1994.

*Federal Register*, National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts; Final Rule. Vol. 63 (No. 241): 69389-69476. 40 CFR Parts 9, 141 and 142, December 16, 1998.

Gallagher, D.L., Hoehn, R.C., and Dietrich, A.M. *Sources, Occurrence, and Control of Chlorine Dioxide By-Product Residuals in Drinking Water*. Denver, CO: AWWARF, 1994.

Gordon, G., and Rosenblatt, A.A. Gaseous Chlorine-Free Chlorine Dioxide for Drinking Water. *Proceedings of the 1995 Water Quality Technology Conference*. Denver, CO: AWWA, 1996.

Granstrom, M.L., and Lee, G.F. "Generation and Use of Chlorine Dioxide in Water Treatment." *Jour. AWWA*, 50:11:1453-1466 (November 1958).

Hoehn, R.C., Dietrich, A.M., Farmer, W.S., Orr, M.P., Lee, R.G., Aieta, E.M., Wood, D.M. III, and Gordon, G. "Household Odors Associated With the Use of Chlorine Dioxide." *Jour. AWWA*, 82:4:166-172 (April 1990).

Masschelein, W.J. *Chlorine Dioxide: Chemistry and Environmental Impact of Oxychlorine Compounds*. Ann Arbor, MI: Ann Arbor Science Publishers, 1979.

McCarthy, J.A. "Chlorine Dioxide for the Treatment of Water Supplies." *Jour. New England Water Works Assoc.*, 58:252-264 (1944).

Novatek Application Note. *Chlorine Dioxide Measurement Using Lissamine Green B.* Miami, OH: Novatek, 1997.

Pfaff, J.D., C.A. Brockhoff, and J.W. O'Dell. 1989. *Test Method: The Determination of Inorganic Anions in Water by Ion Chromatography, Methods 300.0 A&B.* USEPA Environmental Monitoring and Systems Laboratory, Cincinnati, Ohio.

Synan, J.F., MacMahon, J.D., and Vincent, G.P. "Chlorine Dioxide - Development in the Treatment of Potable Water." *Water Works and Sewer*, 91:12:423-426 (December 1944).

United States Environmental Protection Agency (USEPA). Appendix A. In *Methods for Organic Chemical Analyses of Municipal and Industrial Wastewater*. Edited by J.E. Longbottom and J.J. Lichtenberg. Environmental Monitoring and Support Laboratory. EPA-600/4-82-057. Cincinnati, Ohio: USEPA, 1982.

Zika, R.G., Moore, C.A., Gidel, L.T., and Cooper, W.J. Sunlight-Induced Photodecomposition of Chlorine Dioxide. In *Water Chlorination: Environmental Impact and Health Effects*. Vol. 5. Edited by R.L. Jolley, R.J. Bull, W.P. Davis, S. Katz, M.H. Roberts, Jr., and V.A. Jacobs. Chelsea, MI: Lewis Publishers, 1985.

# CHAPTER V
# REFERENCES


Aieta, E.M., and Berg, J.D. "A Review of Chlorine Dioxide in Drinking Water Treatment." *Jour. AWWA*, 78:6:62-72 (June 1986).

Aieta, E.M., Roberts, P.V., and Hernandez, M. "Determination of Chlorine Dioxide, Chlorine, Chlorite, and Chlorate in Water." *Jour. AWWA*, 76:1:64-70 (January 1984).

American Water Works Association. *Treatment Techniques for Controlling Trihalomethanes in Drinking Water*. Denver, CO: AWWA, 1982.

APHA, AWWA, and WEF (American Public Health Association, American Water Works Association, and Water Environment Federation). 1995. *Standard Methods for the Examination of Water and Wastewater*. 19th ed. Washington, D.C.: APHA.

Aston, R.N. "Chlorine Dioxide Use in Plants on the Niagara Border." *Jour. AWWA* 39:7:687-690 (July 1947).

Bellar, T.A., Lichtenberg, J.J., and Kroner, R.C. "The occurrence of Organohalides in Chlorinated Drinking Waters." *Jour. AWWA*, 66:11:703-706 (November 1974).

Bernade, M.A., Israel, B.M., Olivieri, V.P., and Granstrom, M.L. "Efficiency of Chlorine Dioxide as a Bactericide." *Appl. Microbiol.*, 13:776 (September 1965).

Bissonette, E. and Allgeier, S. Summary of Disinfection Application Practices, Evaluated Through the Analysis of ICR Plant Schematics and Small Systems CPRE Data. Presented by the authors at the Disinfectant/Disinfection By-Products Rule meeting of FACA, Office of Ground Water and Drinking Water, Technical Support Center, Cincinnati, Ohio, February, 1997.

Bolyard, M., Fair, P.S., and Hautman, D.P. "Sources of chlorate ion in U.S. Drinking Water." *Jour. AWWA*, 85:9: 81-88 (September 1993).

Bubnis, B. 1997. Personal Communication.

Chemical Manufacturers Association (CMA). 1996. Sodium Chlorite: Drinking Water Rat Two-Generation Reproductive Toxicity Study. Quintiles Report Ref. CMA/17/96.

Chiswell, B., and O'Halloran, K.R. "Use of Lissamine Green B as a Spectrophotometric Reagent for the Determination of Low Levels of Chlorine Dioxide." *Analyst*, 116:6:657-661 (June 1991).

Chow, B.M., and Roberts, P.V. "Halogenated Byproduct Formation by $ClO_2$ and $Cl_2$." *Jour. Environ. Eng. Div., Proceedings of the ASCE,* 107:EE4:609-618 (August 1981).

Cooper, W.J., Zika, R.G., and Steinhauer, M.S. "Bromide-Oxidant Interaction and THM Formation: A Literature Review." *Jour. AWWA,* 77:4:116-121 (April 1985).

Dietrich, A.M., Ledder, T.D., Gallagher, D.L., Grabeel, M.N., and Hoehn, R.C. "Determination of Chlorite and Chlorate in Chlorinated and Chloraminated Drinking Water by Flow Injection Analysis and Ion Chromatography." *Anal. Chem.*, 64:5:496-502 (March 1, 1992a).

Dietrich, A.M., Orr, M.P., Gallagher, D.L., and Hoehn, R.C. "Tastes and Odors Associated with Chlorine Dioxide." *Jour. AWWA,* 84:6:82-88 (June 1992b).

Dixon, K.L., and Lee, R.G. "The Effect of Sulfur-Based Reducing Agents and GAC Filtration on Chlorine Dioxide By-products." *Jour. AWWA,* 83:5:48-55 (May 1991).

Ellenberger, C.S., Hoehn, R.C., Gallagher, D.L., Knocke, W.R., Wiseman, E.V., Benninger, R.W., and Rosenblatt, A. Water Quality Impacts of Pure Chlorine Dioxide Pretreatment at the Roanoke County (Virginia) Water Treatment Plant. In *Proceedings of the 1998 Annual AWWA Conference and Exposition*. Denver, CO: AWWA, 1998.

*Federal Register,* National Secondary Drinking Water Regulations. Vol. 44:42195. 40 CFR Part 140, July 19, 1979.

*Federal Register*, National Primary Drinking Water Regulations; Final Rule. Vol. 54 (No. 124). 40 CFR Parts 141 and 142, June 29, 1989.

*Federal Register,* National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts; Proposed Rule. Vol. 59 (No. 145): 38668-38829. 40 CFR Parts 141 and 142, July 29, 1994.

*Federal Register*, National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts; Final Rule. Vol. 63 (No. 241): 69389-69476. 40 CFR Parts 9, 141 and 142, December 16, 1998.

Finch, G.R., Liyanage, L.R.J., and Belosevic, M. Effects of Chlorine Dioxide on *Cryptosporidium* and *Giardia*. *Proceedings of Third International Symposium on Chlorine Dioxide: Drinking Water, Process Water and Wastewater Issues*. Denver, CO: AWWA and AWWARF, 1995.

Gallagher, D.L., Hoehn, R.C., and Dietrich, A.M. *Sources, Occurrence, and Control of Chlorine Dioxide By-Product Residuals in Drinking Water*. Denver, CO: AWWARF, 1994.

Gates, D.J. *The Chlorine Dioxide Handbook*. Denver, CO: AWWA, 1998.

Glaze, W.H., Schep, R., Chauncey, W., Ruth, E.C., Zarnoch, J.J., Aieta, E.M., Tate, C.H., and McGuire, M.J. "Evaluating Oxidants for the Removal of Model Taste and Odor Compounds From a Municipal Water Supply." *Jour. AWWA*, 82:5:79-84 (May 1990).

Gordon, G., Kieffer, R.G., and Rosenblatt, D.H. "The Chemistry of Chlorine Dioxide." In *Progress in Inorganic Chemistry*. Vol.15. New York, NY: Wiley-Interscience Publishers, 1972.

Gordon, G., and Rosenblatt, A.A. Gaseous Chlorine-Free Chlorine Dioxide for Drinking Water. *Proceedings of the 1995 Water Quality Technology Conference*. Denver, CO: AWWA, 1996.

Gordon, G., Slootmaekers, B., Tachiyashiki, S., and Wood, D. W. III. "Minimizing chlorite ion and chlorate ion in water treated with chlorine dioxide." *Jour. AWWA*, 82:4:160-165 (April 1990).

Grabeel, M.N. "Chlorine Dioxide By-Products in Drinking Water and Their Control by Powdered Activated Carbon." M.S. Thesis. Virginia Polytechnic Institute and State University; Blacksburg, VA (1992).

Granstrom, M.L., and Lee, G.F. "Generation and Use of Chlorine Dioxide in Water Treatment." *Jour. AWWA*, 50:11:1453-1466 (November 1958).

Griese, M.H., Hauser, K., Berkemeier, M., and Gordon, G. "Using Reducing Agents to Eliminate Chlorine Dioxide and Chlorite Ion Residuals in Drinking Water." *Jour. AWWA*, 83:5:56-61 (May 1991).

Griese, M.H., Kaczur, J.J., and Gordon, G. "Combining Methods for the Reduction of Oxychlorine Residuals in Drinking Water." *Jour. AWWA*, 84:11:69-77 (November 1992).

Hautman, D.P., and Bolyard, M. "Using Ion Chromatography to Analyze Inorganic Disinfection By-products." *Jour. AWWA*, 84:11:88-93 (November 1992).

Hettche, O., and Ehlbeck, H.W.S. "Epidemiology and Prophylaxes of Poliomyelitis in Respect of the Role of Water in Transfer." *Arch. Hyg. Berlin*, 137:440 (1953).

Hoehn, R.C. 1993. "Chlorine Dioxide Use in Water Treatment: Key Issues." In *Conference Proceedings: Chlorine Dioxide Drinking Water Issues*. Denver, CO: AWWA Research Foundation, American Water Works Association, May 7-8, 1992, pp. 1-14.

Hoehn, R.C., Dietrich, A.M., Farmer, W.S., Orr, M.P., Lee, R.G., Aieta, E.M., Wood, D.M. III, and Gordon, G. "Household Odors Associated With the Use of Chlorine Dioxide." *Jour. AWWA*, 82:4:166-172 (April 1990).

Hoff, J.C. "Inactivation of Microbial Agents by Chemical Disinfectants." USEPA, EPA/600/2-86/067, 1986.

Hofmann, R., Andrews, R.C., and Ye, Q. "Comparison of Spectrophotometric Methods for Measuring Chlorine Dioxide in Drinking Water." *Environ. Technol.*, 19:761-773 (1998).

Hurst, G.H., and Knocke, W.R. "Evaluating Ferrous Iron for Chlorite Ion Removal." *Jour. AWWA*, 89:8:98-105 (August 1997).

Iatrou, A., and Knocke, W.R. "Removing Chlorite by the Addition of Ferrous Iron." *Jour. AWWA*, 84:11:63-68 (November 1992).

Jensen, J.N. and Johnson, J.D. "Interferences by Monochloramine and Organic Chloramines in Free Available Chlorine Methods. 1. Amperometric Titration." *Environ. Sci. Technol.*, 24:7:981-985 (1990).

Knocke, W.R., Hoehn, R.C., and Sinsabaugh, R.L. "Using Alternative Oxidants to Remove Dissolved Manganese From Waters Laden With Organics." *Jour. AWWA*, 79:3:75-79 (March 1987).

Knocke, W.R., Van Benschoten, J.E., Kearney, M., Soborski, A., and Reckhow, D.A. *Alternative Oxidants for the Removal of Soluble Iron and Manganese*. Denver, CO: AWWARF, 1990.

Korich, D.G., Mead, J.R., Madore, M.S., Sinclair, N.A., and Sterling, C.R. "Effects of Ozone, Chlorine Dioxide, Chlorine, and Monochloramine on *Cryptosporidium parvum* Oocyst Viability." *Appl. Environ. Microbiol.*, 56:5:1423-1429 (1990).

Lalezary, S., Pirbazari, M., and McGuire, M.J. "Oxidation of Five Earthy-Musty Taste and Odor Compounds." *Jour. AWWA*, 78:3:62-69 (March 1986).

Limoni, B., Goldstein, E.C., and Rav-Acha, C. "Determination of Oxidants Formed Upon the Disinfection of Drinking Water with Chlorine Dioxide." *Jour. Environ. Sci. Health*, A19:8:943-957 (1984).

Liyanage, L.R.J., Gyurek, L.L., Belosevic, M., and Finch, G.R. "Effect of Chlorine Dioxide Preconditioning on Inactivation of *Cryptosporidium* by Free Chlorine and Monochloramine: Process Design Requirements." *Proceedings of the 1996 Water Quality Technology Conference*. Denver, CO: AWWA, 1997.

Lohman, S.R., and Rogers, S.E. "Chlorine Dioxide By-Products Reduction by Granular Activated Carbon." *Proceedings of the Water Reuse Symposium IV*. Denver, CO: AWWA, 1987.

Long, B.W., Miller, R.F., and Rosenblatt, A.A. "Pilot Study: The Use of High-Purity Chlorine-Free Chlorine Dioxide to Minimize Trihalomethane Formation." *Proceedings of the 6th International Symposium on Chemical Oxidation: Technology for the Nineties.* Vanderbilt University, Nashville, TN, April 15-17, 1996.

Lykins, B.W. Jr, and DeMarco, J. "Pilot Study on the Use of Chlorine Dioxide." In *Treatment of Water by Granular Activated Carbon.* M.J. McGuire and I.H. Suffet (editors), American Chemical Society Advances in Chemistry Series 202, Washington, D.C. (1983).

Lykins, B.W. Jr, Goodrich, J.A., Koffskey, W.E., and Griese, M.H. "Controlling Disinfection By-Products with Alternative Disinfectants." In *Proceedings of the 1991 Annual Conference of the AWWA*. Denver, CO: AWWA, 1991.

Lykins, B.W. Jr, and Griese, M.H. "Using Chlorine Dioxide for Trihalomethane Control." *Jour. AWWA*, 78:6:88-93 (June 1986).

Masschelein, W.J. *Chlorine Dioxide: Chemistry and Environmental Impact of Oxychlorine Compounds*. Ann Arbor, MI: Ann Arbor Science Publishers, 1979.

McCarthy, J.A. "Chlorine Dioxide for the Treatment of Water Supplies." *Jour. New England Water Works Assoc.*, 58:252-264 (1944).

McGuire, M.J., Lieu, N.I., and Pearthree, M.S. "Using Chlorite Ion to Control Nitrification." *Jour. AWWA*, 91:10:52-61 (October 1999).

Mitchell, R.M. "Evaluation of Different Powdered Activated Carbons in The Control of Chlorite Ion." M.S. Thesis. Virginia Polytechnic Institute and State University; Blacksburg, VA (1993).

National Cancer Institute. *Report on the Carcinogenesis Bioassay of Chloroform*. NTIS PB264018/AS. Washington, D.C.: NCI, 1976.

Novatek Application Note. *The Measurement of Inorganic Species by Ion Chromatography (USEPA Method 300.0 – Revised).* Method C9-02001. Miami, OH: Novatek, January 1993.

Novatek Application Note. *Chlorine Dioxide Measurement Using Lissamine Green B.* Miami, OH: Novatek, January 1997.

Ondrus, M.G., and Gordon, G. "The Oxidation of Hexaquoiron (II) by Chlorine (III) in Aqueous Solution." *Inorganic Chem.*, 11:5:985-989 (May 1972).

Orr, M.P. "Reduction of Odors Associated with Chlorine Dioxide Applications to Drinking Water." M.S. Thesis. Virginia Polytechnic Institute and State University; Blacksburg, VA (1990).

Pfaff, J.D., and Brockhoff, C.A. "Determining Inorganic Disinfection By-products by Ion Chromatography." *Jour. AWWA*, 82:4:192-195 (April 1990).

Pfaff, J.D., C.A. Brockhoff, and J.W. O'Dell. 1989. *Test Method: The Determination of Inorganic Anions in Water by Ion Chromatography, Methods 300.0 A&B.* USEPA Environmental Monitoring and Systems Laboratory, Cincinnati, Ohio.

Rav-Acha, C. "The Reactions of Chlorine Dioxide with Aquatic Organic Materials and Their Health Effects." *Water Res.*, 18:11:1329-1341 (November 1984).

Ridenour, G.M., and Ingols, R.S. "Bactericidal Properties of Chlorine Dioxide." *Jour. AWWA*, 39:561 (1947).

Rook, J.J. "Formation of Haloforms during Chlorination of Natural Waters." *Journ. Society for Water Treatment Exam.*, 23:2:234-243 (1974).

Singer, P.C. and W.K. O'Neil. "Technical Note: The Formation of Chlorate from the Reaction of Chlorine and Chlorite in Dilute Aqueous Solution." *Jour. AWWA*, 79:11:75-76 (November 1987).

Steinbergs, C.Z. "Removal of By-products of Chlorine and Chlorine Dioxide at a Hemodialysis Center." *Jour. AWWA*, 78:6:94 (June 1986).

Synan, J.F., MacMahon, J.D., and Vincent, G.P. "Chlorine Dioxide - Development in the Treatment of Potable Water." *Water Works and Sewer*, 91:12:423-426 (December 1944).

Thompson, A.L. "Chlorine Dioxide Process Treatment Data and Cost." In *Chlorine Dioxide Use in Water Treatment, Second International Symposium*. Denver, CO: AWWA and AWWARF, 1993.

Thompson, A.L., Matthews, N.O., Mittl, A.J., and Owen, D.M. "Chlorite and Chlorate Residuals in the Distribution System." *AWWA Water Quality Technology Conference Proceedings*. Denver, CO: AWWA, 1989.

United States Environmental Protection Agency (USEPA). Appendix A. In *Methods for Organic Chemical Analyses of Municipal and Industrial Wastewater*. Edited by J.E. Longbottom and J.J. Lichtenberg. Environmental Monitoring and Support Laboratory. EPA-600/4-82-057. Cincinnati, Ohio: USEPA, 1982.

United States Environmental Protection Agency (USEPA). *An Evaluation of Alternative Oxidant and Disinfectant Treatment Strategies for Controlling Trihalomethane Formation in Drinking Water*. USEPA Coop. Agreement CR811108 (September 1983).

United States Environmental Protection Agency (USEPA). *Final: Occurrence Assessment for Disinfectants and Disinfection Byproducts in Public Drinking Water Supplies.* Prepared by Science Applications International Corporation (McLean, Va.) for Office of Groundwater and Drinking Water, USEPA, Washington, D.C., November 13, 1997.

Vel Leitner, N.K., De Laat, J., Dore, M., Suty, H., and Pouillot, M. "Chlorite and Chlorine Dioxide Removal by Activated Carbon." *Water Res.*, 26:8:1053-1066 (August 1992).

Voudrias, E.A., Dielmann, L.M.J., Snoeyink, V.L., Larson, R.A., McCreary, J.J., and Chen, A.S.C. "Reactions of Chlorite with Activated Carbon and with Vanillic Acid and Indan Adsorbed on Activated Carbon." *Water Res.*, 17:9:11071114 (September 1983).

Walker, G.S., Lee, F.P., and Aieta, E.M. "Chlorine Dioxide for Taste and Odor Control." *Jour. AWWA*, 78:3:84-93 (March 1986).

Werdehoff, K.S., and Singer, P.C. "Chlorine Dioxide Effects on THMFP, TOXFP, and the Formation of Inorganic By-products." *Jour. AWWA*, 79:9:107-113 (September 1987).

White, G.C. *Handbook of Chlorination*. New York, NY: Van Nostrand Reinhold Company, 1972.

Zika, R.G., Moore, C.A., Gidel, L.T., and Cooper, W.J. Sunlight-Induced Photodecomposition of Chlorine Dioxide. In *Water Chlorination: Environmental Impact and Health Effects*. Vol. 5. Edited by R.L. Jolley, R.J. Bull, W.P. Davis, S. Katz, M.H. Roberts, Jr., and V.A. Jacobs. Chelsea, MI: Lewis Publishers, 1985.

# APPENDIX A

# CHLORITE ION AND CHLORATE ION

# ANALYTICAL DATA

Table A1. Chlorite ion concentration measured throughout the Roanoke County Spring Hollow Water Treatment Plant, September 9, 1997 through February 10, 1998.

| | Concentration, mg/L | | | | |
|---|---|---|---|---|---|
| Date | Dosed Raw | Filter Applied | Filtered | GAC Effluent | Clearwell |
| 9/9/1997 | 0.522 | 0.601 | 0.747 | 0.286 | NS |
| 9/10/1997 | 0.507 | 0.454 | 0.718 | 0.289 | NS |
| 9/11/1997 | 0.292 | 0.348 | 0.303 | 0.142 | NS |
| 9/12/1997 | 0.273 | 0.477 | 0.339 | 0.166 | NS |
| 9/15/1997 | 0.584 | 0.542 | 0.739 | 0.276 | 0.017 |
| 9/16/1997 | 0.362 | 0.420 | 0.354 | NS | NS |
| 9/17/1997 | 0.340 | 0.360 | 0.340 | 0.136 | 0.037 |
| 9/18/1997 | 0.338 | 0.352 | 0.376 | 0.133 | 0.033 |
| 9/19/1997 | 0.360 | 0.383 | 0.361 | 0.129 | 0.042 |
| 9/22/1997 | <DL | <DL | <DL | <DL | <DL |
| 9/23/1997 | 0.360 | 0.430 | 0.370 | 0.160 | <DL |
| 9/24/1997 | 0.374 | 0.422 | 0.438 | 0.156 | 0.096 |
| 9/25/1997 | 0.202 | 0.392 | 0.421 | 0.128 | 0.086 |
| 9/26/1997 | 0.397 | 0.450 | 0.415 | 0.177 | 0.080 |
| 9/29/1997 | 0.429 | 0.399 | 0.414 | 0.186 | 0.090 |
| 9/30/1997 | 0.369 | 0.477 | 0.406 | 0.113 | 0.103 |
| 10/2/1997 | 0.412 | 0.428 | 0.447 | 0.160 | 0.129 |
| 10/3/1997 | 0.547 | 0.580 | 0.553 | 0.098 | 0.104 |
| 10/6/1997 | 0.495 | 0.666 | 0.502 | 0.286 | 0.159 |
| 10/7/1997 | 0.547 | 0.549 | 0.466 | 0.250 | 0.170 |
| 10/8/1997 | 0.582 | 0.549 | 0.586 | 0.257 | 0.172 |
| 10/9/1997 | 0.606 | 0.652 | 0.604 | 0.255 | 0.101 |
| 10/10/1997 | 0.598 | 0.580 | 0.604 | 0.282 | 0.137 |
| 10/14/1997 | NS | NS | 0.576 | 0.228 | NS |
| 10/15/1997 | 0.570 | 0.582 | 0.510 | 0.206 | 0.113 |
| 10/16/1997 | NS | NS | 0.547 | 0.225 | NS |
| 10/17/1997 | 0.471 | 0.540 | 0.482 | 0.185 | 0.119 |
| 10/21/1997 | 0.297 | 0.286 | 0.294 | 0.119 | 0.072 |
| 10/22/1997 | 0.262 | 0.271 | 0.245 | 0.103 | 0.067 |
| 10/23/1997 | 0.233 | 0.203 | 0.237 | 0.092 | 0.052 |
| 10/24/1997 | NS | NS | 0.229 | 0.041 | NS |
| 10/27/1997 | NS | NS | 0.072 | 0.029 | NS |
| 10/28/1997 | NS | NS | 0.121 | <DL | NS |
| 10/29/1997 | NS | NS | 0.108 | 0.030 | NS |
| 10/30/1997 | NO $CLO_2$ | | | | |
| 10/31/1997 | NO $CLO_2$ | | | | |

Table A1. Chlorite ion concentration measured throughout the Roanoke County Spring Hollow Water Treatment Plant, September 9, 1997 through February 10, 1998.

| | Concentration, mg/L | | | | |
|---|---|---|---|---|---|
| **Date** | **Dosed Raw** | **Filter Applied** | **Filtered** | **GAC Effluent** | **Clearwell** |
| 11/4/1997 | NS | NS | 0.105 | 0.008 | NS |
| 11/5/1997 | NS | NS | NS | NS | NS |
| 11/6/1997 | NS | NS | 0.599 | 0.227 | 0.032 |
| 11/7/1997 | NS | NS | 0.525 | 0.218 | 0.125 |
| 11/10/1997 | 0.329 | 0.363 | 0.495 | 0.213 | 0.140 |
| 11/11/1997 | NS | NS | 0.488 | 0.216 | NS |
| 11/12/1997 | NS | NS | 0.486 | 0.212 | NS |
| 11/13/1997 | 0.291 | 0.357 | 0.495 | 0.218 | 0.139 |
| 11/14/1997 | NS | NS | 0.482 | 0.139 | NS |
| 11/17/1997 | NS | NS | 0.521 | 0.242 | NS |
| 11/18/1997 | NS | NS | 0.342 | 0.167 | NS |
| 11/19/1997 | NS | NS | 0.338 | 0.166 | NS |
| 11/20/1997 | NS | NS | 0.174 | 0.133 | NS |
| 11/21/1997 | 0.228 | 0.291 | 0.329 | 0.156 | 0.080 |
| 11/24/1997 | 0.217 | 0.519 | 0.318 | 0.150 | 0.087 |
| 11/25/1997 | NS | NS | 0.433 | <DL | NS |
| 11/26/1997 | NS | NS | 0.342 | 0.082 | NS |
| 11/27/1997 | NS | NS | 0.336 | 0.287 | NS |
| 11/28/1997 | NO $CLO_2$ | | | | |
| 12/1/1997 | NS | NS | 0.369 | 0.159 | NS |
| 12/2/1997 | NS | NS | 0.334 | 0.227 | NS |
| 12/3/1997 | 0.272 | 0.352 | 0.304 | 0.159 | 0.092 |
| 12/4/1997 | NS | NS | 0.331 | 0.071 | NS |
| 12/5/1997 | 0.219 | 0.252 | 0.325 | 0.158 | 0.081 |
| 12/8/1997 | NS | NS | 0.341 | 0.170 | NS |
| 12/9/1997 | NS | NS | 0.320 | 0.171 | NS |
| 12/11/1997 | NS | NS | 0.320 | 0.118 | 0.071 |
| 12/12/1997 | 0.545 | 0.284 | 0.355 | 0.131 | 0.110 |
| 12/15/1997 | NS | NS | 0.357 | 0.193 | NS |
| 12/16/1997 | NS | NS | 0.343 | 0.186 | NS |
| 12/17/1997 | NS | NS | 0.343 | 0.131 | 0.113 |
| 12/18/1997 | NS | NS | 0.343 | 0.181 | 0.096 |
| 12/19/1997 | NS | NS | 0.314 | 0.185 | NS |
| 12/22/1997 | NS | NS | 0.285 | 0.161 | NS |
| 12/23/1997 | 0.163 | 0.185 | 0.279 | 0.152 | 0.097 |
| 12/24/1997 | NS | NS | 0.100 | 0.094 | NS |
| 12/26/1997 | NS | NS | 0.279 | 0.131 | NS |

Table A1. Chlorite ion concentration measured throughout the Roanoke County Spring Hollow Water Treatment Plant, September 9, 1997 through February 10, 1998.

| | Concentration, mg/L | | | | |
|---|---|---|---|---|---|
| Date | Dosed Raw | Filter Applied | Filtered | GAC Effluent | Clearwell |
| 12/29/1997 | NS | NS | 0.215 | 0.066 | NS |
| 12/30/1997 | 0.158 | 0.184 | 0.150 | 0.090 | 0.095 |
| 12/31/1997 | NS | NS | 0.251 | 0.149 | NS |
| 1/1/1998 | NS | NS | 0.253 | 0.095 | NS |
| 1/2/1998 | NS | NS | 0.267 | 0.133 | NS |
| 1/5/1998 | NS | NS | 0.267 | 0.154 | NS |
| 1/6/1998 | NS | NS | 0.259 | 0.150 | NS |
| 1/7/1998 | 0.162 | 0.219 | 0.269 | 0.154 | 0.089 |
| 1/8/1998 | NS | NS | 0.259 | 0.152 | 0.099 |
| 1/9/1998 | NS | NS | 0.263 | 0.145 | NS |
| 1/12/1998 | 0.196 | 0.225 | 0.267 | 0.154 | 0.107 |
| 1/13/1998 | NS | NS | 0.271 | 0.150 | NS |
| 1/14/1998 | NS | NS | 0.271 | 0.151 | NS |
| 1/15/1998 | NS | NS | 0.250 | 0.124 | NS |
| 1/16/1998 | NS | NS | 0.259 | 0.147 | 0.077 |
| 1/20/1998 | NS | NS | 0.247 | 0.147 | NS |
| 1/21/1998 | NS | NS | <DL | 0.059 | NS |
| 1/22/1998 | 0.186 | 0.232 | 0.271 | 0.161 | 0.082 |
| 1/23/1998 | NS | NS | 0.004 | <DL | NS |
| 1/26/1998 | 0.144 | 0.256 | 0.259 | 0.084 | 0.095 |
| 1/27/1998 | 0.124 | 0.232 | 0.234 | 0.082 | 0.113 |
| 1/28/1998 | 0.134 | 0.210 | 0.324 | 0.070 | 0.105 |
| 1/29/1998 | 0.211 | 0.151 | 0.151 | 0.051 | 0.103 |
| 1/30/1998 | 0.127 | 0.145 | 0.207 | 0.069 | 0.115 |
| 2/2/1998 | 0.161 | 0.273 | 0.255 | 0.143 | 0.102 |
| 2/4/1998 | 0.184 | 0.170 | 0.184 | 0.046 | <DL |
| 2/5/1998 | 0.170 | 0.107 | 0.109 | 0.032 | 0.029 |
| 2/6/1998 | NS | NS | 0.255 | 0.092 | NS |
| 2/9/1998 | NS | NS | 0.216 | 0.089 | NS |
| 2/10/1998 | 0.208 | 0.160 | 0.158 | 0.055 | 0.126 |

NS = Not Sampled
<DL = less than detection limit (0.004 mg/L)

Table A2. Chlorate ion concentration measured throughout the Roanoke County Spring Hollow Water Treatment Plant, September 9, 1997 through February 10, 1998.

| Date | Concentration, mg/L | | | | |
|---|---|---|---|---|---|
| | **Dosed Raw** | **Filter Applied** | **Filtered** | **GAC Effluent** | **Clearwell** |
| 9/10/1997 | NS | NS | 0.029 | <DL | NS |
| 9/11/1997 | 0.019 | 0.014 | 0.014 | 0.021 | NS |
| 9/12/1997 | 0.015 | 0.011 | 0.014 | <DL | NS |
| 9/15/1997 | 0.022 | 0.014 | 0.023 | 0.016 | 0.060 |
| 9/16/1997 | 0.019 | 0.011 | <DL | NS | NS |
| 9/17/1997 | 0.016 | 0.021 | <DL | <DL | 0.067 |
| 9/18/1997 | 0.018 | 0.019 | 0.017 | <DL | 0.042 |
| 9/19/1997 | 0.016 | <DL | 0.018 | <DL | 0.067 |
| 9/22/1997 | <DL | <DL | <DL | <DL | <DL |
| 9/23/1997 | 0.014 | 0.019 | 0.014 | <DL | <DL |
| 9/24/1997 | 0.016 | 0.016 | <DL | 0.021 | 0.026 |
| 9/25/1997 | 0.015 | 0.015 | 0.018 | 0.017 | 0.025 |
| 9/26/1997 | 0.022 | <DL | 0.017 | 0.015 | 0.018 |
| 9/29/1997 | 0.015 | 0.018 | 0.017 | 0.014 | 0.019 |
| 9/30/1997 | <DL | <DL | <DL | 0.017 | 0.022 |
| 10/2/1997 | <DL | <DL | <DL | 0.016 | 0.016 |
| 10/3/1997 | 0.024 | 0.011 | <DL | <DL | 0.012 |
| 10/6/1997 | <DL | <DL | <DL | <DL | 0.017 |
| 10/7/1997 | 0.012 | <DL | 0.011 | 0.015 | <DL |
| 10/8/1997 | <DL | 0.017 | 0.017 | <DL | 0.014 |
| 10/9/1997 | 0.015 | <DL | <DL | <DL | 0.011 |
| 10/10/1997 | <DL | <DL | 0.013 | <DL | 0.070 |
| 10/14/1997 | NS | NS | <DL | <DL | NS |
| 10/15/1997 | <DL | <DL | <DL | <DL | <DL |
| 10/16/1997 | NS | NS | <DL | <DL | NS |
| 10/17/1997 | <DL | <DL | <DL | <DL | 0.016 |
| 10/21/1997 | <DL | <DL | <DL | <DL | <DL |
| 10/22/1997 | <DL | <DL | <DL | <DL | <DL |
| 10/23/1997 | <DL | 0.030 | <DL | <DL | <DL |
| 10/24/1997 | NS | NS | <DL | <DL | NS |
| 10/27/1997 | NS | NS | <DL | <DL | NS |
| 10/28/1997 | NS | NS | <DL | <DL | NS |
| 10/29/1997 | NS | NS | <DL | <DL | NS |
| 10/30/1997 | NO $CLO_2$ | | | | |
| 10/31/1997 | NO $CLO_2$ | | | | |

Table A2. Chlorate ion concentration measured throughout the Roanoke County Spring Hollow Water Treatment Plant, September 9, 1997 through February 10, 1998.

| | Concentration, mg/L | | | | |
|---|---|---|---|---|---|
| Date | Dosed Raw | Filter Applied | Filtered | GAC Effluent | Clearwell |
| 11/3/1997 | NS | NS | NS | NS | NS |
| 11/4/1997 | NS | NS | <DL | <DL | NS |
| 11/5/1997 | NS | NS | NS | NS | NS |
| 11/6/1997 | NS | NS | 0.012 | 0.011 | <DL |
| 11/7/1997 | NS | NS | 0.020 | 0.012 | 0.019 |
| 11/10/1997 | 0.018 | 0.023 | <DL | 0.012 | <DL |
| 11/11/1997 | NS | NS | 0.021 | 0.024 | NS |
| 11/12/1997 | NS | NS | 0.029 | 0.011 | NS |
| 11/13/1997 | 0.014 | 0.017 | 0.020 | 0.023 | 0.022 |
| 11/14/1997 | NS | NS | 0.026 | <DL | NS |
| 11/17/1997 | NS | NS | 0.013 | <DL | NS |
| 11/18/1997 | NS | NS | <DL | 0.018 | NS |
| 11/19/1997 | NS | NS | <DL | 0.018 | NS |
| 11/20/1997 | NS | NS | <DL | <DL | NS |
| 11/21/1997 | 0.020 | 0.015 | 0.014 | 0.014 | 0.021 |
| 11/24/1997 | 0.019 | 0.025 | <DL | 0.021 | 0.022 |
| 11/25/1997 | NS | NS | 0.014 | 0.018 | NS |
| 11/26/1997 | NS | NS | <DL | 0.017 | NS |
| 11/27/1997 | NS | NS | <DL | <DL | NS |
| 11/28/1997 | NO $CLO_2$ | | | | |
| 12/1/1997 | NS | NS | 0.014 | <DL | NS |
| 12/2/1997 | NS | NS | <DL | 0.016 | NS |
| 12/3/1997 | 0.018 | 0.020 | 0.017 | 0.016 | 0.023 |
| 12/4/1997 | NS | NS | 0.025 | 0.013 | NS |
| 12/5/1997 | <DL | 0.025 | 0.019 | 0.014 | 0.023 |
| 12/8/1997 | NS | NS | <DL | 0.012 | NS |
| 12/9/1997 | NS | NS | <DL | 0.018 | NS |
| 12/11/1997 | NS | NS | <DL | <DL | <DL |
| 12/12/1997 | 0.031 | 0.017 | <DL | 0.015 | 0.022 |
| 12/15/1997 | NS | NS | <DL | <DL | NS |
| 12/16/1997 | NS | NS | 0.013 | <DL | NS |
| 12/17/1997 | NS | NS | 0.012 | 0.017 | NS |
| 12/18/1997 | NS | NS | 0.011 | <DL | 0.042 |
| 12/19/1997 | NS | NS | 0.016 | <DL | NS |
| 12/22/1997 | NS | NS | 0.011 | <DL | NS |
| 12/23/1997 | 0.014 | 0.011 | 0.017 | <DL | 0.044 |
| 12/24/1997 | NS | NS | <DL | 0.012 | NS |
| 12/26/1997 | NS | NS | 0.018 | 0.014 | NS |

Table A2. Chlorate ion concentration measured throughout the Roanoke County Spring Hollow Water Treatment Plant, September 9, 1997 through February 10, 1998.

| | Concentration, mg/L | | | | |
|---|---|---|---|---|---|
| Date | Dosed Raw | Filter Applied | Filtered | GAC Effluent | Clearwell |
| 12/29/1997 | NS | NS | <DL | 0.011 | NS |
| 12/30/1997 | <DL | 0.016 | <DL | 0.012 | <DL |
| 12/31/1997 | NS | NS | 0.013 | 0.013 | NS |
| 1/1/1998 | NS | NS | 0.014 | 0.015 | NS |
| 1/2/1998 | NS | NS | 0.013 | 0.017 | NS |
| 1/5/1998 | NS | NS | 0.017 | 0.014 | NS |
| 1/6/1998 | NS | NS | 0.016 | 0.014 | NS |
| 1/7/1998 | 0.017 | 0.016 | 0.013 | 0.018 | 0.017 |
| 1/8/1998 | NS | NS | 0.013 | 0.015 | 0.021 |
| 1/9/1998 | NS | NS | 0.017 | 0.016 | NS |
| 1/12/1998 | 0.014 | 0.013 | 0.012 | 0.016 | 0.023 |
| 1/13/1998 | NS | NS | <DL | 0.014 | NS |
| 1/14/1998 | NS | NS | <DL | 0.013 | NS |
| 1/15/1998 | NS | NS | <DL | <DL | NS |
| 1/16/1998 | NS | NS | 0.013 | <DL | NS |
| 1/20/1998 | NS | NS | <DL | <DL | NS |
| 1/21/1998 | NS | NS | <DL | <DL | NS |
| 1/22/1998 | 0.017 | 0.023 | <DL | <DL | 0.021 |
| 1/23/1998 | NS | NS | <DL | <DL | 0.023 |
| 1/26/1998 | <DL | <DL | <DL | <DL | 0.014 |
| 1/27/1998 | <DL | <DL | <DL | <DL | 0.011 |
| 1/28/1998 | <DL | <DL | 0.014 | <DL | <DL |
| 1/29/1998 | NS | NS | <DL | <DL | 0.030 |
| 1/30/1998 | <DL | <DL | <DL | <DL | 0.028 |
| 2/2/1998 | <DL | <DL | <DL | <DL | 0.021 |
| 2/4/1998 | <DL | 0.013 | 0.011 | 0.022 | <DL |
| 2/5/1998 | <DL | <DL | <DL | <DL | 0.011 |
| 2/6/1998 | NS | NS | 0.014 | <DL | NS |
| 2/9/1998 | NS | NS | 0.013 | <DL | NS |
| 2/10/1998 | 0.026 | 0.016 | <DL | 0.015 | 0.027 |

NS = Not Sampled
<DL = less than detection limit (0.011 mg/L)

Table A3. Chlorite ion concentrations in the Roanoke County Distribution System, November 25, 1997 through February 13, 1998.

| Date | Concentration, mg/L | | | | | |
|---|---|---|---|---|---|---|
| | **Hunting Hills** | **Penn Forest** | **Oak Grove** | **Castle Rock** | **Hidden Valley** | **Cherokee Hills** |
| 11/25/1997 | 0.060 | 0.074 | 0.061 | 0.077 | 0.064 | 0.089 |
| 12/2/1997 | 0.011 | 0.026 | 0.044 | 0.054 | 0.077 | 0.109 |
| 12/9/1997 | <DL | 0.070 | 0.070 | 0.010 | 0.050 | <DL |
| 12/11-12/12/1997 | 0.010 | 0.040 | 0.030 | 0.010 | 0.030 | 0.030 |
| 12/17/1997 | 0.090 | 0.070 | 0.080 | 0.070 | 0.090 | 0.130 |
| 1/8/1998 | 0.050 | 0.090 | 0.070 | 0.100 | 0.080 | 0.100 |
| 1/16/1998 | <DL | 0.080 | 0.080 | 0.080 | 0.080 | 0.100 |
| 1/23/1998 | 0.010 | 0.090 | 0.060 | 0.060 | 0.080 | 0.050 |
| 2/13/1998 | 0.080 | 0.080 | 0.060 | 0.100 | 0.090 | 0.090 |

<DL = less than detection limit (0.004 mg/L)

Table A4. Chlorate ion concentrations in the Roanoke County Distribution System, November 25, 1997 through February 13, 1998.

| Date | Concentration, mg/L | | | | | |
|---|---|---|---|---|---|---|
| | **Hunting Hills** | **Penn Forest** | **Oak Grove** | **Castle Rock** | **Hidden Valley** | **Cherokee Hills** |
| 11/25/1997 | 0.035 | 0.046 | 0.025 | 0.040 | 0.040 | 0.032 |
| 12/2/1997 | 0.016 | 0.050 | 0.028 | 0.049 | 0.036 | 0.036 |
| 12/9/1997 | 0.020 | 0.040 | 0.030 | 0.040 | 0.030 | 0.020 |
| 12/11-12/12/1997 | <DL | 0.030 | 0.040 | <DL | 0.020 | 0.020 |
| 12/17/1997 | 0.030 | 0.060 | 0.040 | 0.090 | 0.030 | 0.030 |
| 1/8/1998 | 0.030 | 0.030 | 0.030 | 0.020 | 0.030 | 0.020 |
| 1/16/1998 | 0.025 | 0.015 | 0.043 | 0.022 | 0.012 | 0.022 |
| 1/23/1998 | 0.025 | 0.040 | 0.033 | <DL | 0.023 | 0.023 |
| 2/13/1998 | 0.030 | 0.040 | 0.030 | 0.030 | 0.030 | 0.020 |

<DL = less than detection limit (0.011 mg/L)

Table A5. Data for the calculation of chlorite ion and chlorate ion limits of detection by ion chromatography.

Actual Concentration = 0.02 mg/L

| Replicate | Concentration, mg/L | |
|---|---|---|
| | Chlorite ion | Chlorate ion |
| 1 | 0.0236 | 0.0203 |
| 2 | 0.0248 | 0.0162 |
| 3 | 0.0236 | 0.0155 |
| 4 | 0.0236 | 0.0229 |
| 5 | 0.0225 | 0.0141 |
| 6 | 0.0248 | 0.0264 |
| 7 | 0.0236 | 0.0206 |
| 8 | 0.0214 | 0.0197 |
| 9 | 0.0214 | 0.0163 |
| 10 | 0.0214 | 0.0153 |
| Std dev | 0.0013 | 0.0039 |
| T | 2.8214 | 2.8214 |
| MDL, mg/L | 0.0037 | 0.0111 |
| LOQ, mg/L | 0.0184 | 0.0555 |

Std dev = standard deviation
T = Student's T-value
MDL = method detection limit
LOQ = limit of quantitation

Table A6. Comparison of chlorite ion and chlorate ion concentrations in split samples analyzed at Virginia Tech and Novatek, an independent laboratory.

| Date | Chlorite ion, µg/L | | Chlorate ion, µg/L | |
|---|---|---|---|---|
| | Novatek | Va Tech | Novatek | Va Tech |
| 9/17/1997 | 44 | 37 | 68 | 67 |
| 9/24/1997 | 103 | 96 | 30 | 26 |
| 10/2/1997 | 147 | 129 | 22 | 16 |
| 10/8/1997 | 162 | 172 | 28 | 14 |

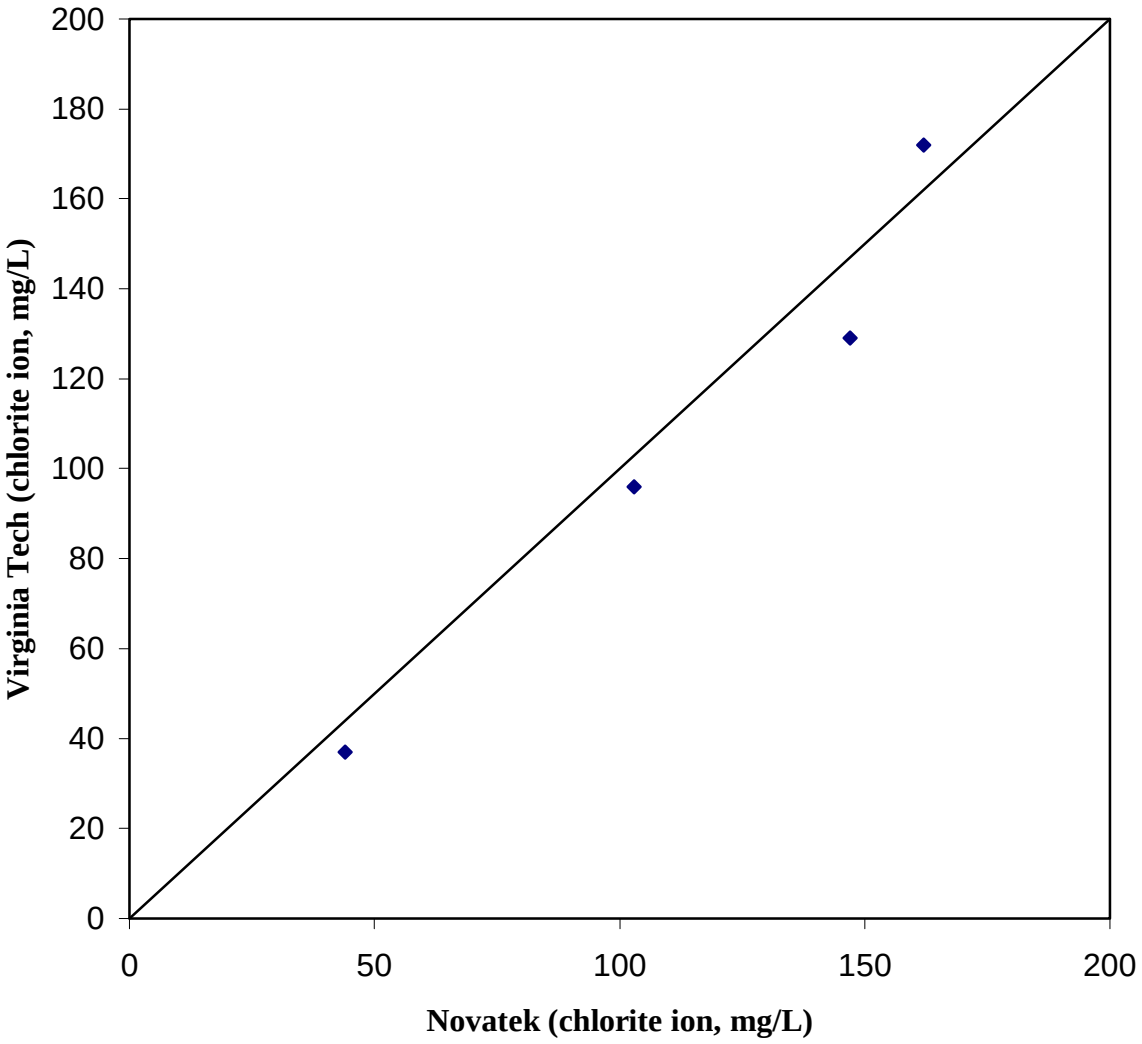


Figure A1. Comparison of chlorite ion concentrations determined at Virginia Tech and Novatek (see Table A8)

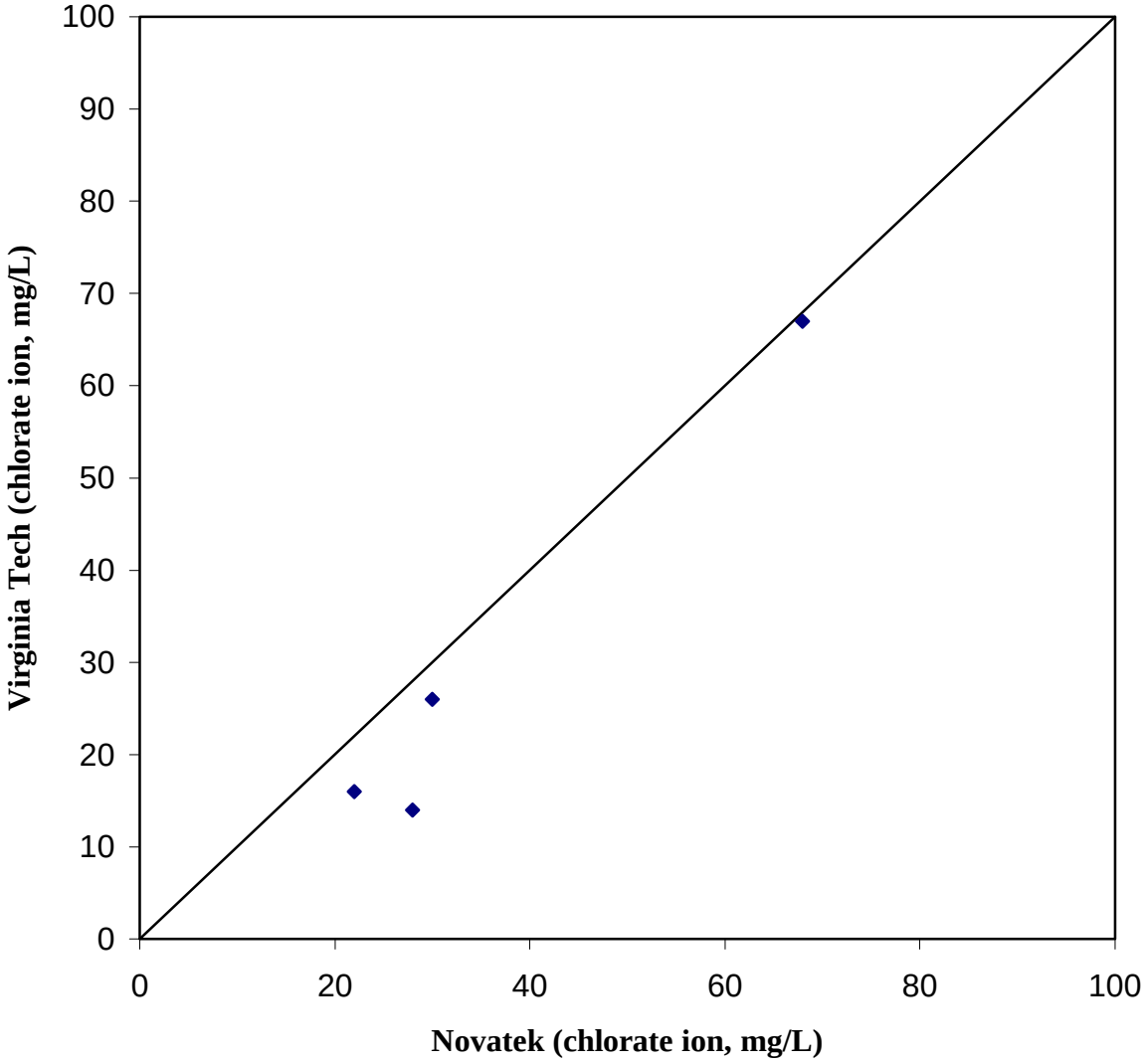


Figure A2. Comparison of chlorate ion concentrations determined at Virginia Tech and Novatek (see Table A8)

# APPENDIX B

# CHLORINE DIOXIDE

# ANALYTICAL DATA

Table B1. Chlorine dioxide concentration measured throughout the Roanoke County Spring Hollow Water Treatment Plant, November 24, 1997 through February 5, 1998.

| Date | Dosed Raw | Filter Applied | Filtered |
|---|---|---|---|
| 11/24/1997 | 0.413 | 0.397 | 0.263 |
| 11/25/1997 | 0.157 | 0.106 | <DL |
| 12/2/1997 | 0.161 | 0.133 | 0.020 |
| 12/3/1997 | 0.150 | 0.069 | <DL |
| 12/4/1997 | 0.111 | 0.163 | 0.021 |
| 12/5/1997 | 0.193 | 0.168 | 0.070 |
| 12/8/1997 | 0.045 | <DL | <DL |
| 12/9/1997 | 0.236 | 0.105 | 0.028 |
| 12/10/1997 | 0.381 | 0.330 | <DL |
| 12/11/1997 | 0.195 | 0.153 | 0.024 |
| 12/12/1997 | 0.440 | 0.092 | <DL |
| 12/16/1997 | 0.191 | 0.159 | <DL |
| 12/17/1997 | 0.207 | 0.169 | 0.025 |
| 12/18/1997 | 0.220 | 0.180 | <DL |
| 12/19/1997 | 0.175 | 0.163 | 0.078 |
| 12/22/1997 | 0.155 | 0.141 | 0.030 |
| 1/5/1998 | 0.137 | 0.109 | 0.041 |
| 1/6/1998 | 0.164 | 0.134 | 0.073 |
| 1/7/1998 | 0.157 | 0.125 | 0.053 |
| 1/8/1998 | 0.107 | 0.088 | 0.052 |
| 1/9/1998 | 0.076 | 0.080 | 0.036 |
| 1/12/1998 | 0.057 | 0.048 | 0.017 |
| 1/13/1998 | 0.121 | 0.097 | <DL |
| 1/15/1998 | 0.117 | 0.103 | 0.032 |
| 1/16/1998 | 0.154 | 0.116 | 0.073 |
| 1/20/1998 | 0.099 | 0.040 | <DL |
| 1/22/1998 | 0.099 | 0.165 | 0.062 |
| 1/26/1998 | 0.054 | <DL | <DL |
| 1/27/1998 | 0.067 | <DL | <DL |
| 1/28/1998 | 0.102 | 0.021 | 0.034 |
| 1/29/1998 | 0.114 | 0.028 | 0.031 |
| 1/30/1998 | 0.108 | 0.038 | 0.025 |
| 2/2/1998 | 0.112 | <DL | <DL |
| 2/4/1998 | 0.102 | 0.025 | 0.028 |
| 2/5/1998 | 0.079 | 0.021 | 0.018 |

<DL = less than detection limit (0.017 mg/L)

Table B2. Chlorine dioxide concentrations in the Roanoke County Distribution System November 25, 1997 through February 13, 1998.

| Date | Concentration, mg/L | | | | | |
|---|---|---|---|---|---|---|
| | **Hunting Hills** | **Penn Forest** | **Oak Grove** | **Castle Rock** | **Hidden Valley** | **Cherokee Hills** |
| 11/25/1997 | 0.157 | 0.069 | 0.063 | 0.083 | 0.086 | 0.095 |
| 12/02/1997 | 0.152 | 0.082 | 0.051 | 0.054 | 0.107 | 0.111 |
| 12/05/1997 | NS | NS | 0.026 | NS | NS | NS |
| 12/09/1997 | <DL | <DL | <DL | <DL | <DL | <DL |
| 12/10/1997 | NS | NS | 0.037 | NS | NS | NS |
| 12/11-12/12/1997 | 0.077 | 0.036 | 0.021 | 0.095 | 0.087 | 0.019 |
| 12/17/1997 | 0.066 | 0.040 | 0.040 | 0.047 | 0.032 | 0.047 |
| 01/08/1998 | 0.044 | 0.035 | 0.023 | 0.071 | 0.020 | <DL |
| 01/16/1998 | <DL | <DL | 0.026 | <DL | <DL | <DL |
| 01/23/1998 | 0.029 | 0.046 | <DL | 0.023 | 0.026 | <DL |
| 02/13/1998 | <DL | 0.036 | <DL | <DL | <DL | <DL |

NS = not sampled
<DL = less than detection limit (0.017 mg/L)

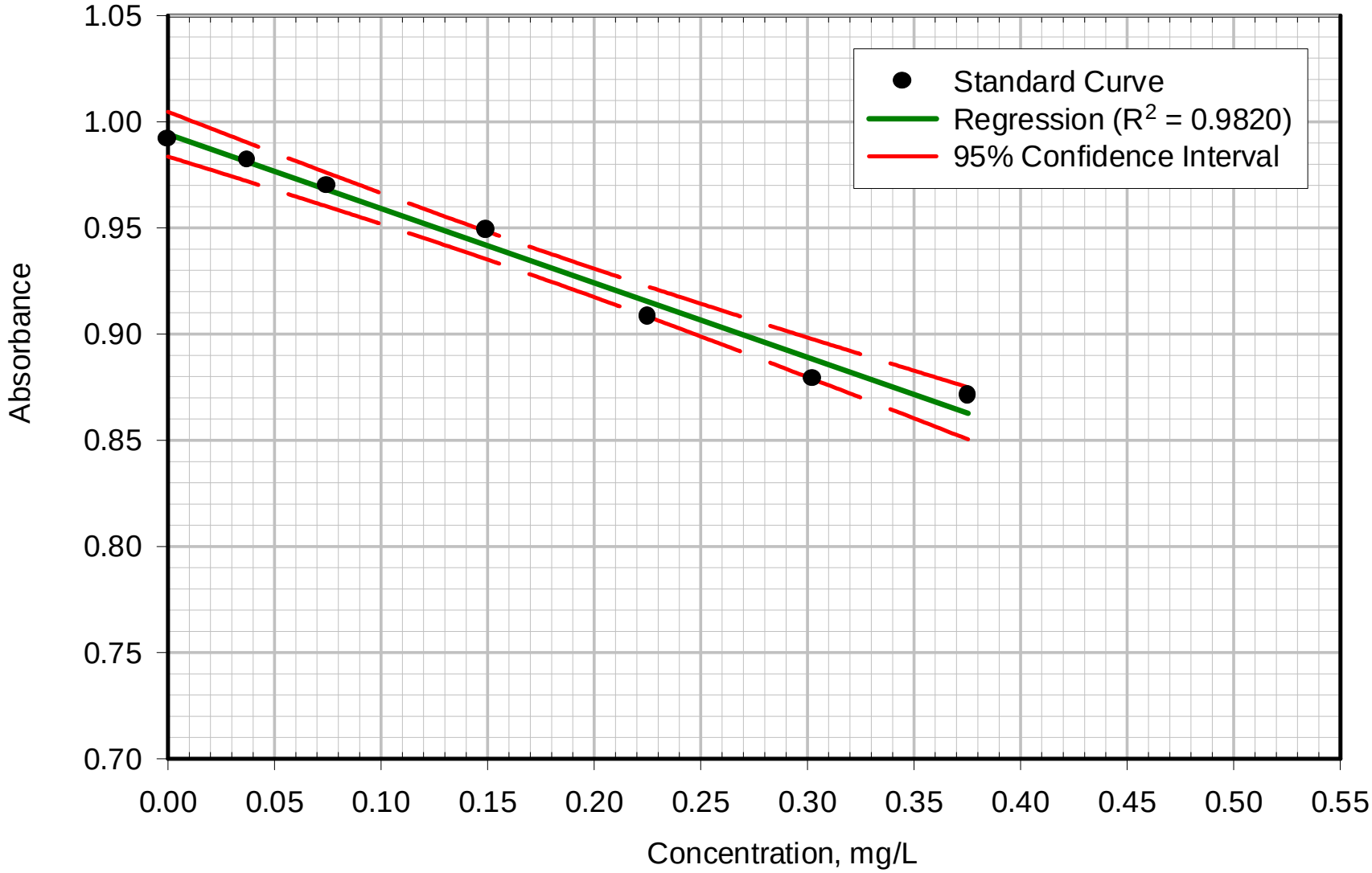


**Figure B1. LGB Standard Curve in Finished Water 11/25/97**

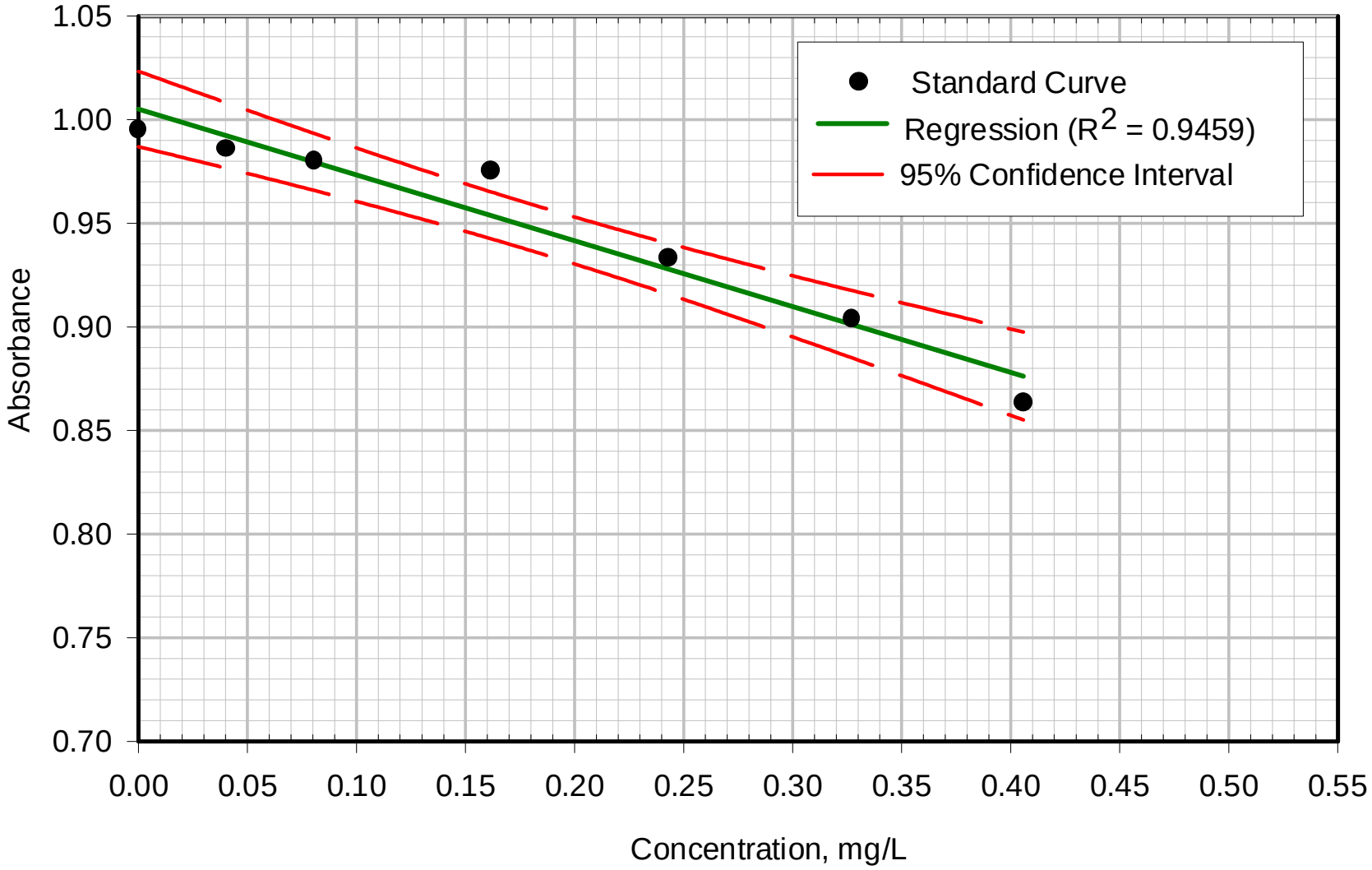


**Figure B2. LGB Standard Curve in Finished Water 12/2/97**

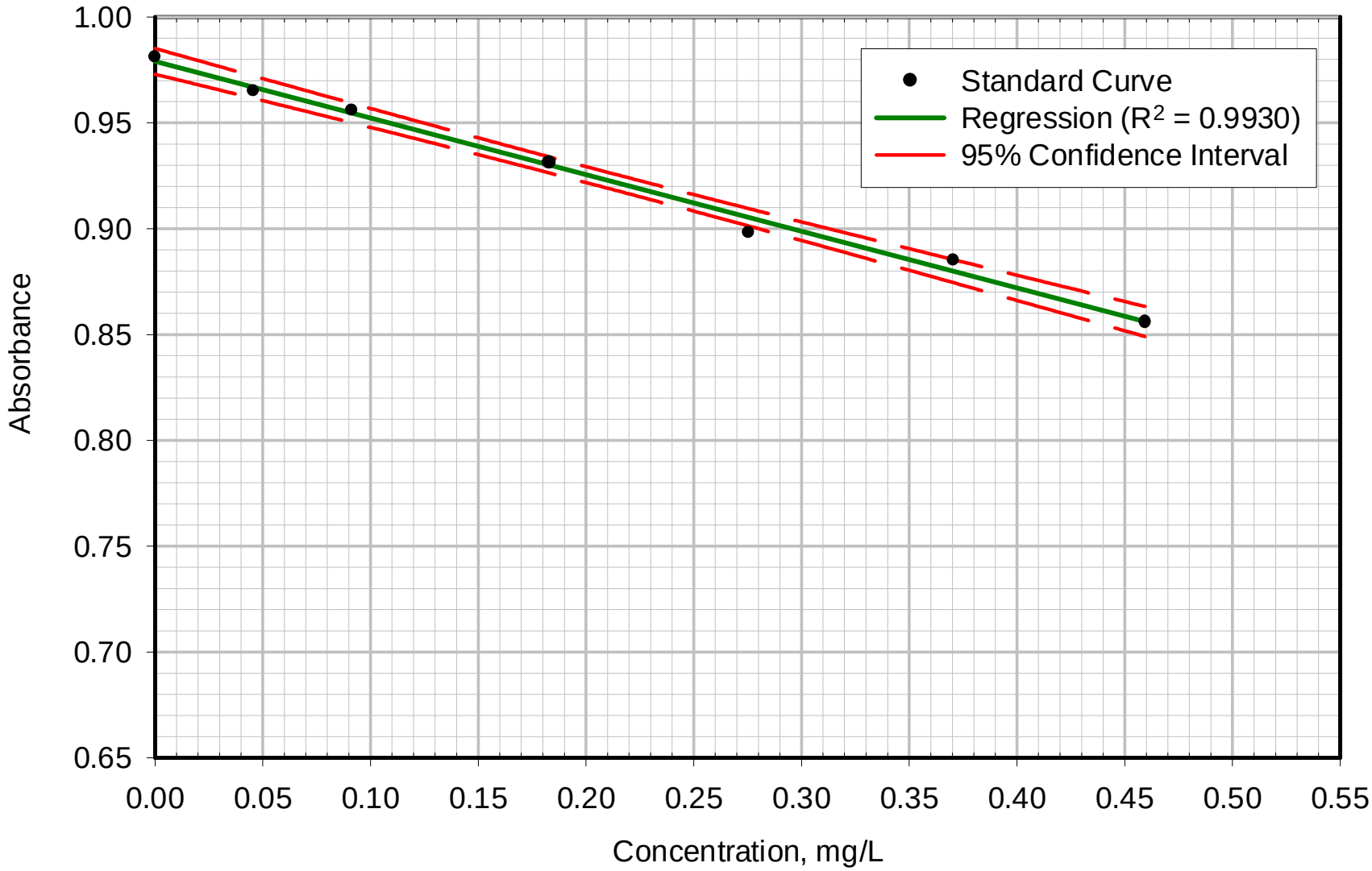


**Figure B3. LGB Standard Curve in Distribution System Water, Vauxhall Road,12/5/97**

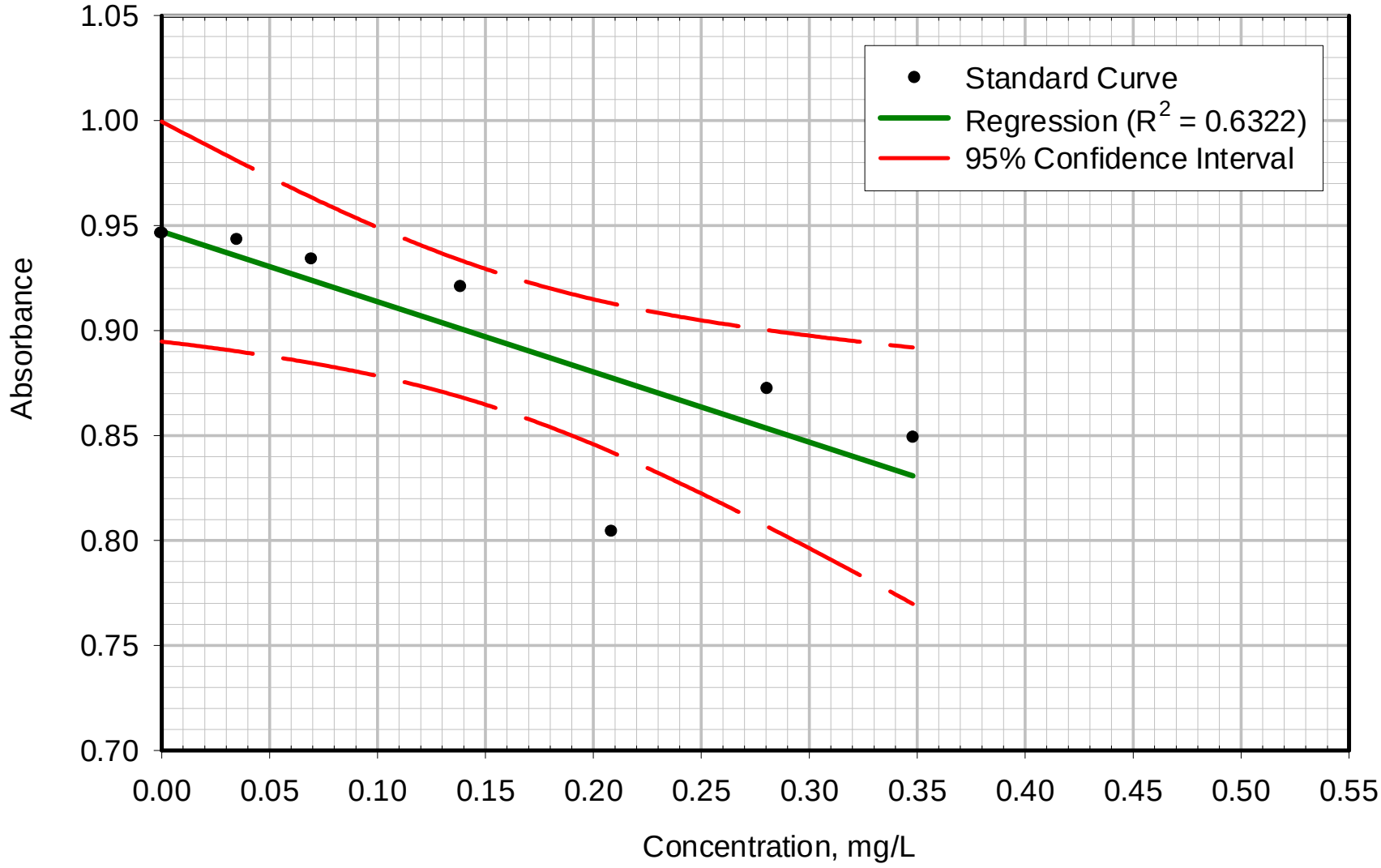


**Figure B4. LGB Standard Curve in Distribution System Water, Vauxhall Road, 12/9/97**

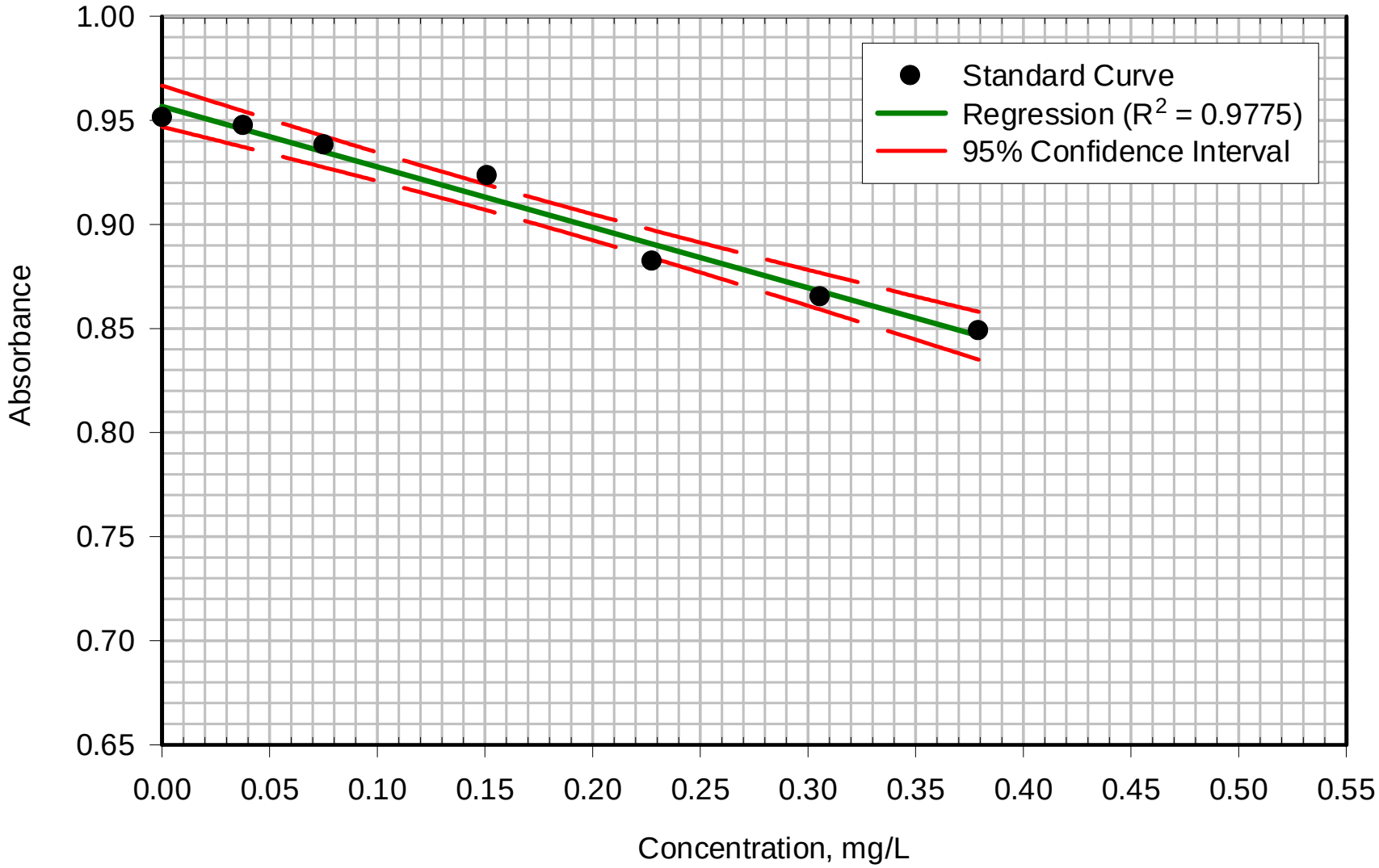


**Figure B5. LGB Standard Curve in Distribution System Water, Cordell Drive, 12/10/97**

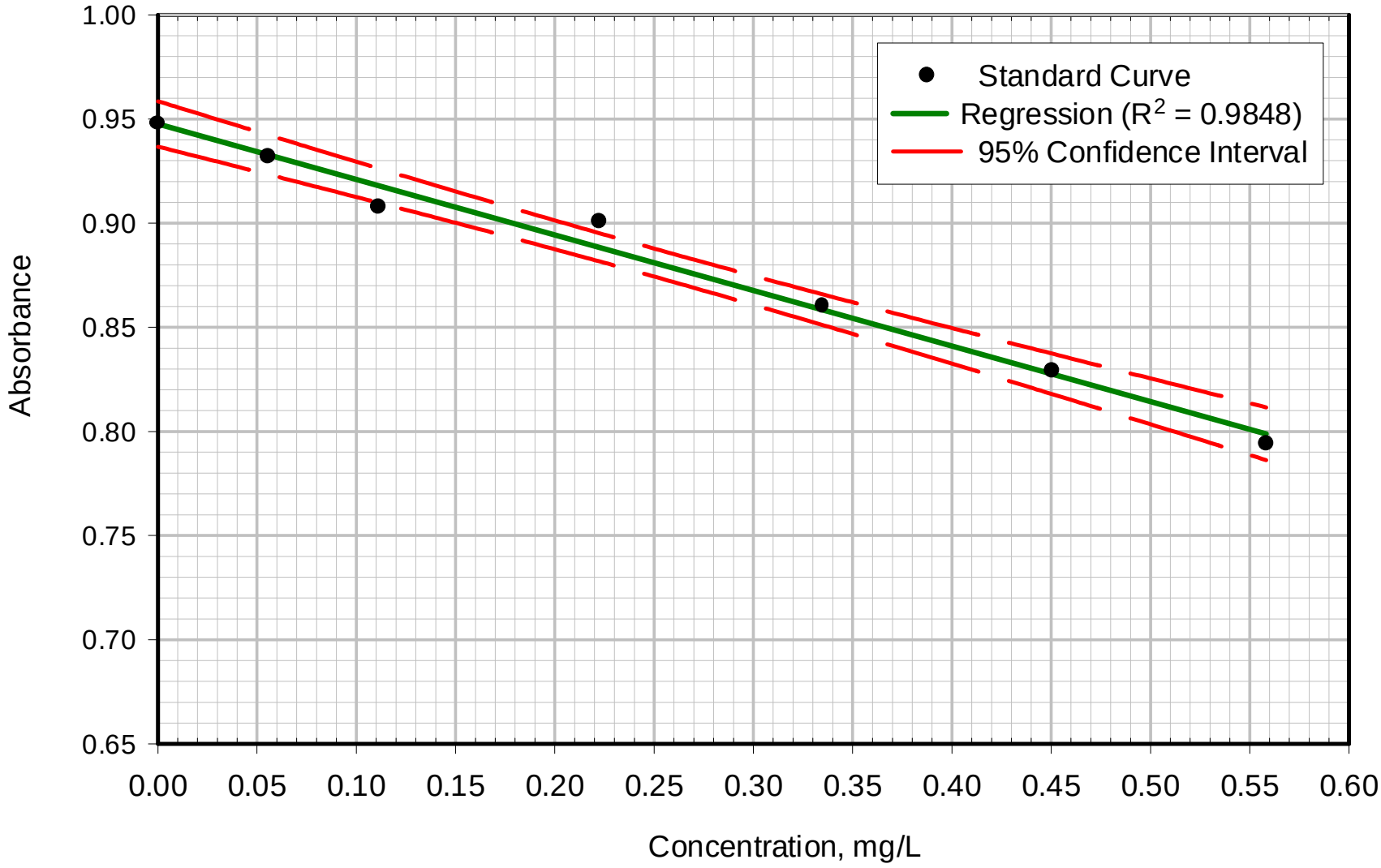


**Figure B6. LGB Standard Curve in Distribution System Water, Cordell Drvie, 12/11/97**

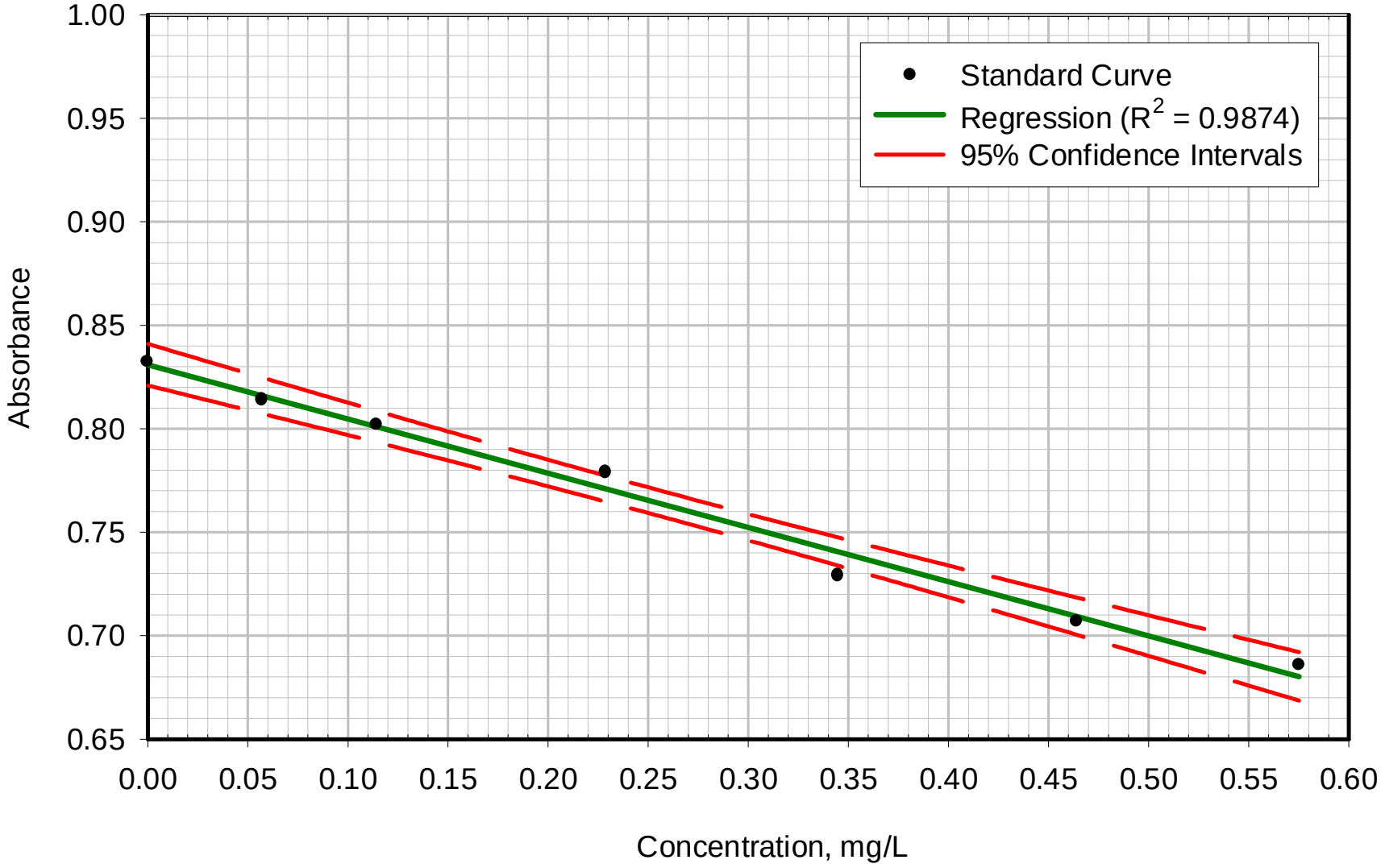


**Figure B7. LGB Standard Curve for Analysis of $ClO_2$ in Distribution System Water from Buckskin Lane, 12/12/97**

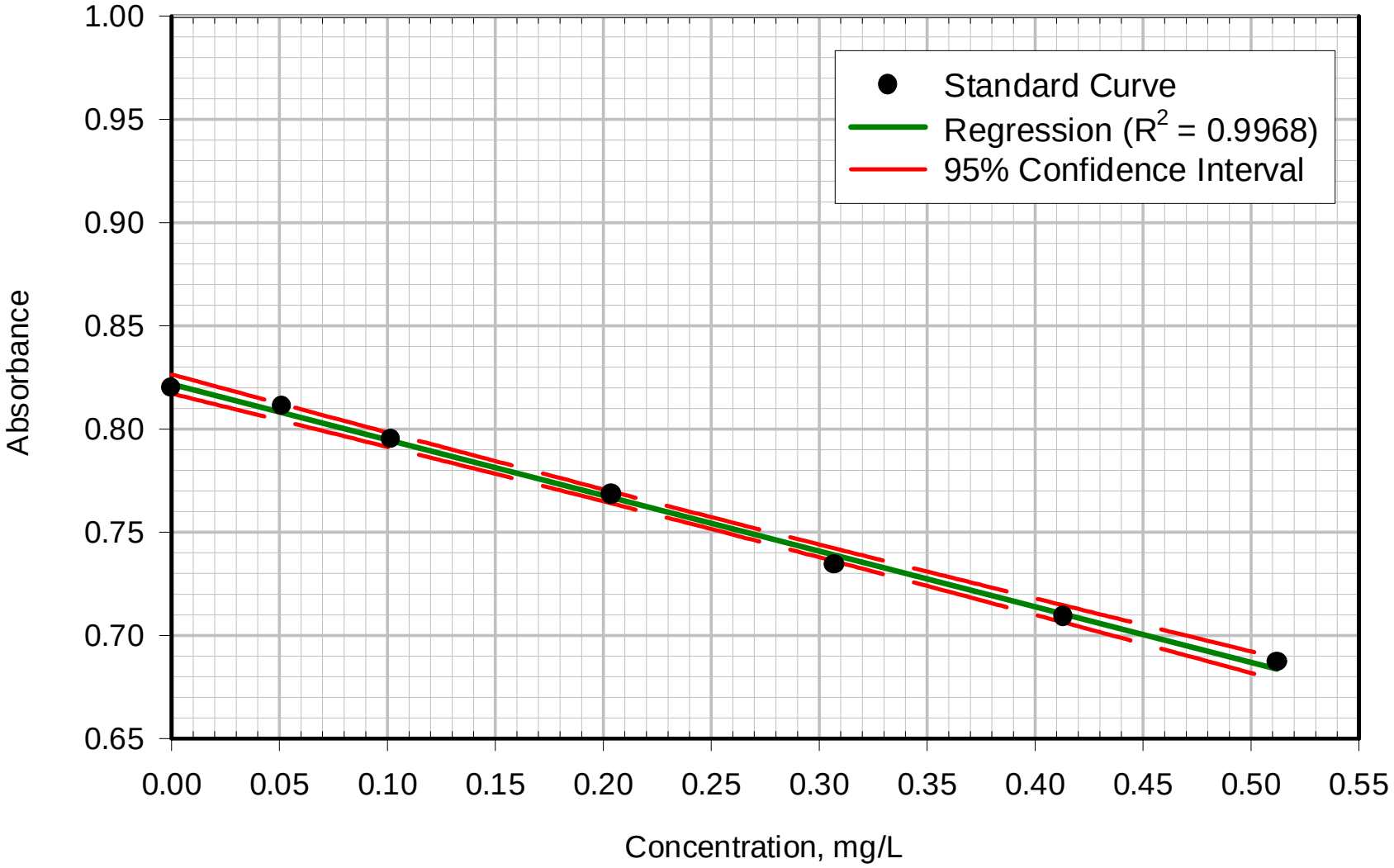


**Figure B8. LGB standard curve in distribution system water, Buckskin Lane, 12/17/97**

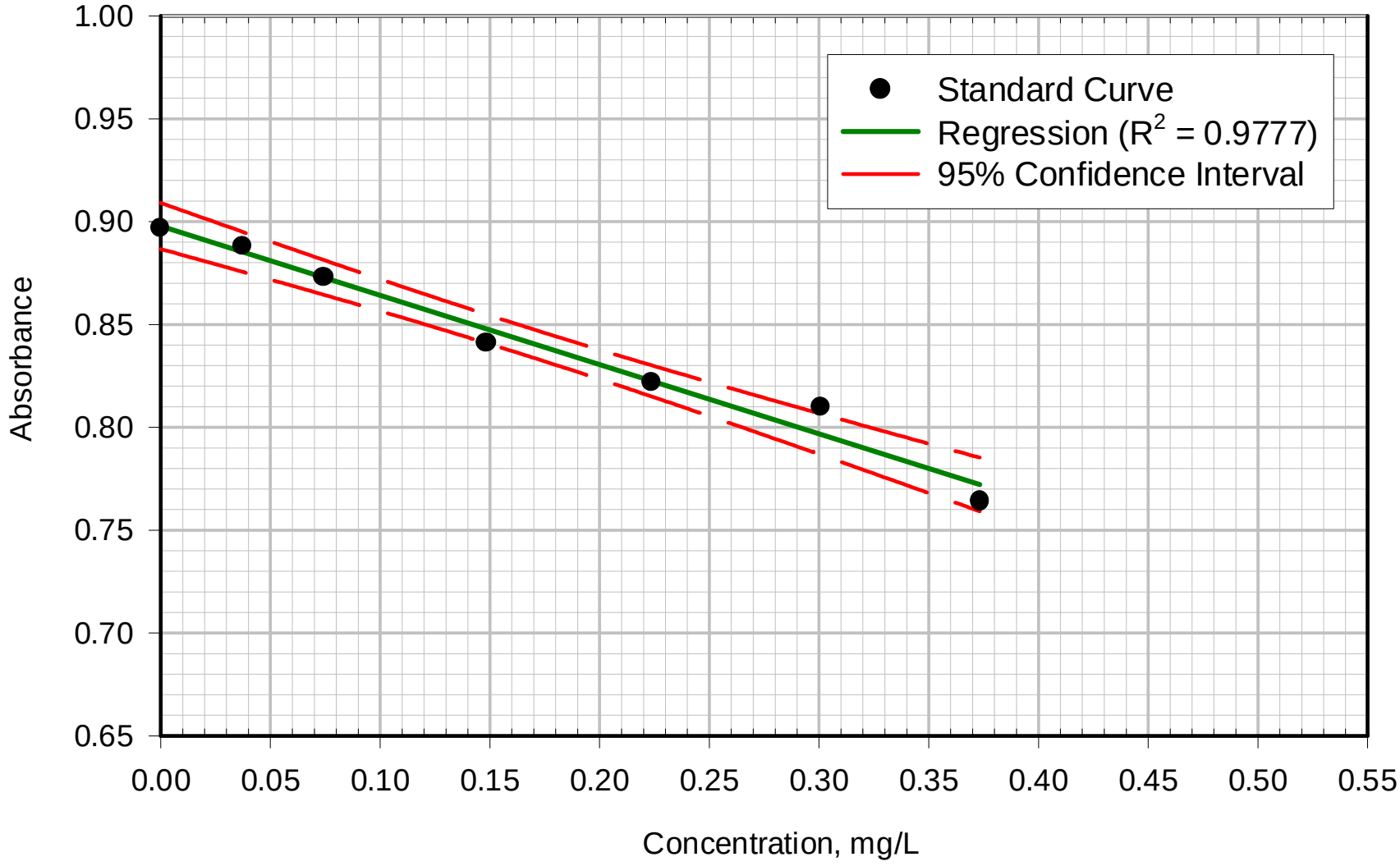


**Figure B9. LGB Standard Curve in Distribution System Water, Cordell Drive, 1/8/98**

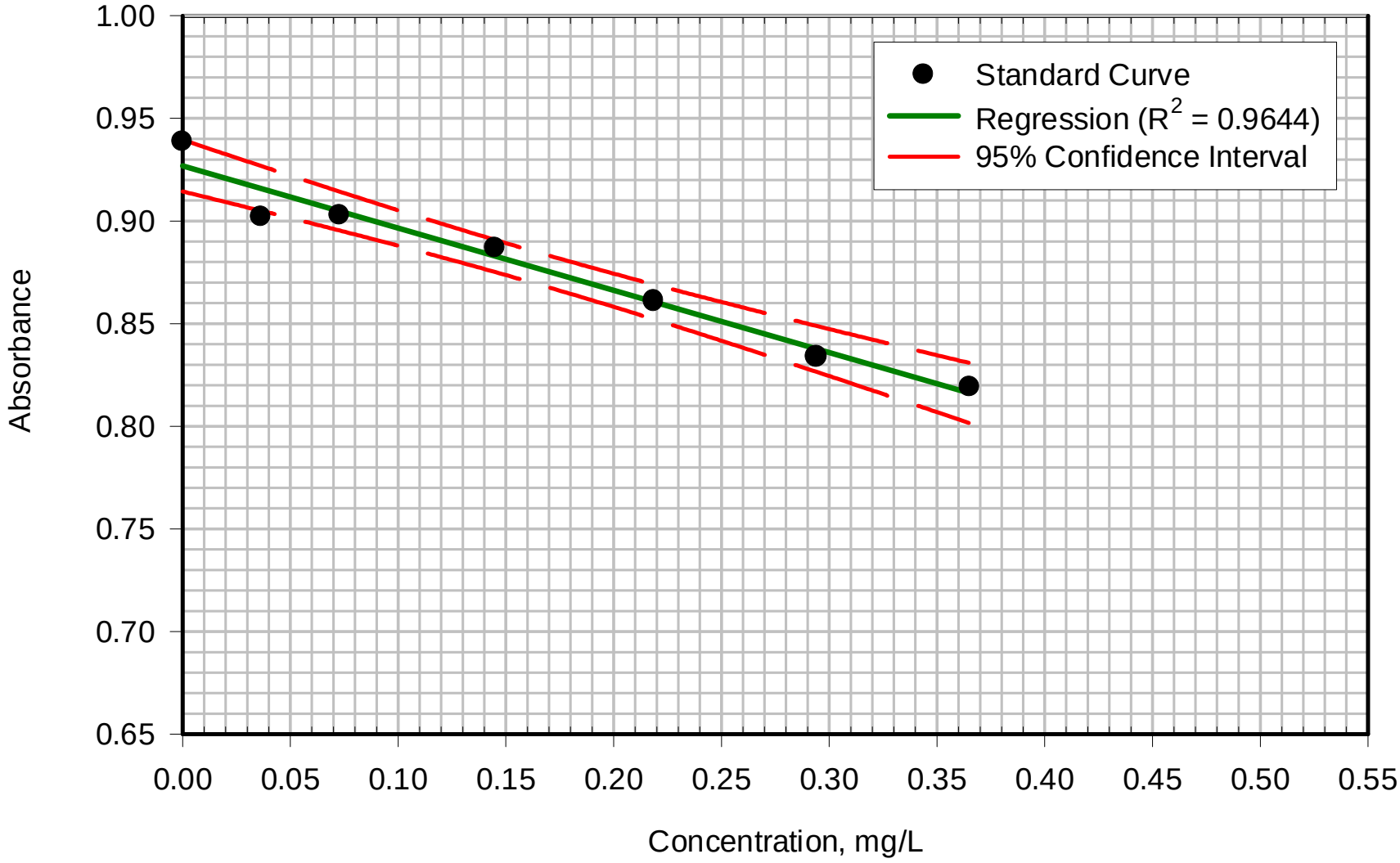


**Figure B10. LGB Standard Curve in Distribution System Water, Fairway Estates Drive, 1/16/98**

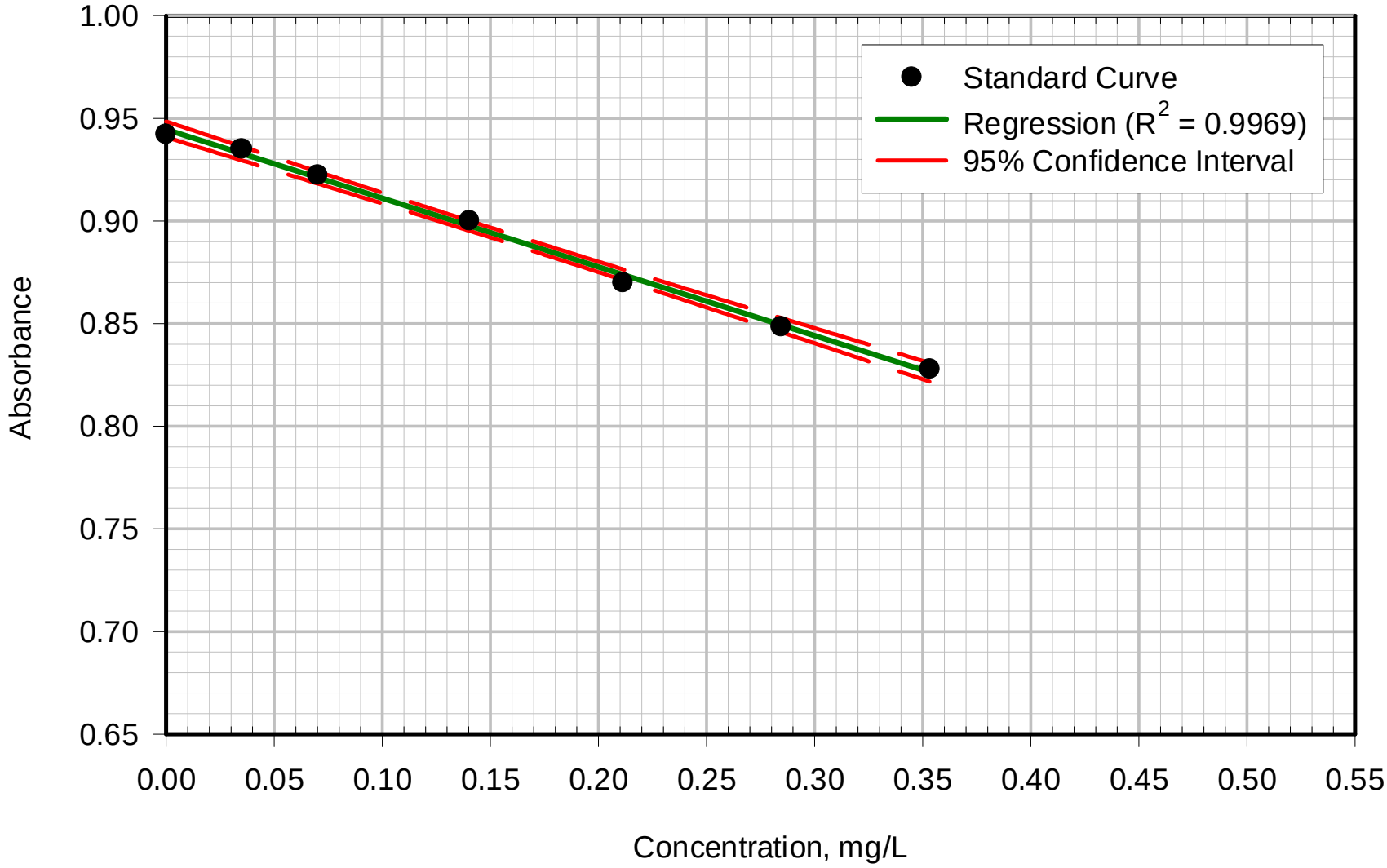


**Figure B11. LGB Standard Curve in Distribution System Water, 1/23/98**

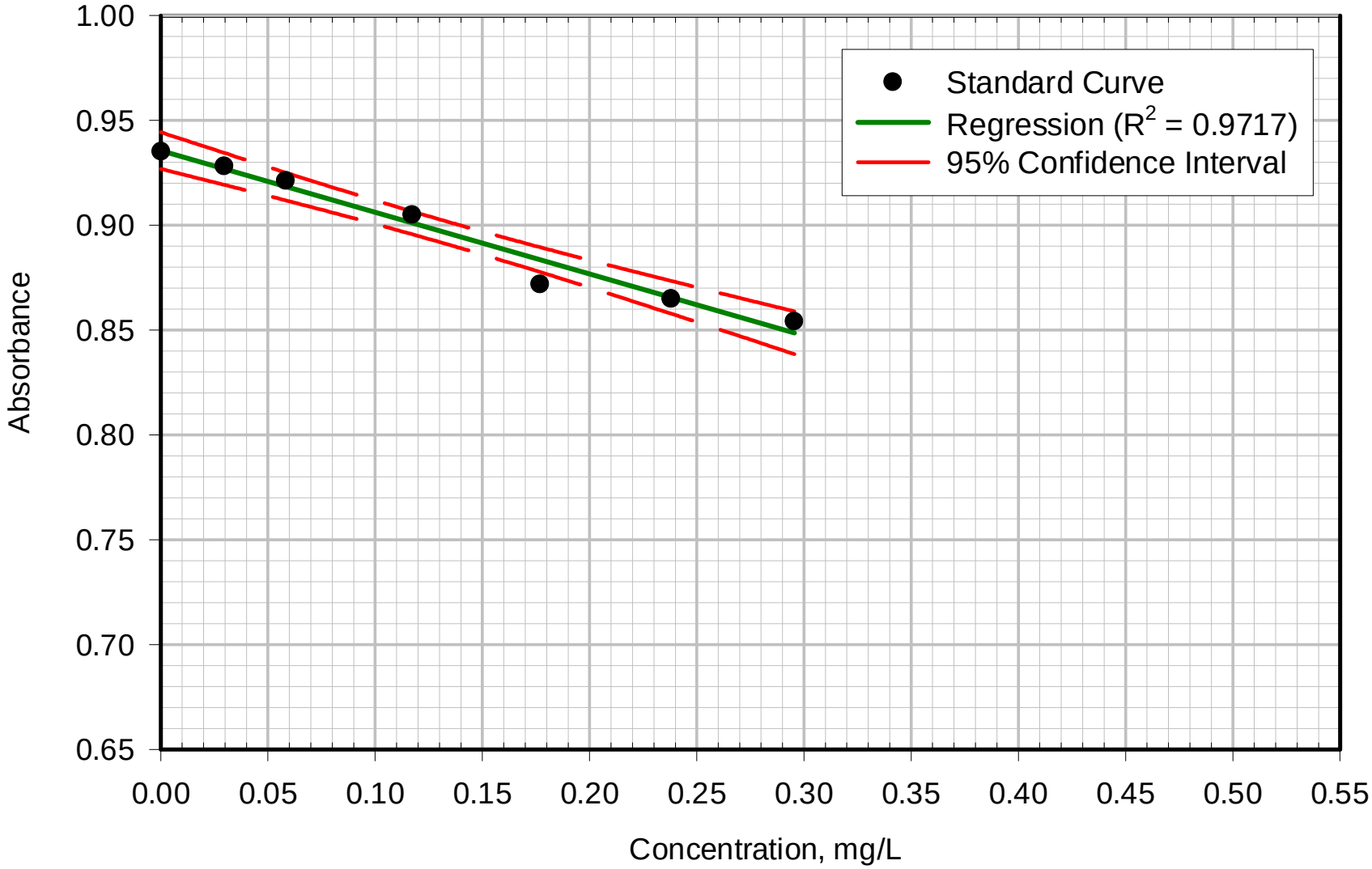


**Figure B12. LGB Standard Curve in Distribution System Water, Perigrine Crest Circle, 2/13/98**

**VITA**

Christine Ellenberger was born September 17, 1974, in Falls Church, Virginia. She received a Bachelor of Science in Civil Engineering from Virginia Polytechnic Institute and State University, Blacksburg, Virginia in the summer of 1996. During her undergraduate curriculum she interned at Montgomery Watson Consulting Engineers in Herndon, Virginia. She stayed at Virginia Polytechnic Institute and State University to earn a Master of Science in Environmental Engineering in the fall of 1999. She worked as both a teaching assistant and a research assistant while completing her degree. She accepted a job as a Civil Engineer with Black & Veatch, Inc. in Greenville, South Carolina.