

**OXIDATION OF TRIHALOMETHANE-PRECURSORS AND MANGANESE(II)
BY CHLORINE DIOXIDE AND PERMANGANATE**

by

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(ABSTRACT)

The objectives were to evaluate permanganate and chlorine dioxide as preoxidants both when they were dosed individually and when they were dosed together, for their abilities to improve water treatment plant performance. The specific goals were to determine the effect of the preoxidant conditions on coagulant requirements, filter operation, and the removals of organic carbon, trihalomethane precursors, iron, and manganese. Also, the interaction of the preoxidants with each other when dosed together was investigated. The preoxidant conditions were evaluated on both plant- and laboratory-scale bases. The plant-scale study focused on the ability of the preoxidants to enhance those aspects of plant performance listed above. The laboratory-scale study reinforced the results of the plant-scale study and included investigations to the interactions between the two oxidants when they were dosed simultaneously. The plant-scale study yielded information regarding the extent to which these oxidants helped remove the raw water constituents listed previously. The laboratory-scale study expanded on these results and included information concerning the reasons why these oxidants performed in the manner that they did.

During the period of lake stratification, when trihalomethane removal caused the greatest treatment concerns, chlorine dioxide provided the greatest removal efficiency (65 percent), but organic carbon removal suffered (45 percent). While the lake was mixing and reduced manganese posed the greatest treatment concerns, the simultaneous use of chlorine dioxide and permanganate resulted in the greatest removal efficiency (95 percent), however, objectionable tastes-and-odors were formed. In

comparison, chlorine dioxide was more apt to oxidize organic compounds (including trihalomethane and taste-and-odor precursors), and permanganate was more apt to oxidize manganese(II). When the two oxidants were dosed simultaneously, chlorine dioxide had the capacity to maintain permanganate for extended periods, possibly beyond the hydraulic retention time of the plant. Methods were developed to measure 1) chlorite concentrations in the presence of oxidized forms of manganese and 2) the relative sizes and shapes of molecular-size distributions of naturally occurring organic matter.

Acknowledgements

The author would like to express his appreciation to his graduate committee members for their assistance in the completion of this project. Dr. Hoehn's suggestions during both the research phase and editing phase were especially helpful. Dr. Knocke's guidance during the period when the manganese work was performed was invaluable. Dr. Novak's ability to see the "big picture" gave direction to the committee on more than one occasion. Drs. Larry Taylor and James Wightman from the Department of Chemistry kept the author honest when it came to manganese and surface chemistry, respectively.

The author would also to thank the County of Stafford, Virginia for providing funding for this project. Also, the following people were helpful in completing this project: _____, who was co-developer of the manganese-species determination procedure, _____, who performed all the metals determinations and suggested the use of hydroxyl amine sulfate to preserve manganese samples, _____ and his staff at the Abel Lake Water Treatment Plant who collected samples, and _____ who helped perform jar-tests. Oh, thanks to my pals - _____, _____, _____, and _____ - who gave me advice, even when it was not solicited.

This dissertation is dedicated to the author's father, _____, who might have also traveled this path were it not for a simple twist of fate.

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INTRODUCTION

Ever since the U.S. Environmental Protection Agency (EPA) established a Maximum Contaminant Level (MCL) for trihalomethanes (THMs), many water treatment plants have stopped prechlorinating their influent waters. Although this seemed the simplest, most cost-effective method of dealing with potential THM problems, the practice has, for certain plants, exacerbated several water quality problems including (a) high reduced metal (Fe and Mn) concentrations in the finished water; (b) increased consumer taste and odor complaints; and (c) decreased filter performance. As a consequence, alternate preoxidants are being sought that have the capability to minimize these problems while still achieving acceptable THM concentrations in the distribution system.

The Abel Lake Water Treatment Plant, in Stafford County, Virginia (about 40 miles southwest of Washington D.C.) is an alum filtration plant that treats 2 million gallons of water per day (MGD). Upon promulgation of the trihalomethane (THM) maximum contaminant level (MCL) of 0.10 mg/L, the plant delayed chlorination until after the settling step to avoid THM formation. This action caused the THM concentrations to decrease but other, unexpected, problems developed.

During the summer of 1984, biological growths, which formerly had been prevented by chlorination, caused periodic episodes of taste-and-odor in the drinking water. Later in the fall, when conditions in Abel Lake changed (as they normally do), manganese removal problems developed. Manganese is a naturally occurring metal in many soils and lake sediments, that can cause

aesthetic problems (brownish discoloration of the water, staining of fixtures and clothing, *etc.*) in concentrations greater than 0.05 mg/L (parts per million).

Permanganate and chlorine dioxide are two preoxidants that offer a short term solution to the problem. Neither of these oxidants form trihalomethanes when they react with organic materials, and are fairly inexpensive to use. Because chlorine dioxide and permanganate have previously taken a secondary role to chlorine as preoxidants and disinfectants in water treatment, information concerning their benefits and problems regarding water treatment is not well documented.

In this research study, chlorine dioxide and potassium permanganate were first evaluated on a plant-scale basis for their effect on the removals of 1) THM formation potential (THMFP), 2) organic carbon, 3) reduced iron and manganese. In addition, the effects of these oxidants on the coagulation and filtration processes was investigated. Second, a laboratory study was performed to determine the ability of both of these oxidants to remove organic carbon, THM-precursors, iron, and manganese. Third, the oxidation/reduction relationship between a) the oxidants themselves and b) the oxidants and two reducing agents (manganese(II) and organic carbon) was explored. Finally, the interference of manganese in chlorine dioxide, chlorite and chlorine determinations and the use of ultrafilters for sizing naturally occurring organic molecules were investigated.

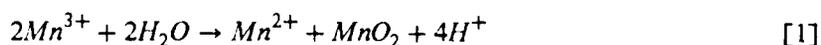
In this study, the oxidants were often referred to as preoxidants. This term, preoxidant, was meant to imply the method with which the oxidant was used. Preoxidation refers to oxidants dosed to the raw water, prior to any other treatment. Preoxidation was only appropriate in the context of plant-scale studies. In the laboratory-scale studies, permanganate and chlorine dioxide were referred to as oxidants.

LITERATURE REVIEW

General Chemistry of Manganese and Iron

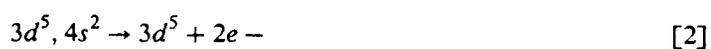
Manganese has an atomic weight of 54.94 amu and an atomic number of 25. As a member of the transition series, it can exist in several oxidation states. The species found in aqueous solutions include II, III, IV, VI, and VII. Manganese(II) and manganese(IV) are most common in natural waters (1). Manganese(VII) (permanganate) is important in its role as an oxidant in water treatment and more will be said about this species in the section on permanganate.

The chemistry of manganese(III) is not extensive. In the presence of a reductant, it is easily reduced to manganese(II). If no reductant is present, manganese(III) disproportionates as follows:

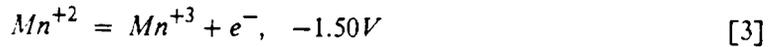


The equilibrium constant for this reaction is approximately 10^9 (1).

Manganese(II) is the most stable oxidation state of manganese in the natural environment. Its stability has been attributed to its half-filled d-level:



In neutral and acid solutions manganese(II) occurs as the hexaquo complex $[\text{Mn}(\text{H}_2\text{O})_6^{+2}]$ (1). Compared to Fe^{+2} , Mn^{+2} is quite resistant to oxidation as shown by the standard oxidation potentials listed below (2):



Manganese(IV) is most commonly found in nature as MnO_2 (1). This compound is relatively inert to most acids, but, if dissolved, it will react with strong reducing agents (3).

Iron, atomic weight 55.85 amu and atomic number 26, is also a member of the transition series. Because it has fewer stable oxidation states, iron is chemically simpler than manganese. Its position on the periodic table indicates that it differs from manganese by the addition of one electron in its d-orbital, a neutron and a proton. The oxidation states most important to its aqueous chemistry are iron(II) and iron(III).

Iron(III) is much more stable than its manganese counterpart (equations [2] and [3]). The removal of a 3d electron is relatively easy because a half-filled, stable 3d-orbital is left. The reaction is as follows:



In solutions of pH greater than two to three, colloidal gels of hydrous ferric oxide are precipitated (3).

Iron(II) is also found in neutral to acidic solutions as the hexaquo complex $[\text{Fe}(\text{H}_2\text{O})_6^{+2}]$. This oxidation state is less stable than manganese(II) because of the extra electron in the d-orbital. iron(II) has six electrons in its d orbital. As a consequence, iron(II) is less resistant to oxidation by a half (equations [3] and [4]).

Occurrence of Manganese and Iron

Manganese is a relatively abundant element, second only to iron in the order of abundance of heavy metals. Among the more important mineral forms are pyrolusite [MnO_2], manganite [$\text{MnO}(\text{OH})$], rhodonite [MnSiO_3], braunite [$3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$], hausmannite [Mn_3O_4], pyrochroite [$\text{Mn}(\text{OH})_2$], and rhodochrosite [MnCO_3] (3). Manganese is an essential nutrient for many plants and animals.

Manganese is found in many surface waters and groundwaters. Its oxidation state in natural waters varies and is normally manganese(II), manganese(III) or manganese(IV) (1). The concentration of manganese in water is usually less than 1.0 mg/L but may be as high as 10 mg/L (4). At these concentrations, the element is not toxic but can present secondary water-quality problems, including the staining of clothes and porcelain fixtures, unpleasant tastes, increased turbidity, and the precipitation into and fouling of distribution systems. In 1962, the U.S. Public Health Service established a standard of 0.05 mg/L for manganese (1).

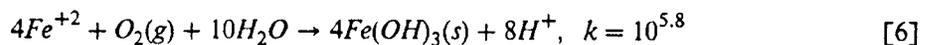
Iron is the most common heavy metal and the fourth most abundant element in the earth's crust. The important mineral forms are hematite [Fe_2O_3], magnetite [Fe_3O_4], limonite [$\text{FeO}(\text{OH})$], and siderite [FeCO_3] (3). Iron, the most important transition metal to living systems (3), is found in both surface waters and groundwaters at concentrations that vary greatly from a trace to 10 mg/L (4). At these concentrations iron is not toxic but will impart turbidity, stain clothing and porcelain fixtures, and taste unpleasant. Because the chemistries of iron and manganese are similar, the elements often occur together, though not chemically bound. The species and concentrations of both iron and manganese encountered in nature are dependent upon the type of water in which it is found (i.e., lake, river or groundwater). For example, iron in an unpolluted, well oxygenated stream is usually present as either a suspended ferric hydroxide or an organic complex, which will decrease in concentration by sedimentation when flushed into quiescent waters.

Reduced iron and manganese (Fe^{+2} and Mn^{+2}), which are the most soluble forms of these elements, occur at greater concentrations in surface and ground waters than do the more oxidized

forms (Fe^{+3} , Mn^{+3} and Mn^{+4}). Figures 1 and 2 show that the oxidation states of these metals are determined by the specific pH and redox potential of the solution (5). Reduced forms are most common in waters with a low pH and a low redox potential. These conditions, pH and redox, can vary dramatically in lakes and reservoirs. Many lakes in temperate climates stratify thermally, preventing oxygen from reaching the lower waters (hypolimnion). Biological activity, prevalent in the sediment and hypolimnion of enriched (eutrophic) lakes, causes reduction of both pH and redox potential (6). Under these conditions, the oxidized precipitates of iron and manganese [$Fe(OH)_3$, $MnO(OH)$ and MnO_2] are reduced to the (II) oxidation state [i.e., $Mn(II)$ and $Fe(II)$] (6, 7). Sediments in natural lakes and older reservoirs contain reserves of manganese and iron that have previously been precipitated and entombed. The low redox conditions in the sediment shift the equilibria towards the reduced species [manganese(II) and iron(II)], which migrate upward through the interstitial waters of the sediment (8). The manganese and iron remain dissolved in the lake's hypolimnion until the fall when, due to decreasing temperatures, the water becomes homeothermal and begins to mix (6). When the iron- and manganese-laden lower waters mix with the oxygen-rich upper waters, most of the iron and manganese are oxidized and precipitated (7). In this way, the oxidation states and concentrations of both manganese and iron in eutrophic, temperate lakes and reservoirs vary with season.

Removal of Iron(II) and Manganese(II)

Water treatment plants treating waters rich in manganese or iron typically oxidize the reduced species to a form which can be removed by adsorption to a solid phase (9, 10). Iron is more easily oxidized than manganese, and many times aeration of the water at a pH greater than 7 or 8 is sufficient. The stoichiometry of iron oxidation is as follows (11):



Manganese is more stable in the manganese(II) state than is the ferrous ion and is thus more difficult to oxidize from both a thermodynamic and a kinetic standpoint (12). Because it is more dif-

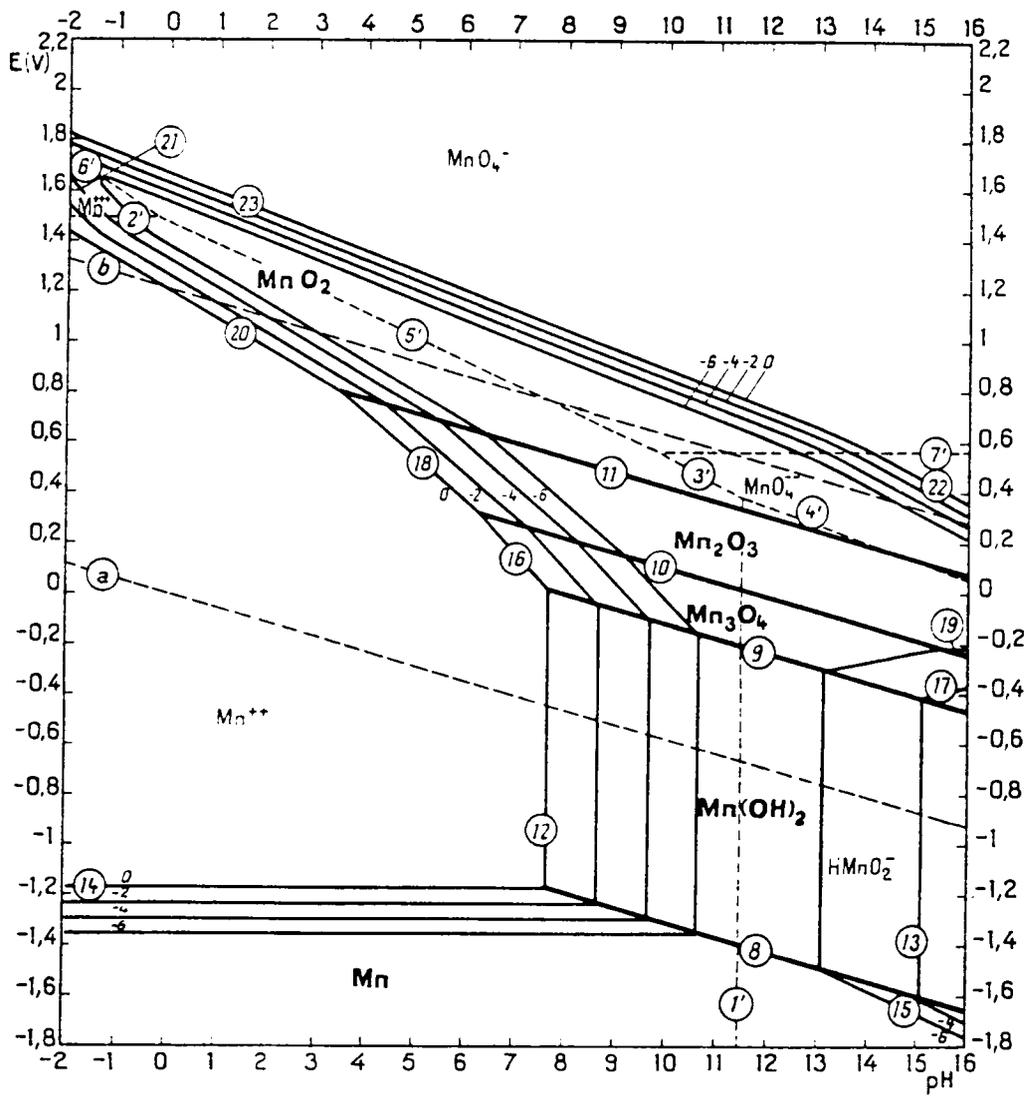
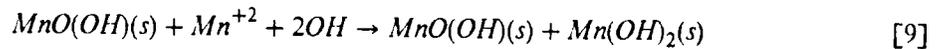
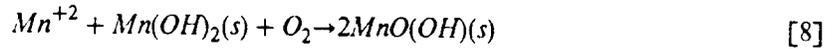


Figure 2. Pourbaix diagram for manganese (5).

difficult to oxidize manganese than to oxidize iron, manganese oxidation has been the subject of more research. The proposed mechanism for the oxygenation of manganese is as follows (13):



During these reactions, the rate of manganese oxygenation depends on the rate of formation of the initial hydroxide as a catalyst surface in equation [7]. Upon formation of the surface, the oxidation proceeds first by the instantaneous adsorption of Mn^{+2} to the surface, then by the oxidation to $MnO(OH)$ (7). This mechanism is more favored at higher pHs. Thus, to optimize manganese removal, some water treatment plants elevate the pH to about 10 and add an oxidant.

Particles of oxidized manganese can adsorb cations such as manganese(II) (14). This adsorption phenomenon influences the nature of the manganese precipitate and the stoichiometry of manganese oxidation. (The reaction stoichiometry of chlorine dioxide and permanganate oxidation of manganese(II) is presented in later sections.) Stumm and Morgan (12) have demonstrated that particles of oxidized manganese range in oxidation state from 1.6 to 3.8 depending on such reaction conditions as the pH, the rate of particle growth, and the rate of oxidation. They theorized that manganese(II) adsorbs to the insoluble manganese particles and becomes incorporated into the particle matrix without being oxidized. This occurs only when the growth rate of the particles is greater than the rate of oxidation (13). The reaction stoichiometry is changed because some manganese(II) is removed by adsorption subsequent and incorporation into a manganese oxide particle, not by oxidation. Thus, less oxidant is needed than is predicted by stoichiometric requirements. The product of manganese oxidation is probably a combination of $Mn(OH)_2$, $MnO(OH)$ and MnO_2 (13-15).

The zero point charges of manganese oxide particles (MnO_x) and aluminum hydroxides (used as a coagulant to remove turbidity in water treatment) are roughly 3 to 4 and 7 to 8, respectively (15).

Thus, between pH three and pH eight, MnO_x and $\text{Al}(\text{OH})_3$ will have an electrostatic attraction. This is beneficial to manganese removal because the MnO_x particles adsorb to the aluminum hydroxides, which precipitate from solution. In addition, MnO_x can be removed on the filter (10). In both cases, manganese removal is optimized when the particle sizes are increased. Calcium reduces the surface charge of MnO_x particles, thus allowing Van der Waals attraction forces to dominate, which result in larger particles. Thus, cation concentration is important to manganese removal (16).

Organic Compounds

In the mid-70s, two independent studies (28, 29) reported the existence of chloroform, a trihalomethane (THM) in chlorinated drinking water. Rook (29) postulated that the naturally occurring organic materials were the major precursors of THMs that were found in the drinking water. Subsequent studies have verified this postulate, and investigations into the nature and origin of naturally occurring organic compounds intensified.

Origin and Classification

Compared to inorganic compounds, the information regarding naturally occurring compounds in water supplies is relatively ambiguous. The organic carbon concentration in surface and groundwaters is highly variable, but some generalizations can be made. Groundwaters typically have low concentrations of organic carbon (0.5 to 1.0 mg/L) because they are reduced by bacterial decay and adsorption to soil. Groundwater in states such as Florida are atypically high in organic compound concentrations. Surface water has substantially more organic carbon; concentrations range from 1 to 10 mg/L and can be as high as 30 to 50 mg/L in marshes and bogs (17).

Dissolved organic matter in lakes is either of allochthonous or autochthonous origin. Outside sources include leaching of soil organic matter (17, 18), and trace quantities in rain directly entering the basin (19) or tributaries. From inside the lake basin, organic matter is released by algae (20), aquatic macrophytes (21) and the sediment (17). Mouchet (22) has found that terrestrial vegetation not removed from reservoirs prior to inundation can add to the dissolved organic carbon (DOC) concentration of the lake. Once in a lake, organic matter is removed by adsorption to sediment (especially high molecular weight organic materials) (23), photodegradation (23) or biodegradation (17).

The organic material in natural waters has been classified on the basis of either chemical characteristics or chemical identification. Figure 3 shows a histogram of the classifications of organic compounds in a river water. As is shown, the organic compounds that can be identified comprise only 20 percent of the total quantity of organic matter and are typically the byproducts of biological activity (17). The remaining 80 percent is composed of large, amorphous, organic compounds called "humic substances" and "hydrophilic acids". Humic substances result from the degradation of plant remains and are defined by Thurman (17) as being polyelectrolytic acids retained by XAD resin at pH 2. In solution, humic substances are colored, nonvolatile, and range in molecular weight from 500 to 5,000 (17). Humic substances are further categorized on the basis of solubility in an acid solution. At pH 1.0, humic acid precipitates and fulvic acid remains in solution (24).

Hydrophilic acids comprise about 30 percent of the total nonidentifiable organic carbon concentration. They derive their name from their high degree of water solubility, and they are not retained by XAD resin at pH 2. This characteristic makes the isolation, purification and subsequent analysis of these compounds difficult (17). Consequently, relatively few studies into the nature of these compounds have been performed.

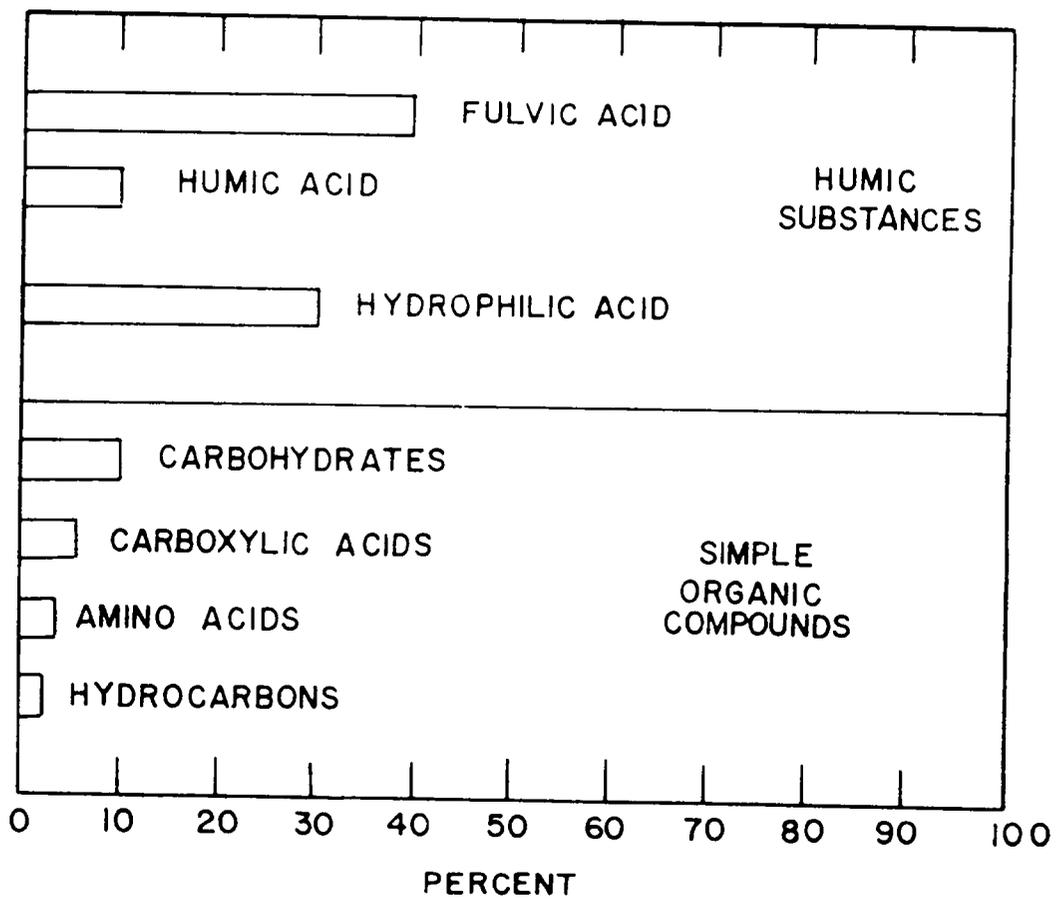


Figure 3. Dissolved organic carbon (DOC) histogram for average river water with a DOC concentration of 5 mg/L (17).

Characterization of Humic Materials

Beyond the operational definitions described above, humic substances comprise an ill-defined constituent of natural waters. No exact molecular formula of humic substances is available, but many researchers agree that they are dominated by aromatic rings containing hydroxyl and carboxyl groups (17, 23-27). Several models of humic substances have been proposed; two of which are illustrated in Figure 4 (26, 27). Elemental analysis (17) reveals the approximate composition as follows: 50 percent carbon, 5 percent hydrogen, 40 percent oxygen, and 1 to 2 percent nitrogen. Humic acids have a higher ash content (5 percent) than fulvic acids (1 percent), but otherwise the two forms are of similar composition.

Molecular Size

Four methods have been used to determine the molecular size of dissolved organic matter, and a good review of these is given by Thurman (17). The molecular sizes are often expressed in atomic mass units or daltons when in actuality some methods (gel permeation chromatography and ultrafiltration) measure the size, not the weight, of the molecules. Evidently this has been done for several reasons: to aid in the comparison to previous studies, for convenience and because it has been accepted in previous literature. This practice has been continued in this text for these three reasons, but the reader should remember that different molecular geometries make the extrapolation of molecular weight data to molecular size ambiguous, at best.

The molecular weights of dissolved organic carbon (DOC) vary with the water source and the sizing method employed. Probably the most accurate method involves the use of x-ray diffraction and yields molecular weights substantially lower than either gel permeation chromatography or ultrafiltration. X-ray diffraction showed that fulvic acids were typically 500 to 2,000 daltons and humic acids were about 2,000 to 5,000 daltons (17). Analysis by ultrafiltration resulted in a size

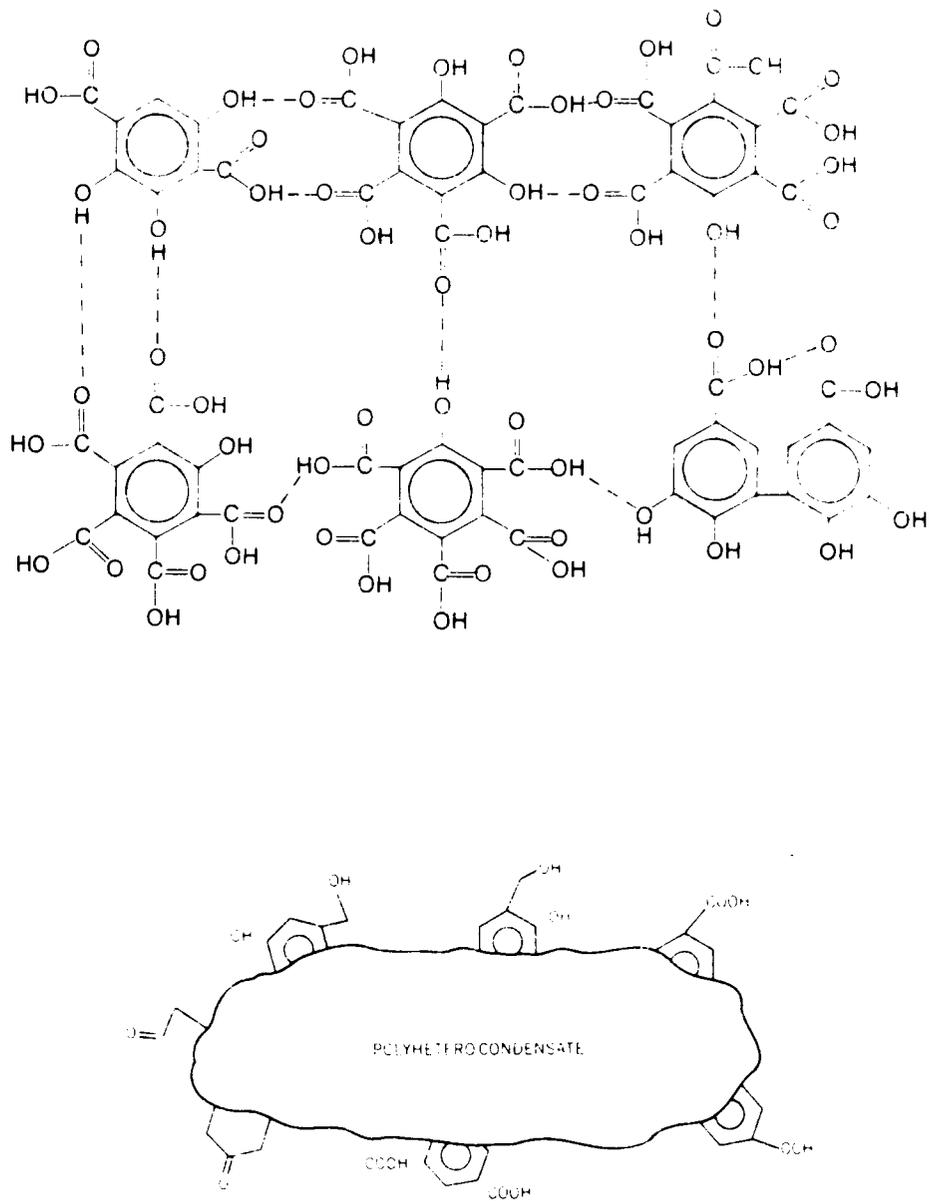


Figure 4. Proposed structures of humic substances from reference 27 (top) and reference 26 (bottom).

range of 5,000 to 20,000 daltons for unprocessed solutions containing all classes of organic material (17).

Chlorinated Organics

In the mid-1970s, two major studies reported the occurrence of halogenated organic materials in chlorinated waters that contained humic substances (28, 29). In the United States, Bellar *et al.* (28) detected chloroform in treated drinking water at concentrations ranging from 37 to 150 ug/L. The highest concentrations were found in finished waters having surface waters as a source. In the Netherlands, Rook (29) substantiated this find and explored the effects of pH, reaction time, chlorine concentration and fulvic acid concentration on the formation of trihalomethanes (THM). Rook found a positive correlation between each parameter tested and the final THM concentration. The yield of THMs from the DOC was found to range from about 50 to 100 ug THM/mg DOC.

The results of two epidemiological studies caused the occurrence of organic chemicals in drinking water to take on added significance. First, in 1976 a correlation between organic chemicals in water supplies and cancer mortality among white males was established (98); second, chloroform was found to be carcinogenic to rats (100). In response to mounting evidence of widespread THM contamination, the EPA published a proposed interim maximum contaminant level (MCL) for total trihalomethanes of 0.10 mg/L in 1979 (100). In most water supplies, the THMs of concern are, in decreasing order of occurrence, chloroform (CHCl_3), bromodichloromethane (CHCl_2Br), chlorodibromomethane (CHBr_2Cl) and bromoform. In its November 29, 1979, publication, the EPA mandated compliancy by water utilities serving more than 10,000 customers by November 1983.

Using model compounds, Rook developed a reaction mechanism that explained the effects of pH and concentration (29). Subsequent study of the reactions between chlorine and model compounds has revealed two reaction pathways for chlorine and humic materials, oxidation and substitution (31). Substitution reactions result in chlorinated organic compounds, and oxidation does not. In

general, chlorine oxidizes aldehydes and organic nitrogen to carboxylic acid and nitrogen gas, respectively. In substitution reactions, chlorine is attracted to electrophilic sites on aromatic rings or double bonds (31, 32). Studies with model compounds revealed several reaction mechanisms leading to the formation of chlorinated hydrocarbons. Two of the most widely accepted are shown in Figures 5 and 6 (30, 32).

Studies involving the chlorination of naturally occurring organic compounds from different origins also have been performed. Fulvic acids from regions that varied in their geochemistry showed little difference in either their rates of reaction with chlorine (18, 34) or their reaction products upon chlorination (35, 36). When naturally occurring organic materials were separated by size instead of by geochemistry of origin, the THM yield was greater for the larger organic molecules (34, 36). The correlation between the molecular size and THM production upon chlorination has been substantiated by a few subsequent studies (44, 45) but may not hold for all types of DOC (92).

Metabolic by-products of algal activity, or extracellular products (ECP), also produce THMs upon chlorination (20, 37, 38). Algae have been found to produce seasonal shifts in the THM precursor content of lakes (39). In general, the blue-green algae, which typically bloom in mid-summer, produce greater quantities of THM precursors than green algae, which predominate in the spring and fall (38). Molecular-size determinations by ultrafiltration have shown algal ECP to range from 10,000 to 30,000 daltons with little seasonal variation (37).

Removal of DOC by Water Treatment Plants

The study of dissolved organic carbon (DOC) removal processes was accelerated when DOC was implicated as precursors to halogenated organic materials. As a short-term solution, many water treatment plants delayed chlorination until after flocculation and sedimentation (after which most DOC is removed) (40). This method was helpful in reducing both the amount of precursor material that reacted with chlorine and the contact time between chlorine and organic material, but it was not sufficient for many plants. The removal of DOC by coagulation was optimal at pH 5.0 to 6.0

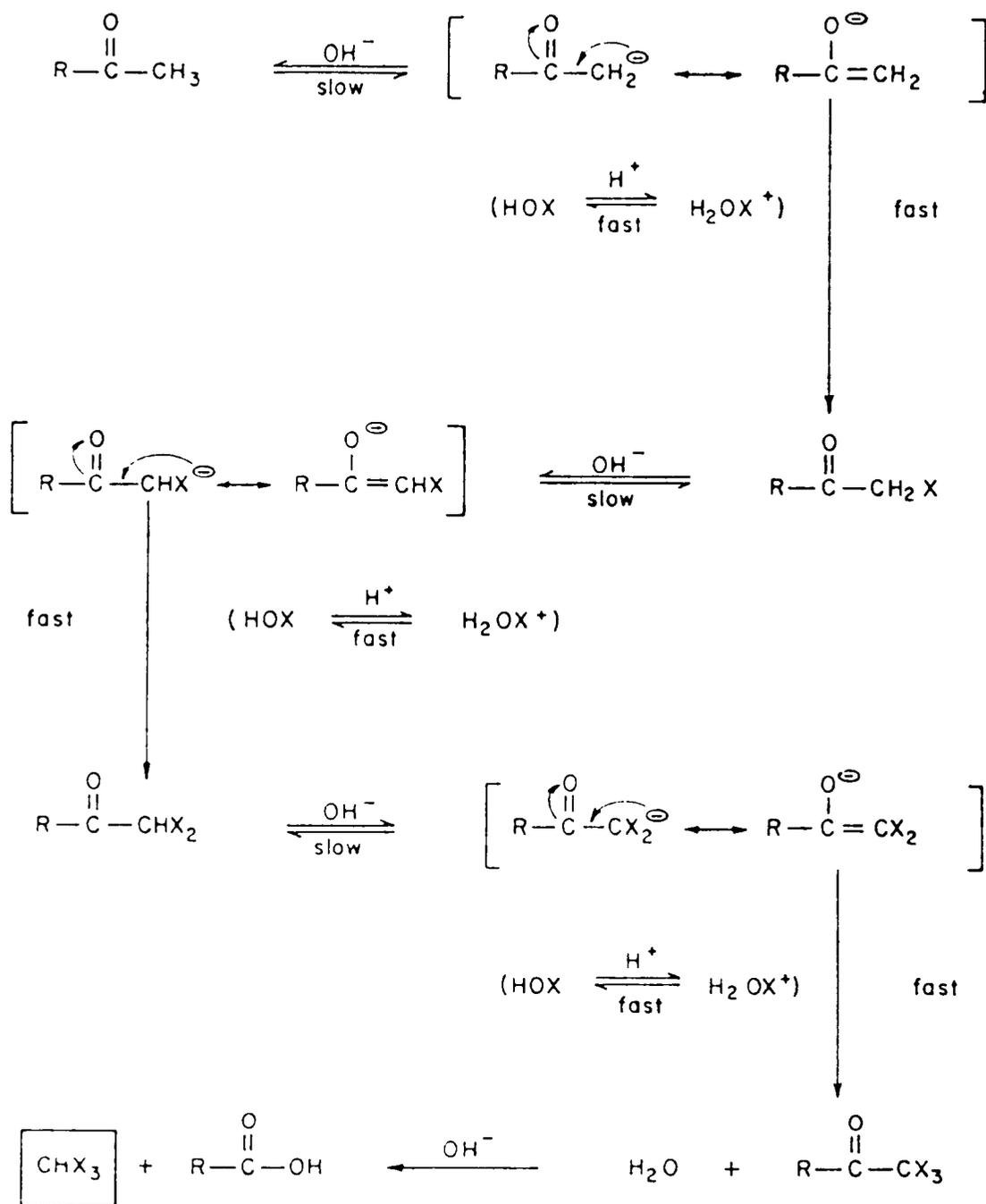


Figure 5. Haloform reaction proposed by Morris (32).

(41-44). Two removal mechanisms based on the aluminum concentration were proposed by Dempsey (41): adsorption and formation of a humic-aluminum complex. At high concentrations, aluminum hydroxide forms large, amorphous flocculent particles which enmesh suspended particulates and act as substrate to which the organic material can adsorb (41, 42). At the lower concentrations of aluminum required for charge neutralization, organic materials act as ligands to complex the aluminum in a humic-aluminum complex (41). Edwards and Amirtharajah (42) found that pH, in addition to aluminum concentration, influenced the mechanism. At pH 6.0 to 8.0, adsorption predominated, and at pH 4.0 to 6.0 humic-aluminum complex formation predominated.

Studies have shown that in some cases the differences in DOC removal can be attributed to the characteristics of the organic molecules. The most important characteristic is molecular size; large molecules are removed more efficiently than small ones (43-45). In a thorough study, Sinsabaugh (45) determined that charge and solubility, in addition to size, were influential factors in DOC removal by coagulation. Ionic molecules were more easily removed than neutral ones, and less soluble molecules were more easily removed than soluble ones. These results have demonstrated that the optimization of the coagulation process will not meet with the same success at all water treatment plants because of differences that may exist in the dissolved organic molecules.

Chlorine Dioxide and Permanganate

Many water treatment plants still had some difficulties meeting the 0.10 mg/L THM MCL after postponing chlorination and optimizing the coagulation process for organics removal. Many other plants experienced other problems associated with delaying chlorination and reducing pH, including poor manganese removal, taste-and-odor problems and septic sludge (46). In response, many oxidants, alternative to chlorine, were given closer consideration, among them chlorine dioxide and permanganate.

Chlorine Dioxide Chemistry

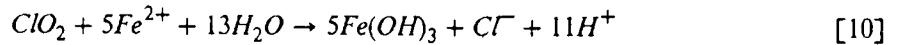
For two of the best reviews of chlorine dioxide chemistry and the use of chlorine dioxide in water treatment, see Masschelein (47) and Ajeta and Berg (48), respectively. Chlorine dioxide, a yellow gas at room temperature, is a strong and rapid oxidant (49). The molecule is paramagnetic, implying that it has one unpaired electron. The structure of the molecule is angular (118°) with Cl-O bond length of 14.7 nm (3). Chlorine dioxide is one of the few species that exists entirely as a monomeric free radical in nature (48). Solution concentrations up to 8 g/L are stable in the dark, but in the light ClO_2 decomposes to HCl and HClO_3 (3).

In alkaline solutions, chlorine dioxide rapidly disproportionates to chlorite (ClO_2^-) and chlorate (ClO_3^-). In acidic solutions decomposition also occurs, but much more slowly; initially chlorite forms, which then disproportionates to hydrochloric acid and chlorate (3). The rate of decomposition is faster at high initial concentrations of chlorine dioxide. However, alkaline solutions (pH 12) containing 5 to 10 mg/L chlorine dioxide remained stable for periods between 20 minutes and three hours (50). Under conditions more typical of water treatment (pH 6 to 10, $\text{ClO}_2 = 0.1$ to 3 mg/L) chlorine dioxide would presumably remain stable for even longer periods.

Chlorine dioxide can be oxidized by chlorine to chlorate (48); however, at the low initial concentrations of chlorine and chlorine dioxide used for water treatment this reaction is quite slow. For example, at concentrations in the 0.5 to 1.0 mg/L range, the half life of a chlorine/chlorine dioxide solution is 15 to 20 days, an indication that this reaction is of little importance to water treatment (48):

Oxidation Reactions with Iron(II) and Manganese(II)

Chlorine dioxide rapidly oxidizes ferrous iron to the iron(III) state. Chlorite also reacts with reduced iron producing iron hydroxide and chloride. The overall reaction is shown in equation [10] (48).



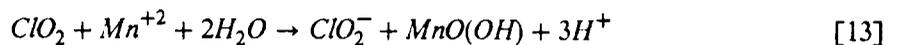
As implied by La Chatlier's Principle, this reaction is favored at neutral to alkaline pHs. There is some evidence that chlorine dioxide can oxidize organically bound iron (47). Chlorine dioxide reacts with manganese(II) to form chloride and manganese dioxide, as is shown in equation [11] (47):



However, using relatively dilute solutions typically used in water treatment, only about 30 percent of the chlorine dioxide is reduced to chloride, and 70 percent remains as chlorite (48, 50). If chlorine dioxide is reduced to chlorite, the stoichiometry of manganese oxidation would be as follows:



In his review of manganese chemistry, Morgan presented the oxidation product of Mn^{+2} as $\text{MnO}(\text{OH})$ (1). If this were the reaction product, the stoichiometry of the reaction would be as is shown in equation [13]:



Obviously, there is much confusion regarding the oxidation of manganese. One of the major textbooks in the water-treatment field (15) reports the product of Mn^{2+} oxidation to be MnO_2 and the primary precipitate of the same reaction to be $\text{MnO}(\text{OH})$.

Oxidation of Organic Compounds

When discussing organic matter reactions, one naturally compares chlorine dioxide to chlorine because the former is often used as an alternative to chlorine to avoid the formation of organic halogens. In its reactions with DOC, chlorine dioxide primarily acts as a one-electron acceptor (52, 53) in contrast to chlorine, which acts by way of a variety of electrophilic, oxidative and radical pathways (31, 53). As a consequence, chlorine dioxide is more selective, more specific, and produces considerably fewer chlorinated products than does chlorine (53). The chlorinated products that are produced in chlorine dioxide reactions are formed by secondary reactions between residual DOC and chlorine that is released from the initial reaction of chlorine dioxide and DOC (51, 53, 54). Typically, chlorine produced in this manner is short lived in solution because it is almost immediately incorporated into the organic material (51). It should be emphasized that the concentration of organic halogens produced by chlorine from chlorine dioxide is considerably less than what would be produced if an amount of chlorine equivalent to the initial chlorine dioxide concentration were used. The main products of chlorine dioxide oxidation of naturally occurring organic materials include aldehydes, carboxylic acids, chloroacetic acids, quinones and hydroquinones (53).

One of the main benefits of chlorine dioxide as a preoxidant is that it removes THM precursors by oxidation (31, 48). The range of THM precursor reduction due to oxidation by permanganate is broad, ranging from 15 to 60 percent at pH 7 (48, 51, 55). The extent of this range is probably due to differences in such reaction conditions as THM precursor concentration, chlorine dioxide dose, chlorine dose, reaction time and temperature. In any case, many water treatment plants have initiated the use of chlorine dioxide to decrease the concentrations of THMs in the finished water with varying degrees of success (46, 56).

Chlorine dioxide has been used also to oxidize organic materials that cause taste-and-odor problems. It has two advantages over chlorine for this purpose. First, chlorine dioxide will not form THMs and, second, unlike chlorine, chlorine dioxide will not react with phenol moieties to form

chlorinated phenolics (48, 57). Also, a direct comparison of chlorine, chlorine dioxide, and permanganate revealed chlorine dioxide to be superior for the oxidation of the unsaturated taste-and-odor compounds geosmin, 2,3,6-trichloroanisole (TCA), 2-isopropyl-3-methoxy pyrazine (IPMP), 2-isobutyl-3-methoxy pyrazine (IBMP) and 2-methylisoborneol (MIB). These unsaturated oils, excreted by algae, were oxidized to saturated forms by chlorine dioxide doses typically used in water treatment (58). Chlorine dioxide will not oxidize all odor-producing compounds. On a plant-scale basis, chlorine dioxide (as well as powdered activated carbon) was found to be ineffective for the removal of "hydrocarbon"-type odors from urban runoff (57).

Other Effects on Plant Performance

Among other reasons, chlorine dioxide is an attractive alternative to chlorine because it is a good disinfectant. There is some controversy concerning its exact rank with respect to other disinfectants, but Table 1 shows a representative list of relative potencies. As is seen, chlorine dioxide ranks between HOCl and OCl⁻ in its effectiveness. As a pre-disinfectant (i.e., disinfection in the plant as opposed to in the distribution system) chlorine dioxide performed adequately at concentrations of 0.6 to 0.8 mg/L but not as effectively as chlorine (59). The advantage in this instance was the avoidance of THMs.

In other studies on plant performance, chlorine dioxide has provided some unexpected benefits and some unexpected problems. One study reported that chlorine dioxide prevented the release of manganese from sedimentation basins and improved the dewatering characteristics of the sludge. In addition, the filters had to be backwashed less often (46). In a separate study, chlorine dioxide treatment, as well as ozone treatment, increased the turbidity of the finished waters (60). In a review of several water treatment plants that used alternative oxidants including chlorine dioxide, Singer (61) asserted that chlorine dioxide was of limited use when treating water which contained more than about 5 mg/L DOC. This conclusion was based on 1) a state recommendation limiting the treated waters to 1.0 mg/L combined ClO₂, ClO₂⁻, and ClO₃⁻ and 2) the rapid reduction of

Table 1.
Relative potencies of disinfectants used in water treatment (93).

Species	Relative Potency	
	E. Coli	Poliovirus
HOCl	1	1
ClO ₂	1/12	1/3
OCl ⁻	1/23	1/7
NHCl ₂	1/100	1/8900
NH ₂ Cl	1/4400	1/570

chlorine dioxide to chlorite in the presence of DOC. (That is, with more than 5 mg/L DOC, chlorine dioxide would have a negligible residence time in a water treatment plant.)

As was mentioned previously, many states regulate the use of chlorine dioxide for water treatment. The most common limit is 1.0 mg/L combined chlorine dioxide, chlorite, and chlorate in the distribution system. This limit was originally an EPA recommendation that cited concerns over hematopoietic and thyroid effects of ClO_2 and ClO_2^- (62). Chlorate is included in this limit because it can readily be converted to ClO_2^- by the body (63).

The health effects of chlorine dioxide may be greater than those associated with chlorinated organic matter. In a 1982 review article, Bull (64) reported that the health problems associated with chlorinated organic materials might be a more reasonable health risk than those associated with ClO_2 and ClO_2^- . More recently, chlorine dioxide has been found to alter the metabolism and bioavailability of iodine by oxidizing it to its elemental state. This reactive form of iodine then undergoes substitution reactions *in vivo* resulting in iodinated organic compounds, the health effects of which are under investigation (63). At this point, all investigators emphasize the need for further research.

Permanganate Chemistry

Permanganate represents manganese at its highest oxidation state. With a molecular weight of 158.08 amu, potassium permanganate is a solid, deep purple, almost black crystal at room temperature. In solution, the color changes with concentration from a light pink at low concentrations to a deep purple resembling grape juice at concentrations greater than 150 mg/L. The visible-light spectrum of permanganate shows two, fairly sharp peaks at 525 nm and 545 nm (65). The geometry of the permanganate molecule is tetrahedral with an average Mn-O bond length of 16.3 nm. The bond angles are not yet known (66). The schematic of potassium permanganate in Figure 7 shows the tetrahedral geometry.

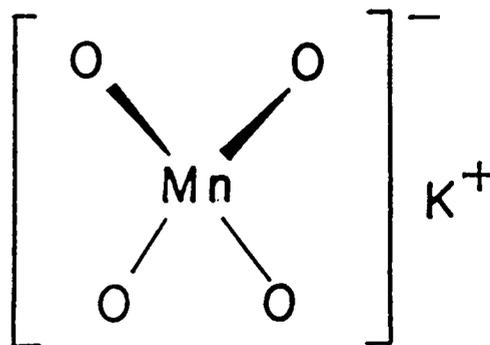
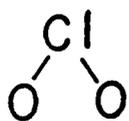
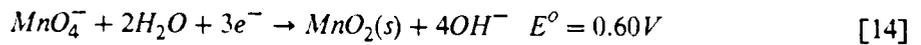


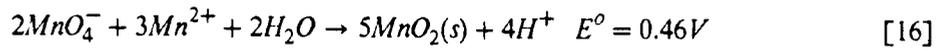
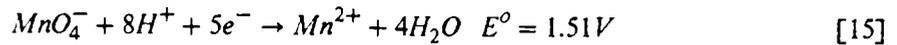
Figure 7. Structures of chlorine dioxide and potassium permanganate from reference 47 (left) and reference 66 (right).

Because permanganate is a strong oxidizing agent, it will oxidize water in aqueous solutions. However, the kinetics of this reaction are sufficiently slow, especially under neutral-to-slightly alkaline conditions, that permanganate is used as an analytical titrant (67). Permanganate solutions are subject to light-catalyzed decomposition, and should be stored in dark bottles. Potassium and sodium salts of permanganate are prepared by electrolytic oxidation of basic solutions of MnO_4^- .

In basic solutions, permanganate is a strong oxidizing agent as is seen from equation [14] (2):



In acidic solutions, permanganate is reduced to Mn^{2+} , as is shown in equation [15] (2). However, if excess permanganate is present, it will react as shown in equation [16] (3).



These reactions are generally not important in water treatment. As is seen in equations [14] to [16] the oxidation potentials increase with decreasing pH, but many permanganate oxidation reactions are faster in basic solutions than in neutral-to-acidic ones (68).

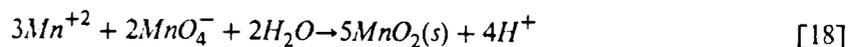
Oxidation Reactions with Iron(II) and Manganese(II)

Permanganate undergoes many reactions with inorganic compounds, but the oxidation of iron(II) and manganese(II) are relevant to this study. The oxidation of iron (II) by permanganate is fairly rapid over a pH range of 6 to 10 (68). The stoichiometry of this reaction is as follows (68):



In general, the oxidation of manganese(II) by permanganate is rapid but shows a strong dependence on pH. At pHs values greater than 8, oxidation is almost immediate, and at pH 5 oxidation is

complete in approximately 10 minutes. Oxidation time increases sharply when pH is decreased past pH 5 (68). The stoichiometry of this reaction is as follows (67):



Reactions with Organic Matter

Permanganate readily oxidizes many types of organic materials. Good reviews of the use of permanganate oxidation in synthesis procedures are given by Lee (69) and Arndt (70). This discussion focuses on the general reactions between MnO_4^- and naturally occurring organic materials. At the concentrations used in water treatment, permanganate oxidation is restricted to functional groups and double bonds (68). Some functional groups are more susceptible to oxidation than are others. When applied to natural waters, permanganate showed a preference for m-dihydroxyl phenyl moieties (74). Using organic materials extracted from the Missouri River, Spicher and Skrinkle (71) found that permanganate reacted with aldehydes, esters, and keto acids but not with carboxylic acids, ketones, or aliphatic alcohols. The reaction rate increased with pH, permanganate concentration, and temperature. The organic products were not identified. Liao (72) found that permanganate oxidized alkyl side chains of arenes to aromatic acids.

Permanganate also oxidizes THM precursors but to a lesser extent than does chlorine dioxide. The range in THM reduction is reported to be from 2 to 35 percent, the magnitude dependent upon permanganate dose, reaction time, and pH. As permanganate concentrations increase, THM-precursor reduction increases. At a pH of 6.3, increasing the permanganate concentration from 2 to 10 mg/L increased the THM-precursor reduction from 15 to 30 percent (74). These reductions were consistent in waters with both a low (3 mg/L) and a high (9 mg/L) DOC concentration. In a separate study, Werdehoff and Singer (51) reported the THM-precursor removal increased from 5 to 15 percent when the permanganate dose increased from 5×10^{-3} to 2×10^{-2} milliequivalents MnO_4^- per mg carbon (meq/mg C). (For a three electron transfer and an assumed organic carbon concentration of 5 mg/L, these doses correspond to concentrations of 1.3 and 5.3

mg/L.) Normally, increases in pH result in increases in the rate of permanganate oxidation, but for THM-precursor oxidation, the effect of pH is unclear. Symons (74) found that increasing the reaction pH from 7.4 to 10.0 caused THM precursor oxidation to decrease about 13 percent. Singer (73) found that increasing the pH from 6.5 to 10.3 caused THM precursor oxidation to increase anywhere from 3 to 16 percent, with an average of about 10 percent.

The adsorption capacity of manganese oxide particles formed upon the reduction of permanganate may also be responsible for THM-precursor removal (75); however, at pH values greater than 3 to 4, cations are required to decrease the electrical double layer created by the negative charges on the surfaces of the manganese oxide particles and the THM-precursors (75).

Permanganate has been known to oxidize odorous organic matter (e.g., aldehydes, amines and phenols) to nonodorous products (77). In one drinking water plant, potassium permanganate successfully oxidized sewage waste odors introduced when a sewage outfall was diverted to a location near the water intake (76). Many odors in water are byproducts of algae that can be detected by humans in the ug/L range (78). Using closed loop stripping, Lalezary *et al.* (58) found that rather than oxidation, the major mechanism for the removal of low concentrations of taste-and-odor compounds by permanganate was the adsorption of the organic compound to the resulting manganese dioxide particles.

Permanganate is not generally regarded as an effective disinfectant in water treatment. It has been used to disinfect water mains, but concentrations on the order of 30 mg/L were required for about 24 hours to be effective (79). Permanganate was found to be effective in reducing the coliform count of water contaminated by sewage (77). In general, disinfection is normally incidental to the use of permanganate as an oxidant (78).

Oxidation of Manganese(II) and DOC

In natural waters, manganese(II) and DOC are usually both present, sometimes in high concentrations. With respect to oxidation by permanganate or chlorine dioxide, manganese(II) and DOC can be considered as competing reducing agents. The compound first oxidized depends upon many factors, such as 1) the nature of the organic carbon, 2) the concentrations of manganese and DOC (9), 3) the oxidant used (9), and 4) whether the manganese is free or bound by the organic compounds (80). Knocke *et al.* (9) found that at pH 5.0, manganese(II) oxidation by permanganate was ineffective until the permanganate demand of the organic matter was satisfied. Oxidation reactions with chlorine dioxide showed that the same requirement must be met, except the chlorine dioxide demand was less than that for permanganate. The corresponding effects of the oxidants on the DOC with different concentrations of manganese(II) were not determined.

Combined use of Chlorine Dioxide and Permanganate

There are no known examples in the literature of the combined use of chlorine dioxide and permanganate as preoxidants in water treatment. At best, the combined use of chlorine dioxide and permanganate would permit an increase in overall oxidation potential without either exceeding the 1.0 mg/L state recommendation for combined ClO_2 , ClO_2^- and ClO_3^- or releasing MnO_4^- into the distribution system. The benefits of an increased oxidation potential would be to enhance the oxidation of iron, manganese (9) and THM-precursors. In addition, using permanganate and chlorine dioxide together would enhance disinfection over that which is possible with permanganate alone. There may be other unexpected benefits.

One of the potential drawbacks of the combined use of chlorine dioxide and permanganate is the oxidation of manganese oxides, derived from the reduction of permanganate, by chlorine dioxide back to permanganate. This phenomenon occurs when waters containing manganese are ozonated (81, 94). The thermodynamics of this reaction can be investigated for various reaction conditions.

A sample calculation of this type follows, and Figure 8 shows the results of this analysis. Because there is some controversy over the oxidation state of the manganese oxide formed in water treatment conditions, two sets of calculations were performed, one considered the oxidation of MnO_2 and the other considered the oxidation of $\text{MnO}(\text{OH})$. The following assumptions are made: 1) ClO_2 loses one electron, forming ClO_2^- upon reduction and 2) the solution pH will be varied. The concentrations are typical of either water treatment plants or the laboratory tests performed in this study. The calculation below was performed using concentrations typical at a water treatment plant, coagulating at a pH of 9.0. The thermodynamic constants, assumed concentrations, and calculation procedures for the other data used for Figure 8 are listed in Appendix A.

Half reactions:	Oxidation Potential (V)
$\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{MnO}_2(\text{s}) + 4\text{OH}^-$	0.59
$\text{ClO}_2 + \text{e}^- \rightarrow \text{ClO}_2^-$	1.16

Combined reaction:



Nernst equation:

$$E = E^\circ - (0.059/n)\log Q$$

where:

$$\begin{aligned} E^\circ &= 0.57, \\ n &= \text{electrons transferred} = 3 \text{ and,} \\ Q &= [\text{ClO}_2^-]^3[\text{MnO}_4^-]/[\text{ClO}_2]^3[\text{OH}^-]^4. \end{aligned}$$

Assuming:

$$\begin{aligned} [\text{ClO}_2^-]^3 &= 3.3 \times 10^{-18} (\approx 0.1 \text{ mg/L as } \text{ClO}_2^-), \\ [\text{MnO}_4^-] &= 4.4 \times 10^{-6} (\approx 0.7 \text{ mg/L as } \text{KMnO}_4), \\ [\text{ClO}_2]^3 &= 3.3 \times 10^{-15} (\approx 1.0 \text{ mg/L as } \text{ClO}_2), \text{ and} \\ [\text{OH}^-]^4 &= 1 \times 10^{-20} (\text{pH} = 9.0). \end{aligned}$$

$$E = 0.38$$

A redox potential greater than 0 indicates the reaction is thermodynamically favored, thus, ClO_2 has the potential to oxidize MnO_2 to MnO_4^- at pH 9. As is seen in Figure 8, the dominant parameter in this system is pH. Alkaline conditions promote oxidation of both species of manganese [MnO_2 and $\text{MnO}(\text{OH})$]; acidic conditions prohibit both species of manganese from being oxidized to MnO_4^- . However, the reduction potentials are close to zero, and may change sign if there is any change in the thermodynamic constants. In addition, these relationships are based on equi-

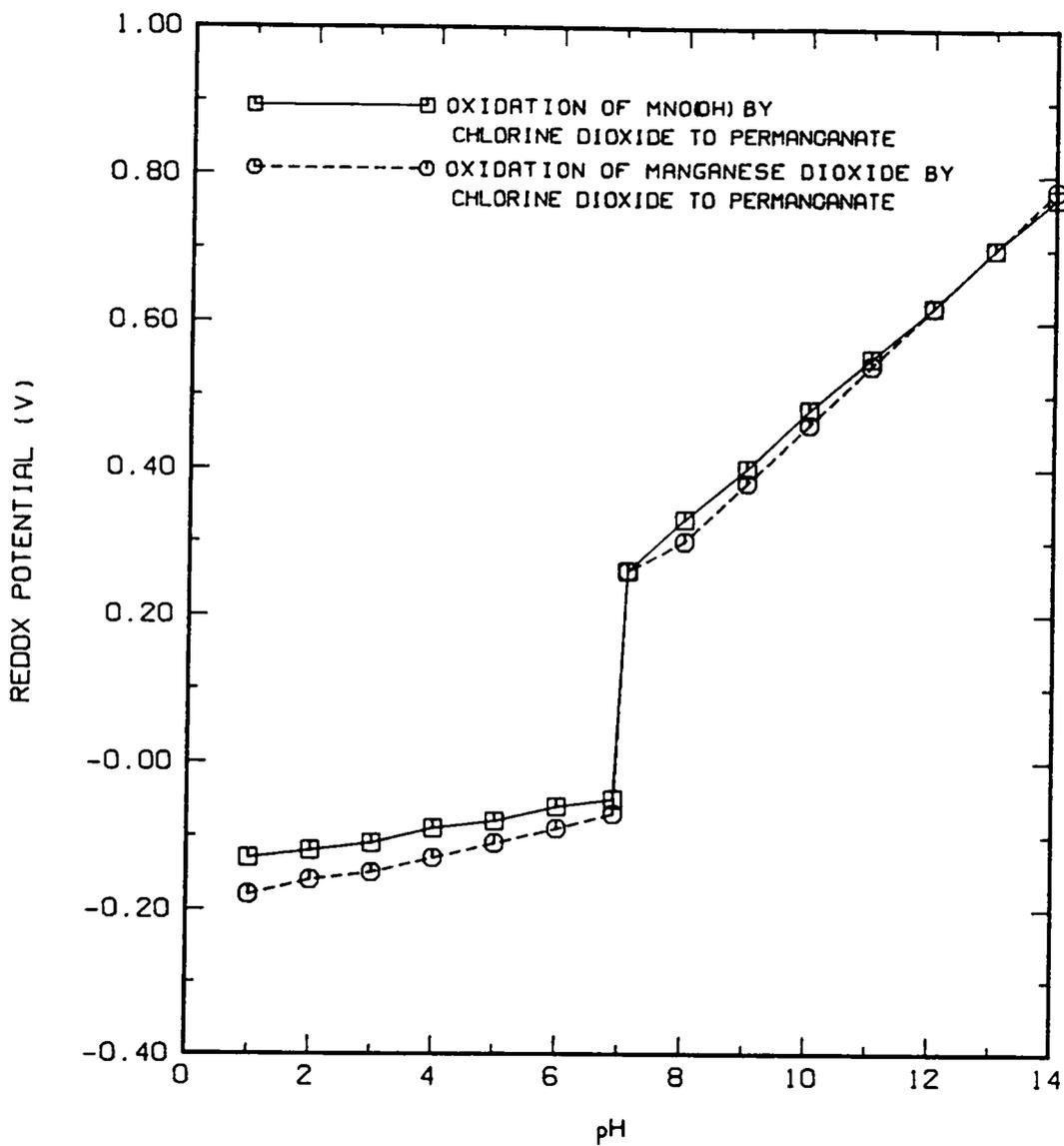


Figure 8. Variation in redox potential with increasing pH for oxidation of $MnO(OH)$ and MnO_2 by ClO_2

librium conditions and do not consider the rate of the reaction. Thus, a positive E° is not an indication that the reaction will spontaneously occur.

The practical ramification is that permanganate, added in conjunction with chlorine dioxide, may persist for an extended period of time, possibly beyond the hydraulic retention time of a treatment facility. Subsequent reduction in a distribution system to an insoluble form [MnO_2 or $MnO(OH)$] may lead to pipe deposition and consumer complaints related to water discoloration.

Review of Nonstandard Methods

This section reviews the evaluations presented in the literature for 1) determinations of different manganese species and 2) ultrafiltration of naturally occurring organic matter for size determination. These techniques are not well defined in methods manuals, and part of this project was an attempt to expand and refine them. The determination of manganese species will be reviewed first.

Determination of Manganese Species

For the purposes of this discussion, manganese species will include manganese(II), solid manganese oxides and manganese(VII). Probably the most popular method for measuring aqueous manganese concentrations is atomic adsorption spectrophotometry (AAS). This method is popular for good reason, but its virtues will not be extolled here. One of the chief disadvantages of this technique is that it is unable to differentiate between the various oxidation states of manganese (or of any metal). As a means to separate dissolved manganese [manganese(II)] from colloidal manganese [manganese(IV)] in natural waters, the American Public Health Administration, the American Water Works Association and the Water Pollution Control Federation (84) recommend the use of a filter with pore diameter of 450 nm (450 nm filter). This is an operational difference meant to set

a standard, not a theoretical difference based on the minimum size of insoluble metals. For experimental and theoretical purposes, this arbitrary standard is insufficient.

In a good review of the techniques available prior to 1964, Morgan and Stumm (95) evaluated the following methods to separate manganese(II) from manganese oxides: 1) solvent extraction of complexed manganese(II), 2) flocculation and centrifugation of suspended oxidation products and 3) filtration of suspended manganese. Filtration through a 220 nm membrane filter was the most effective separation technique.

The presence of permanganate in solution would interfere with this technique because it would not be separated from manganese(II) upon filtration. The determination of manganese concentrations when all three species are in solution requires either a separation technique for manganese(VII) and manganese(II) or a method for measuring manganese(II) and manganese(VII) without mutual interference. In the literature, there are two techniques available to determine manganese(VII) in the presence of manganese(II): amperometric titration and colorimetry.

Initially, amperometric titration was proposed as a method of permanganate determination in 1952 (82). This method was considered advantageous because it was relatively insensitive to the effects of impurities and was accurate to within 5 percent for concentrations as low as 0.005 mg Mn/L (82). In the two reports reviewed (83, 83) the solution conditions and the number of equivalents transferred per mole of permanganate were not reported. Thus, titration of permanganate is a promising, but not well established, technique.

Determination of permanganate by colorimetric means is well documented (65, 84, 85) but it is primarily a means of measuring total manganese following persulfate oxidation of the solution. Peak absorbance of permanganate solutions occurs at 526 nm and 546 nm. The absorbance at 526 nm is slightly greater than that at 546 nm, and, at this wavelength, the method is accurate to concentrations of 0.04 mg Mn^{+7} /L with a 4 cm path length (84). In a 33 laboratory evaluation, this technique was found to have 0 percent error for solutions containing no interferences. Both turbidity (e.g., suspended manganese oxides) and color (e.g., humic substances) interfere with this

technique; therefore, this method is not appropriate for permanganate determinations in the presence of colloidal manganese.

Ultrafiltration

Theoretically, the separation of dissolved organic molecules by ultrafiltration is based upon molecular size. Organic molecules smaller than the membrane pores migrate through the filter by a combination of diffusion and convection. The rate of flux is directly related to the area of the membrane, pressure applied, and diffusion gradient. The larger the concentration gradient between the filtrate and the retentate, the greater the diffusion rate (86).

Some phenomena have been recorded that show deviations from theory. Buffle *et al.* (87) found the major drawback to ultrafiltration to be the interaction of organic molecules with 1) other colloidal particles, 2) each other, and 3) the membrane. Organic molecules can adsorb to colloidal particles too large to pass the membrane, resulting in their errant retention. They can also destabilize and precipitate if stored too long before filtration. Adsorption to the filter can prevent the passage of organic molecules that are actually smaller than the pores. Other authors have also documented this latter phenomenon (88, 89). Reinhard *et al.* (90) found adsorptive losses to the filter ranged from four to 10 percent. The adsorptive losses were greater for solutions containing greater concentrations of organic material. Reinhard did not report whether all sizes of organic molecules were adsorbed to the filter in equal proportions. Thus, the significance of molecular size data was uncertain without an evaluation of a mass balance (90).

Another, perhaps related, problem with ultrafiltration concerns two aspects of the interpretation of results. First, the true molecular weights of organic compounds are not reflected by retention on ultrafilters (i.e., known organic compounds that should pass do not). After determining the molecular weight distribution of three known organic compounds, Buffle (87) found that ultrafiltration was not an accurate measure of molecular weight, but a robust one that might serve as a surrogate measure of molecular weight. He found that changes in neither solution pH,

electrolyte concentration nor pressure affected retention. Ogura (88) evaluated the precision of ultrafiltration and found that retention by filters with the same pore size varied only 2 to 8 percent. Based upon these results, Amy (86) reported that the ultrafiltration of organic material results in an index of the true molecular weight that can be used as a basis for comparison.

Second, it is difficult to compare the results of separate studies if a different number of filters or different filter sizes were used. It would be convenient to be able to express a value, based upon the molecular-weight distribution, that represents a weighted mean molecular weight. In the mineral processing literature (91), equations have been developed to describe particle-distribution curves. The Rosin Rammler equation (91), a generalized method for linearizing sigmoidal curves, is one of the most popular. It takes the following form:

$$Y = 1 - \exp\left(-\frac{X}{X_0}\right)^n \quad [19]$$

The equation can be linearized as follows:

$$\begin{aligned} \frac{1}{1-Y} &= \exp\left(\frac{X}{X_0}\right)^n \\ \ln\left(\frac{1}{1-Y}\right) &= \left(\frac{X}{X_0}\right)^n \\ \log \ln\left(\frac{1}{1-Y}\right) &= n(\log X - \log X_0) \end{aligned} \quad [20]$$

where:

Y = the cumulative weight (DOC concentration) less than size x (i.e., filtrate-X DOC/total DOC),

X = the molecular weight cut off size for the filter,

n = a dimensionless constant characterizing the shape of the molecular-weight distribution (wide versus a narrow bell shape), and

X₀ = a measure of the particle (molecular) size.

By equation [20], X₀ is defined as the characteristic particle (molecular) size where 63.2 percent (1 - 1/e = 0.632) of the particles (molecules) are smaller (most easily seen in Figure 9). The

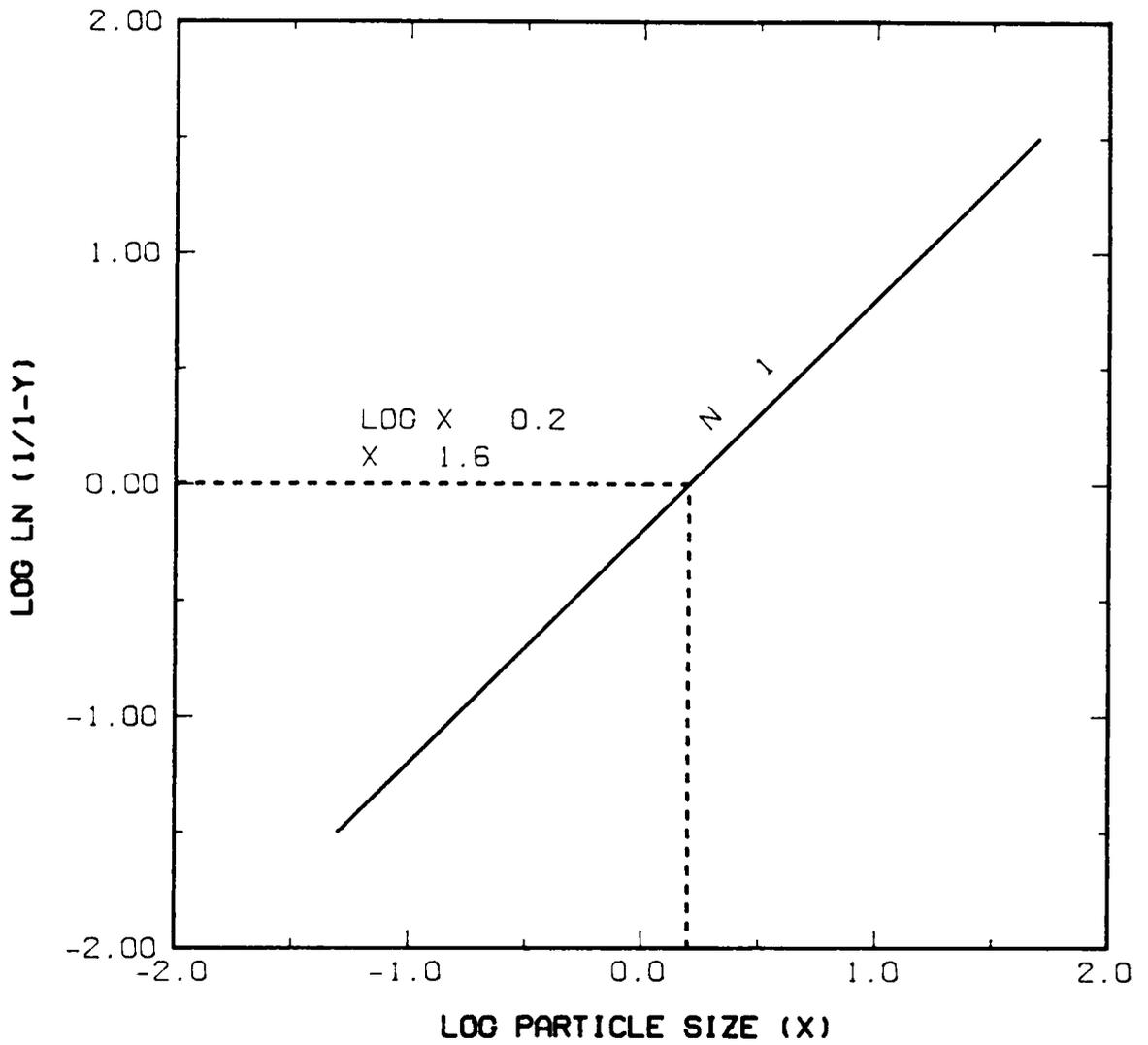


Figure 9. Example plot of Rosin Rammler particle-size distribution equation (91).

dimensionless constant, n , is a measure of how widely distributed are the particles (molecular weights). The greater the value of n , the greater the range in molecular sizes.

METHODS AND MATERIALS

Experimental Design

The plant-scale study was performed at the Abel Lake Water Treatment Plant (Figure 10) in Stafford County Virginia (about 40 miles southwest of Washington, DC). The plant study was performed to evaluate problems and benefits associated with the preoxidation of the raw water with chlorine dioxide and permanganate. Specific questions were raised in the plant-scale study regarding oxidation by permanganate and chlorine dioxide and these were addressed the the laboratory-scale study. Trihalomethanes and manganese(II) provided the major treatment concerns in the Abel Lake Water Treatment Plant. During the summer months, Abel Lake was thermally stratified, effectively sealing the manganese(II)-laden waters in the bottom of the lake. During this period, THM-precursor removal was the greatest treatment concern. Abel Lake normally destratified at the end of November, and did not restratify until the first week of May. During the six months that the lake was not stratified, manganese(II) concentrations increased and caused the major treatment concerns.

The strategy used to evaluate permanganate and chlorine dioxide as preoxidants was to apply them separately, and together in two-week intervals. Water samples were collected at various stages of

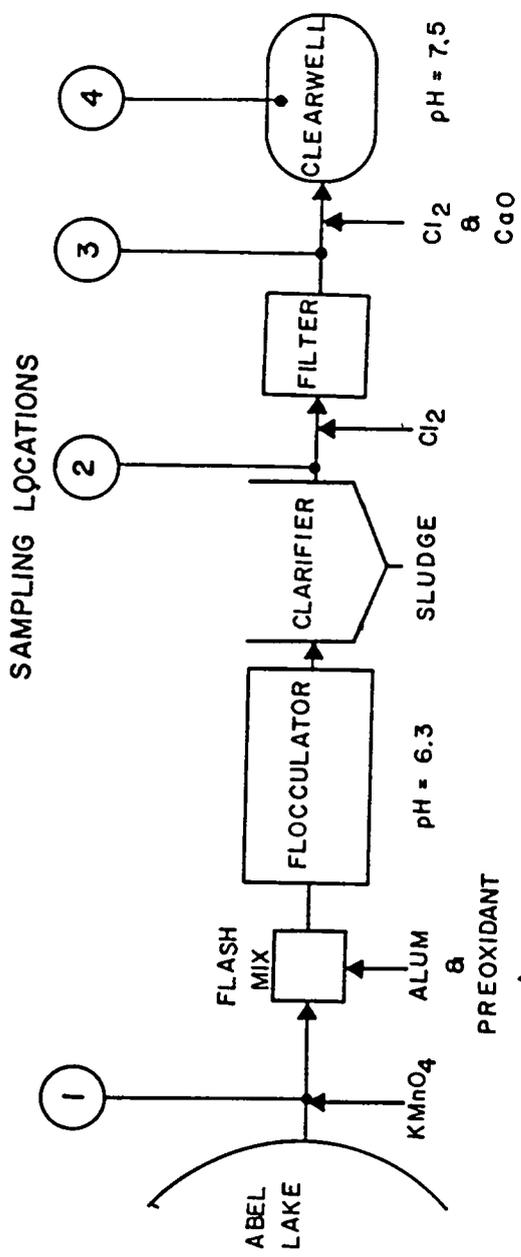


Figure 10. Schematic of Abel Lake Water Treatment Plant. Numbers in circles indicate sampling points.

treatment and analyzed for THM-formation potential, DOC concentration, soluble iron, and soluble manganese concentrations. In addition, the plant records of filter operation times, coagulant requirements and consumer complaints were surveyed. The filter operation times and coagulant doses were categorized by the preoxidant being applied at the time the data was collected and statistical tests were performed to help determine if any of the preoxidant conditions positively or negatively correlated with longer filter operation times or with lower coagulant requirements.

The laboratory phase of this investigation was divided into separate procedures based upon five objectives as follows:

- To evaluate the jar-test data for variability and to compare the jar-test data to the water treatment plant data.
- To determine the effect of the various preoxidants on the optimum coagulant dose for the removal of DOC and THM precursors.
- To compare the removals of iron, manganese, DOC and THM-precursors under flocculation conditions similar to those in the water treatment plant when chlorine dioxide and permanganate were used.
- To analyze the interactions between chlorine dioxide and permanganate when they are used simultaneously for manganese oxidation.
- To determine the effect of permanganate and chlorine dioxide oxidation on the permeability of naturally occurring organic materials through molecular sieves.

The first jar-test was designed to compare the removals of DOC, THMFP, soluble manganese and, soluble iron obtained by the Abel Lake Water Treatment Plant to those obtained by the jar-tests. The strategy was to treat raw water in the jar-test using the chemicals and doses used by the Water Treatment Plant. In addition, water from the rapid mix and the three flocculators was collected and allowed to mix and settle alongside the jars containing raw water treated solely with the jar-test procedure described later.

The next three jar-tests were designed to mimic plant performance under more controlled conditions in an attempt to verify the results obtained in the plant-scale study. The advantage of the jar-test format was that separate aliquots of the lake water could be treated simultaneously with the four preoxidant conditions (no preoxidant, chlorine dioxide by itself, permanganate by itself, and chlorine dioxide with permanganate). The strategy was to measure the concentrations of DOC THMFP, soluble iron, and soluble manganese in the raw water and in the water after treatment.

The removals obtained by treatment with the four different preoxidant conditions were compared. Also, the rate of floc formation, floc size and rate of settling were compared.

The fourth laboratory-scale experiment was performed to more closely examine a) the mechanism by which DOC affected manganese(II) oxidation and b) the interaction between chlorine dioxide and permanganate when in solution together. The design of this experiment, shown in Figure 11, was as follows. Waters with three concentrations of DOC were treated separately with chlorine dioxide alone, permanganate alone, and chlorine dioxide and permanganate together. The concentrations of manganese(II), manganese(VII), particulate manganese, chlorine dioxide, and chlorite were measured through time.

The last experiment was designed to examine the effect of the oxidants on naturally occurring organic materials, which vary greatly in size and structure. Because there is no such thing as a standard humic substance, it is difficult to measure changes that may occur upon oxidation. A common strategy is to characterize the molecules by their permeability through molecular sieves. Because there is a functional relationship between the permeability of organic materials and the ability to remove them (45), this parameter (permeability through molecular sieves) was used in this experiment. It is assumed in this report that the permeability was determined in part by the size of the organic material. Thus, data resulting from measuring the permeability of the organic materials through ultrafilters with different pore sizes was used as an index of the molecular-size distribution of the organic materials.

Several aliquots of water from Abel lake were collected and treated with no oxidant, chlorine dioxide, and permanganate. After treatment, the water was filtered through molecular sieves. The molecular-size distributions of the organic materials in the untreated water were compared to those of the waters treated with the oxidants being evaluated.

To determine chlorite concentrations in the presence of oxidized forms of manganese, it was first necessary to examine the reaction between different forms of manganese (particulate manganese and permanganate) and iodide at pH 7 and at pH 2. This was accomplished by allowing the manganese

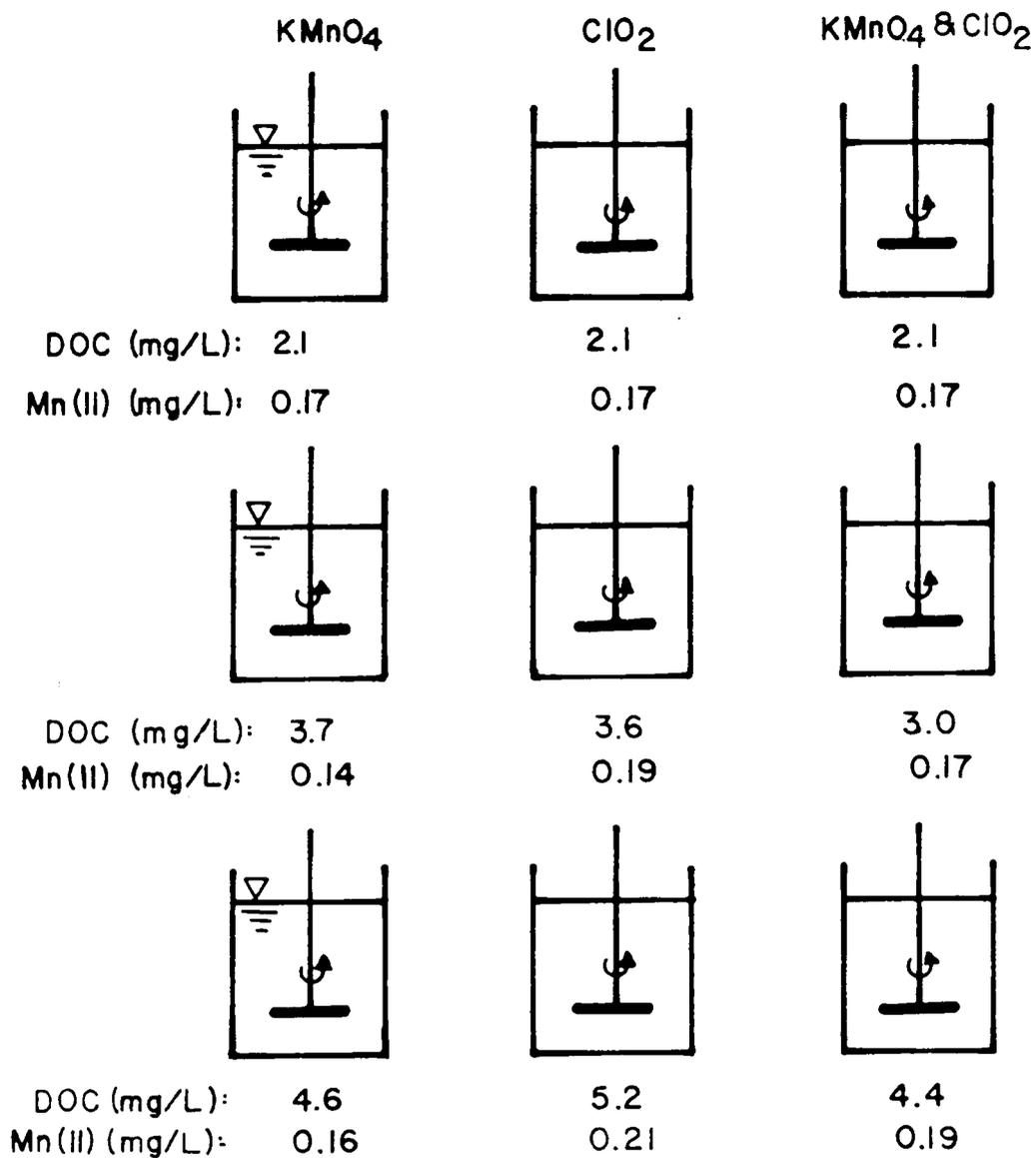


Figure 11. Experimental matrix of study performed to determine effect of DOC concentration on manganese(II) oxidation.

to oxidize iodide at pH 7 to iodine which was then titrated amperometrically with phenylarsine oxide. After the endpoint was reached, the pH was decreased to 2 and titrated again. This procedure allowed the determination of the number of equivalents of manganese that were transferred at each pH used in the chlorine dioxide and chlorite determination procedure that was used in this study. Once the concentrations of the interfering forms of manganese were known, the interference in the titration procedure could be calculated and subtracted. The details of this procedure are presented later in this chapter.

Plant Study

The Abel Lake Water Treatment Facility (Figure 10) is a traditional alum (aluminum sulfate) filtration plant. Coagulation was performed at a pH of 6.3 with aluminum sulfate $[\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}]$. Chlorine dioxide and chlorine were introduced to the flash mix basin with alum, and permanganate was added prior to the flash mix basin near the raw-water intake. If no preoxidant or permanganate were used, chlorine was dosed at a concentration of one to two mg/L (as Cl_2) just prior to filtration to avoid bacterial colonization of the filter media (coal and sand). Post treatment applications of chlorine (1 to 2 mg/L) were used to maintain a residual in the distribution system. To allow for an adequate comparison of both preoxidants, the plant operating scheme (a. no preoxidant added; b. potassium permanganate added alone; c. chlorine dioxide added alone; and d. combined use of both oxidants) was changed every two weeks during both seasonal periods. While the lake was stratified, the typical preoxidant doses, when used alone, were 1.0 to 1.3 mg ClO_2/L and 0.6 to 0.8 mg KMnO_4/L . When used together, the doses were 1.0 to 1.3 mg ClO_2/L and 0.6 to 0.8 mg KMnO_4/L . During overturn the doses, when used alone, were 0.5 to 1.5 mg ClO_2/L and 1.0 to 2.0 mg KMnO_4/L .

Stafford County Water Treatment Plant personnel collected samples from the plant at the locations indicated in Figure 10 by the circled numbers as follows: 1) from the raw-water intake, 2) after

coagulation, 3) after filtration and 4) from the clearwell. The samples were shipped to Virginia Tech, usually by bus, after appropriate steps to preserve them had been taken. The samples were normally three days in transit. Determinations of soluble manganese, soluble iron, DOC and THM formation potential (THMFP) were performed within one week of arrival at Virginia Tech.

The procedures used to prepare containers in which the samples were collected, and the sample preservation techniques were as follows:

- Samples for metals determination were collected in 35 mL plastic containers cleaned in 10 percent nitric acid (HNO_3) for a minimum of 48 hours and then rinsed with distilled water (104). The metals samples were preserved by lowering the pH to < 1.5 with nitric acid (a few drops to ≈ 25 mL) (105).
- Samples for DOC analysis were collected in 120-mL, glass bottles that were cleaned with hot ($\approx 35^\circ \text{C}$) chromic acid for the removal of residual organic material (84). The samples were preserved by the addition of phosphoric acid to a pH of < 2.0 (84).
- Samples for determination of THMFP were shipped in 30-mL, glass vials that had been cleaned with a commercial detergent and rinsed thoroughly (84). No preservative was added.

Laboratory Procedures

In all but one of the laboratory experiments, the test waters originated from Abel Lake. The jar tests were performed with a model 300 six-paddle jar stirrer (Phipps and Byrd, Inc., Richmond, VA 23228). The pH was monitored throughout the experiments with a Corning (Medfield, MA 02052) Model 610-A pH meter and was adjusted with sodium hydroxide (NaOH) and hydrochloric acid (HCl) to maintain a pH of 6.3.

Three phases of the laboratory experiments were performed at the Abel Lake facilities under conditions meant to recreate the conditions of the plant. The objectives of these three experiments

were first, to evaluate the jar test procedure, second to determine the optimum alum dose for DOC and THM-precursor removal and, third, to examine the removal efficiency of manganese, iron, DOC and THMFP using different oxidants. These investigations were performed on-site to avoid changes in manganese(II) concentrations that can occur when water is transported for several hours (103). First, the conditions common to all of these experiments will be presented, then the conditions specific to each will be reviewed.

In these three experiments, the jar tests were performed using water from the raw water intake (at 22° to 25° C) as follows:

- The alum and oxidant(s) (if any) were introduced while the stirring speed of the jar-test paddles was at maximum (> 100 rpm). The solution was mixed at this rate for 45 to 60 seconds.
- The solutions were then flocculated for 20 minutes at a paddle rate of 10 to 20 rpm.
- The floc was allowed to settle for 20 to 30 minutes (depending upon the amount of time required for the floc to completely settle).

Upon completion of the above procedure, the supernatant was filtered through ashed (550° C for one hour) glass-fiber filters (type A/E Gelman, Ann Arbor, Michigan). Aliquots of this filtered sample were then dispensed into separate containers and preserved (following the methods described later) for determinations of DOC, THMFP, Mn and Fe. This procedure, recommended by plant personnel, represented the conditions present in the water treatment plant.

The first experiment evaluated the reproducibility of the data generated by this jar-test procedure. Water from the plant's intake was used to perform four replicate jar tests with 20 mg/L alum, three replicates with 40 mg/L alum and four replicates with 60 mg/L alum. Also, four replicate jar tests were performed on a mixture of surface and bottom waters with 50 mg/L alum. As is more fully described later in this section, the surface and bottom waters were combined to recreate the water quality conditions experienced during overturn. No oxidants were used in any of these jar tests.

In a second step in the evaluation procedure, the data resulting from the jar tests were compared to those obtained from the plant. Two jar tests were performed with the same alum dose as that

used in the water treatment plant (53 mg/L), along side jar tests containing water from the plant. The four locations from which water was obtained were the flash mix basin and the three flocculators. No oxidants were added during this evaluation.

In the second set of experiments, the effects of the oxidants on the optimum aluminum sulfate (alum) dose were evaluated. In each case, the alum concentration was varied from 20 mg/L to 60 mg/L. The oxidants and their doses were as follows:

- 1.5 mg/L ClO_2
- 0.8 mg/L KMnO_4
- 1.5 mg/L Cl_2
- 0.8 mg/L KMnO_4 and 1.0 mg/L ClO_2
- 0.8 mg/L KMnO_4 and 1.0 mg/L Cl_2

After the floc had settled, the samples were collected. These jar tests were performed in triplicate.

In the third experiment, the effect of the oxidant dose was examined. The alum dose was relatively constant (between 40 and 50 mg/L). (The dose used during any particular jar test was the same as the alum dose that was currently being used by the water treatment plant.) The oxidant doses varied from zero (no oxidant) to approximately seven milliequivalents per liter (meq/L). The oxidants used and the range of doses were as follows:

- 0.0 to 7.4×10^{-2} meq/L (5 mg/L) ClO_2
- 0.0 to 4.4×10^{-2} meq/L (2 mg/L) KMnO_4
- 0.0 to 7.4×10^{-2} meq/L (5 mg/L) ClO_2 with 2.2×10^{-2} meq/L (1 mg/L) KMnO_4

The oxidant doses were expressed in meq/L to allow direct comparisons among jar-tests. The normalities were calculated by assuming transfers of 1 equivalent per mole for chlorine dioxide, and 3.5 equivalents per mole for permanganate. In addition, the third experiment included jar tests performed on a mixture of surface water (from the raw-water intake) and bottom water. The proportions of each were adjusted to best represent the raw-water quality during periods when the lake

was not stratified. In the water samples collected when the lake was not stratified, the soluble manganese concentration was greater (0.4 mg/L) and the temperature was lower (5° to 10° C) than that of the surface water alone. The jar-tests in the third experiment were also performed in triplicate.

The fourth and fifth experiments were performed at the Virginia Tech Environmental Engineering laboratory. The fourth series of experiments was designed to evaluate manganese oxidation in solutions with three different DOC concentrations. The three solutions were prepared with deionized water (DOC = 2.1 mg/L), Abel Lake surface water (DOC = 3.0 to 3.7 mg/L), and Abel Lake surface water dosed with fulvic acid (DOC = 4.2 to 5.2 mg/L). The Mn(II) concentration was adjusted to 0.14 to 0.19 mg/L by the addition of manganous sulfate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$). The low DOC water (2.1 mg/L) was prepared by adding salts to deionized water to obtain a moderately hard water (102). The salts added were as follows:

- 96 mg/L NaHCO_3
- 60 mg/L $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
- 60 mg/L MgSO_4
- 4 mg/L KCl

This water had an ionic strength of 0.0045 and a hardness of 90 mg/L as CaCO_3 . The DOC in this deionized water was naturally occurring organic matter present in the source water (Blacksburg tap water from the New River) before the deionization process (which does not remove DOC). The fulvic acid, a reference material extracted from the Suwannee River, was purchased from the International Humic Substance Society (5293 Ward Road, Arvada, Colorado). This source of DOC was used in place of a commercially available humic material because often the commercial products bear little resemblance to a true aquatic humic substance (95).

As is shown in Figure 11, three oxidation strategies to oxidize manganese(II) were tested as follows:

- Potassium permanganate at a dose of 1.0 mg/L as KMnO_4 , except in the waters with 2.1 mg/L DOC, in which case a dose of 0.63 mg/L as KMnO_4 was used.

- Chlorine dioxide at a dose of 3.0 mg/L.
- Doses of 3.0 mg/L chlorine dioxide and 1.0 mg/L potassium permanganate.

The initial concentrations of DOC, manganese(II), and manganese(VII) were measured in duplicate for verification of the desired chemical concentrations. During the course of the reaction, the levels of the reduced and oxidized manganese and of the oxidant(s) were monitored. In the case where chlorine dioxide was used as an oxidant, its concentration was measured by an amperometric titration technique discussed in the next section. Also, the vessels dosed with chlorine dioxide were covered to prevent the volatilization of this gas.

The second of these (the fifth set of experiments) was performed on surface water from Abel Lake, which was subsequently passed through ultrafilters for molecular-size determinations. The water was filtered to exclude particulate matter with a 100K nominal MW exclusion ultrafilter prior to the introduction of an oxidant. Two jar-tests were performed in this phase. The first one included three vessels, one with raw water only, a second with 1.5 mg/L chlorine dioxide (ClO_2) and a third with 1.0 mg/L potassium permanganate (KMnO_4). The second jar-test included one vessel with raw water and four vessels containing raw water dosed with alum plus the oxidants as follows:

- No oxidant
- 1.5 mg/L ClO_2
- 1.0 mg/L KMnO_4
- 0.5 mg/L KMnO_4 and 1.0 mg/L ClO_2

The water that was flocculated was not filtered. In both experiments, the oxidants were allowed to dissipate before the samples were passed through the ultrafilters (about one day). The ultrafiltration methods and materials will be presented later.

Reagents: Preparation and Determination

The chlorine dioxide stock solution was prepared by modifying the procedure suggested in *Standard Methods* (84). The sodium chlorite (NaClO_2) concentration was doubled, and 4.0 mL sulfuric acid was added to 36.0 mL distilled water. Both positive and negative pressures were applied to the system to ensure a steady gas flow. (The positive pressure was always adjusted so that the acid could be introduced safely.) The collection flask contained chilled (4° to 6° C) water purified by the Milli-Q system (Millipore, Inc., Bedford, Massachusetts) and was placed in an ice bath during the entire collection period. The reaction was carried out in the dark. A flask of potassium iodide (KI) served both as an oxidant trap (to protect the vacuum pump) and as an indicator. After the last aliquot of acid was added to the NaClO_2 , the color of the KI solution was checked every 15 minutes. When the color of this solution became brownish red, the gas flow was stopped and the chlorine dioxide solution was capped. Care was taken to prevent the backflow of the KI solution into the chlorine dioxide collection bottle. The ClO_2 was collected and stored in an opaque glass reagent bottle with a ground glass stopper at 2° to 6° C. Typical concentrations were 600 to 800 mg/L ClO_2 , 20 to 60 mg/L ClO_2^- and 20 to 50 mg/L Cl_2 . The solutions prepared and stored as described were fairly stable for about three months (Figure 12).

The method presented by Aieta *et al.* (50) for the determination of oxy-chlorine species was used throughout this study because it offered several advantages, such as superior precision and the ability to determine the concentrations of chlorine dioxide, chlorite and chlorine when they were all in solution. Figure 13 is a simplified schematic of this procedure. The determinations are performed by amperometric titration in the presence of potassium iodide using either sodium thiosulfate or phenyl arsine oxide as titrants. As is illustrated in Figure 13, titration steps A and B and titration steps C and D were performed in series. Titration steps A and C were performed at pH 7 and titration steps C and D were performed at pH 2. As is shown in Figure 13, the pH is then decreased to two, usually by the addition of ≈ 2 mL of ≈ 2.5 M HCl. The solution is allowed to

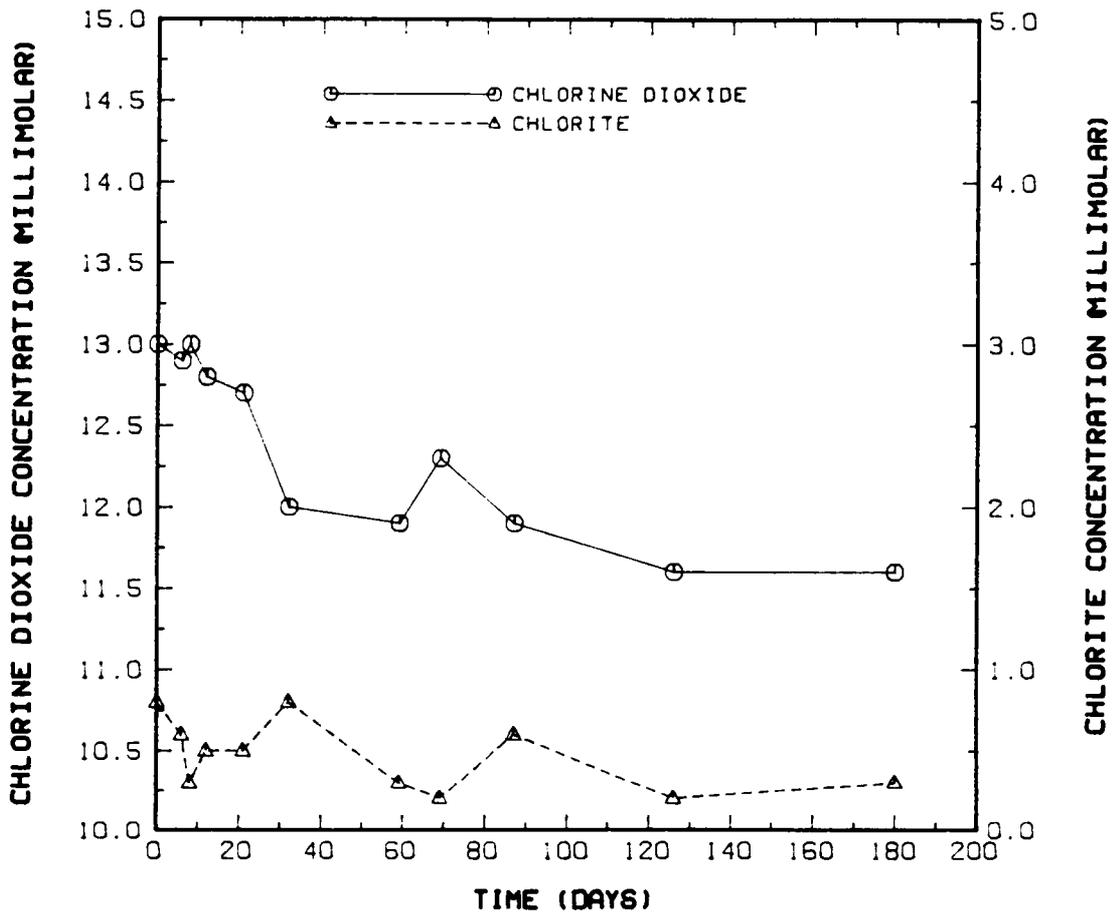


Figure 12. Temporal stability of chlorine dioxide stock solution.

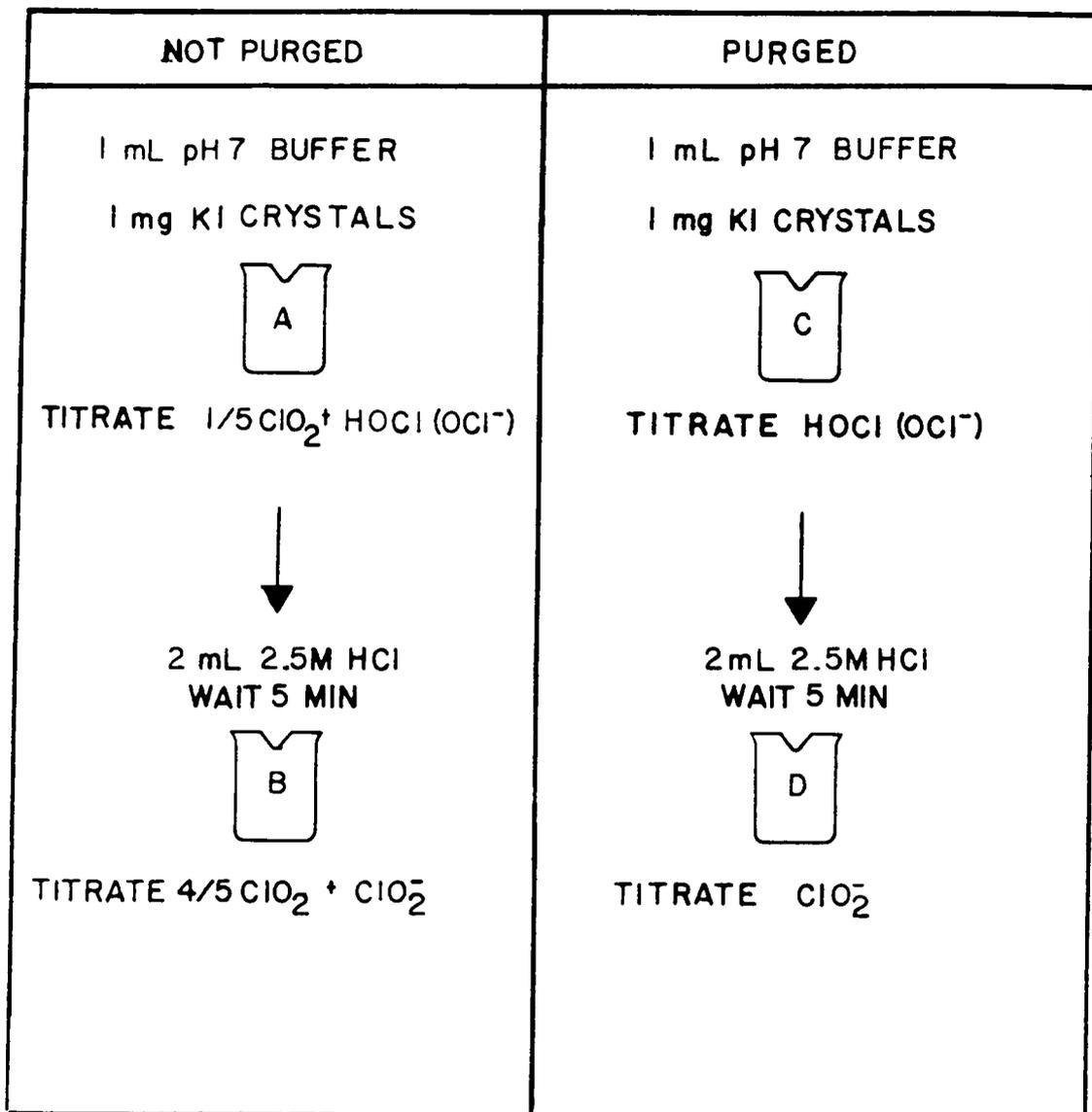


Figure 13. Schematic of method for determination of chlorine species (50).

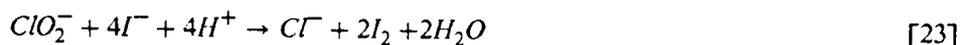
equilibrate before titration. At pH 7 (step A) ClO_2^- does not react with I^- but ClO_2 does, as follows:



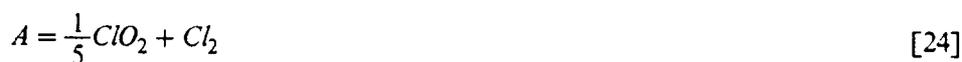
and HOCl reacts with I^- as follows:



At pH 7, some of the chlorine will be present as OCl^- and this will also transfer two electrons per molecule of iodide. If step A (pH 7) was performed properly, only chlorite remains in solution. Some of the chlorite was formed upon the reduction of ClO_2 by I^- during step A and is designated in equations [25] and [29] as ClO_2 to differentiate this chlorite from that which was in solution prior to the addition of KI. The chlorite reacts with I^- at pH 2 as follows:



Steps A and B were performed on an unpurged sample and steps C and D were performed on a sample that had been purged with argon or nitrogen for 15 minutes to remove ClO_2 . The solution titrated in step C contained ClO_2^- and some HOCl that was not removed by purging. Typically, the concentration of HOCl after purging was negligible. At pH 7, the residual HOCl reacted with the I^- as is shown in equation [22]. At pH 2 (step D) the ClO_2^- reacts with I^- as shown in equation [23]. The species that react with I^- , and the fraction of the total number of electrons transferred per molecule for each of the steps of the titration procedure are listed in equations [24] to [27]. For example, in step A (pH 7, ClO_2 not purged) one electron out of a total of five was transferred per mole of ClO_2 , and two electrons out of a total of two were transferred per mole of HOCl. In step B (pH 2, ClO_2 not purged) the remaining four electrons were transferred per mole of ClO_2^- .



$$C \simeq Cl_2 \quad [26]$$

$$D = ClO_2^- \quad [27]$$

This method was also used for chlorine dioxide concentrations during the jar tests. Due to interferences, corrections in final calculations of chlorine dioxide and chlorite had to be made when permanganate or $MnO_2(s)$ was present. The interference from oxidized forms of manganese commonly encountered in water treatment and the nature of these corrections were discussed later in the section of the Results chapter entitled "Manganese: Interference in Determination of Oxy-Chlorine Species and Species Determinations".

The manganous sulfate and permanganate stock solutions were prepared by dissolving reagent grade $MnSO_4 \cdot H_2O$ and $KMnO_4$ into water purified by the Milli-Q water purification system. After preparation, the concentrations of both solutions were verified by atomic absorption spectrophotometry (AAS). The permanganate solution was stored in a dark glass bottle, and its concentration was verified prior to use either by colorimetric means (84) or by amperometric titration.

Samples Analyses

Determinations of manganese, iron, DOC and THMFP were performed on the samples generated from both the plant and laboratory studies. Dissolved iron and manganese were measured by AAS with a Perkin-Elmer (Norwalk, Connecticut) Model 703 AA spectrophotometer. Organic carbon determinations were performed on either a Dohrmann (Fullerton, California) Model DC 40 or Dohrmann Model DC 80 total organic carbon analyzer. Determinations of THMFP required the water first be chlorinated at a 3:1 chlorine-to-DOC weight ratio at pH 7. After incubation for seven days at 22° to 26° C, the THM concentration in the water was measured with a Tracor (Austin,

Texas) Model 560 gas chromatograph equipped with Tracor LSC-2 Purge-and Trap Module and a Hall Electrolytic Conductivity Detector. If it was not possible to perform the determinations on the seventh day, the chlorination reaction was quenched by the addition of sodium sulfite (Na_2SO_3). Also, 0.1 mL of nitric acid (HNO_3) was added to prevent the hydrolysis of organic halide intermediates. The samples were refrigerated at 22°C to 24°C until the THM determinations could be performed, which typically occurred less than one week after the reaction had been quenched.

Ultrafiltration

The size distribution of dissolved organic matter was determined by passing the solutions through the following Amicon (Danvers, Massachusetts) ultrafilters: series YC05, MY2, YM5, YM10 and YM30. The approximate pore sizes and nominal exclusion limits are listed in Table 2. The filters were stored in a sodium azide solution (≈ 1 g/L) to prevent bacterial growth on the membrane.

Prior to use, the filters were mounted in stirred, 200 mL, Amicon 8200 ultracells (Danvers, Massachusetts) and flushed with organic-free (Milli-Q) water under the same conditions that the sample was to be filtered. When the DOC concentration of the filtrate equalled that of the original Milli-Q water (Millipore, Bedford, Massachusetts), filtering was terminated and the ultracell and filter were rinsed with the sample water. Filtration through the membranes was performed under a pressure of 2.8 kg/cm² nitrogen at a temperature of 22° to 24° C. The organic carbon concentrations of the filtrates and the bulk solutions were determined as previously described. In most cases, a separate aliquot was saved for THMFP determinations.

Prior to their use as an analytical tool, the ultrafilters were evaluated for precision and for the extent to which the filters adsorbed DOC. A 50-mL volume of lake water was introduced to the ultracells and allowed to pass the ultrafilter. The effluent was collected in either 5 mL or 10 mL increments and the volume of flow, flow rate and effluent DOC concentration were monitored. This step was

Table 2.
Pore size and nominal molecular-weight exclusion limit of the filters used in this study (114).

Membrane	Approximate pore size (nm)	Nominal molecular-weight exclusion limit (daltons)
YC05	1.1	500
YM2	1.4	1,000
YM5	1.5	5,000
YM10	1.6	10,000
YM30	2.1	30,000
YM100	5.1	100,000

repeated ten times for each size membrane. For the 30K and 10K nominal molecular weight (MW) exclusion ultrafilters, the solution passed the same filter several times. For the 500, 1K and 5K nominal MW exclusion ultrafilters the solution passed five, three and two filters, respectively. In one case, 100 mL of bulk solution was filtered through the 1K nominal MW exclusion membrane. This procedure was followed because it was assumed that the ultrafilter membranes with the smallest pore sizes were more difficult to manufacture with precision and thus, a greater variation in pore sizes (and effluent DOC concentrations) among separate membranes would exist. In addition, the low flow rate made it more convenient to filter several samples in parallel through separate filters, which had a nominal MW-exclusion limit of 500 daltons, than it would have been to filter the solution in series through the same membrane. The information gained by this evaluation was used to determine the methods for obtaining maximum precision and the variability inherent to this technique.

The same procedures as described in the previous paragraphs were used to determine the molecular size distributions of lake water or water from jar tests as when the lake water was passed through the ultrafilters for evaluation. Before the samples from the lake were transported back to the facilities at Virginia Tech, the particulate matter was first excluded by filtering water through Gelman (Ann Arbor, Michigan) Metricell membrane filters with a pore size of 450 nm. It was necessary to rinse these filters with approximately 750 mL organic-free water (purified by the Milli-Q system) to remove organic filter preservatives just prior to sample filtration. Also, the filtrate was discarded until a gel layer had formed on the filter, after which the filtrate was collected. Upon return to the facilities at Virginia Tech, it was found that filtering the lake water through a 100K nominal MW exclusion membrane was equivalent to filtering the lake water through the 450 nm filters with gel layer. Because using a 450 nm filter was much slower (often taking up to 10 hours per liter), and punishing to the vacuum pumps, the 100K dalton nominal MW exclusion limit ultrafilter was subsequently used to filter the raw water collected while the lake was not stratified.

Rosin Rammler Analysis of Molecular-Size Data

In previous studies (21, 44, 45) molecular-weight data have been presented in the manner shown in Figure 14. This style of presentation was not used in this report because it had the following two disadvantages. First, it was difficult to use a single value to express the approximate size of the organic molecules commonly found in most natural waters. Second, it was difficult to determine the significance of the differences observed between two such curves. To overcome these difficulties, the Rosin Rammler (91) method of linearizing particle size data (presented in the literature review) was adopted to linearize molecular-weight data. The straight line equation resulting from the Rosin Rammler analysis and the resulting descriptors of molecular size and distribution lend themselves to a statistical evaluation.

Figure 15 shows a typical Rosin Rammler (91) plot applied to the same data shown in Figure 14 molecular size data. The original form as proposed by Rosin Rammler (94) and as presented in Figure 10, was adjusted as follows:

$$\log \ln\left(\frac{1}{1-Y}\right) = n(\log X - \log X_0) \quad [28]$$

$$\frac{1}{n} \log \ln\left(\frac{1}{1-Y}\right) = \log X - \log X_0 \quad [29]$$

$$\log X = \frac{1}{n} \log \ln\left(\frac{1}{1-Y}\right) + \log X_0 \quad [30]$$

where:

Y = the DOC concentration of the permeate from filter size X divided by the DOC of the bulk solution,

X = the molecular cutoff of any filter,

X₀ = the size of the dissolved organic molecules greater than or equal to 63 percent of all the organic molecules present. It is used as a measure of the molecular size of the organic compounds present. (See Figure 16.), and

n = a measure of the width of the molecular size distribution. (See Figure 16.)

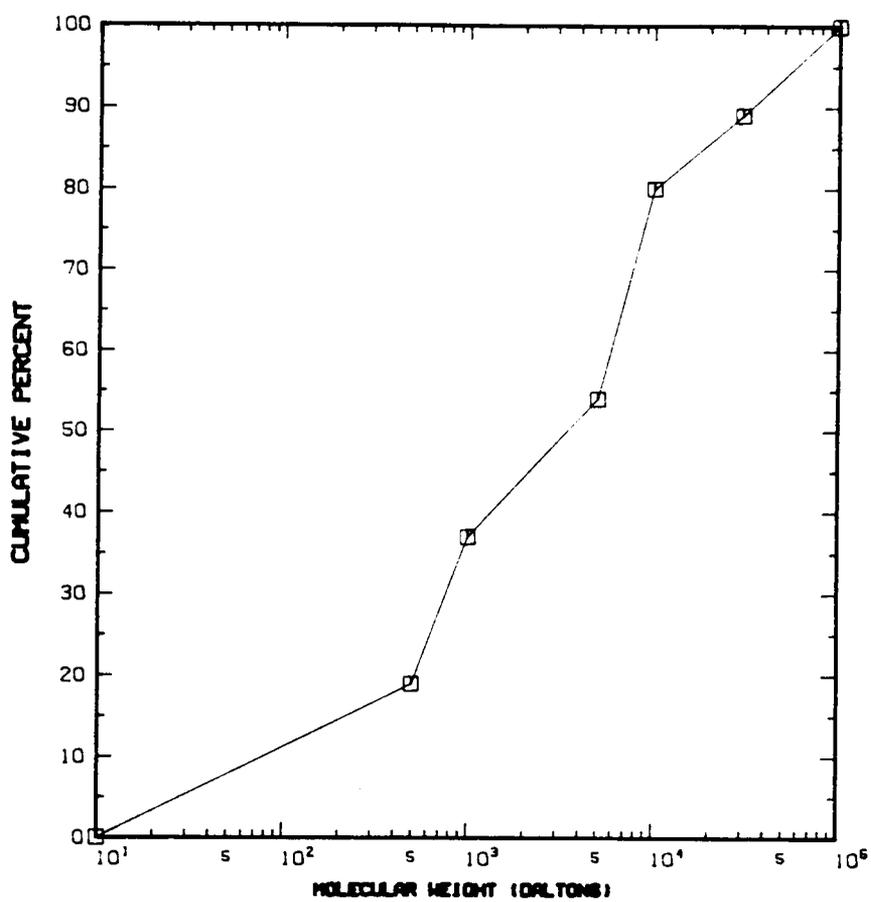


Figure 14. Typical graph of cumulative molecular weight (MW) as a function of the MW exclusion limit of the filter.

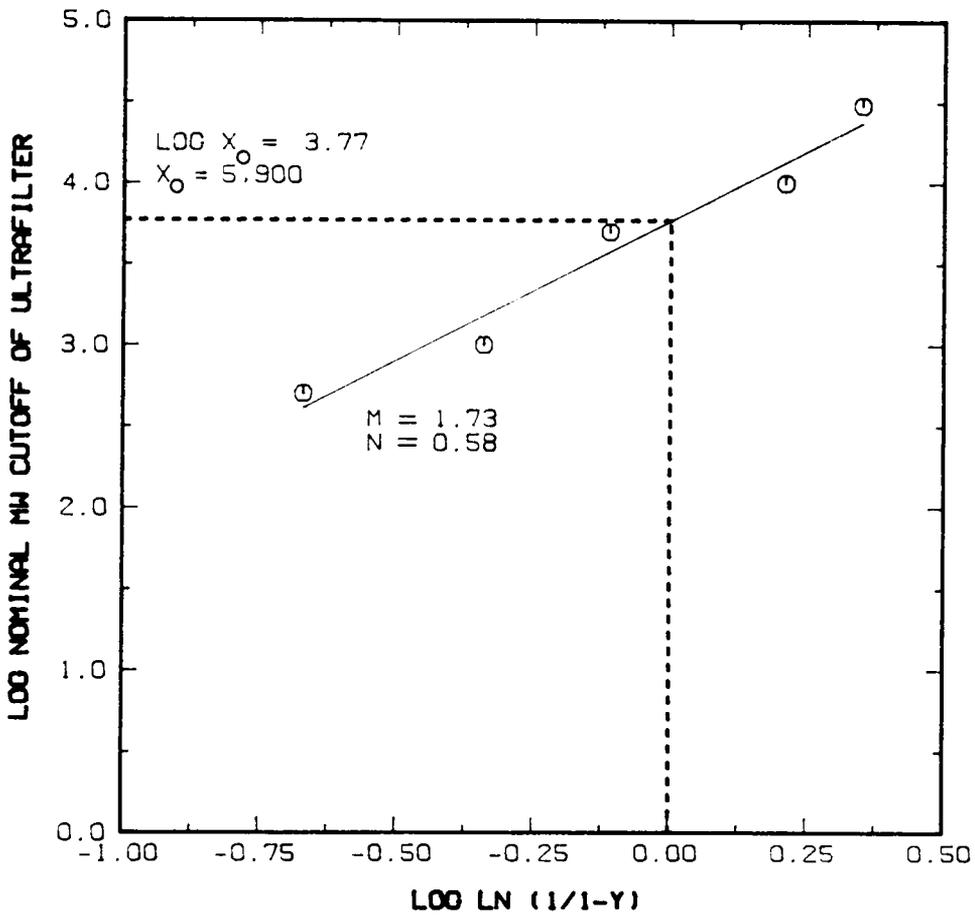


Figure 15. Rosin Rammler particle-size analysis applied to molecular size data.

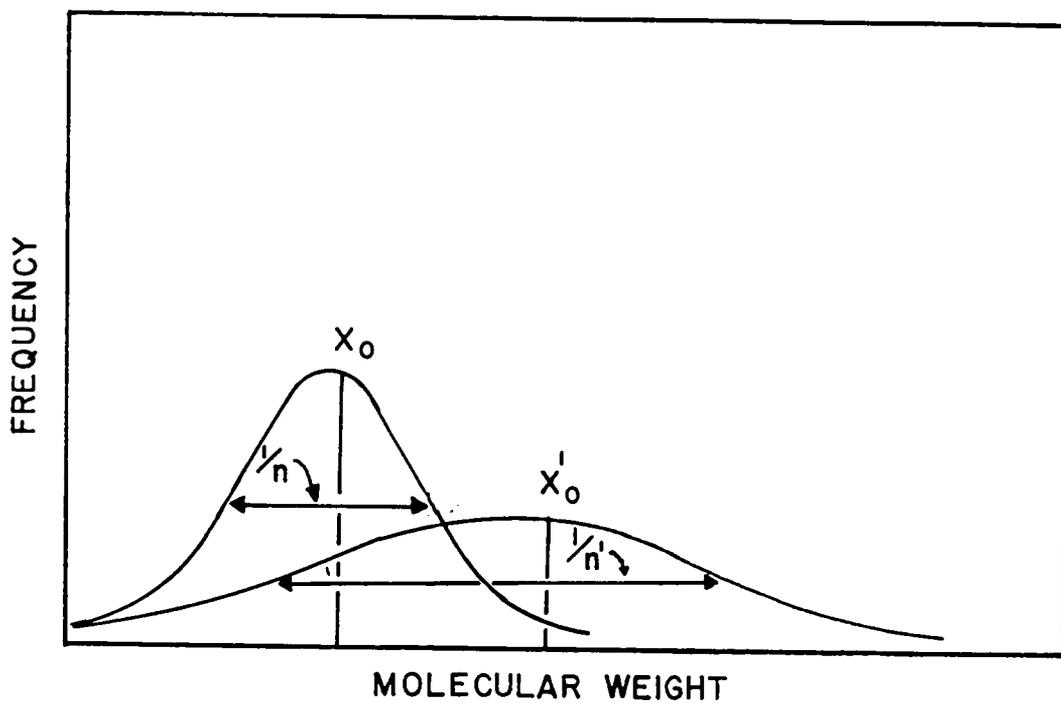


Figure 16. Illustration of how X_0 and n describe the molecular-size distribution of naturally occurring organic materials.

The quantity used for the bulk DOC concentration is critical for the calculation of Y and, thus, on the values obtained for X_0 and n. As previously described, the water was passed through either a 450 nm pore size filter or a 100,000 MW nominal exclusion limit filter (pore size of 5.1 nm).

Figure 16 shows how X_0 and n describe a molecular-weight distribution. The value for X_0 was used as the logarithm of a measure of the molecular size and the reciprocal of the slope (n) was used as a measure of how well distributed in size the organic molecules were. Mathematically, X_0 is the Y-intercept and its value represents the molecular weight equal to or larger than 63 percent of the organic molecules present. A high value for X_0 represents larger organic molecules and a low value represents smaller organic molecules. Mathematically, n is the reciprocal of the slope and represents the width of the molecular weight range for the solution. A high value of n indicated that the organic molecules exhibited a narrow size distribution, and a low value for n indicated that the organic molecules had a wide size distribution.

RESULTS

Overview

This chapter is divided into two main sections: 1) the results of the plant study and 2) the results of the laboratory study. The plant study focused on the effect of various preoxidants on the performance of the Abel Lake Water Treatment Plant, including 1) the removal of iron, manganese, THM precursors, organic carbon, and tastes and odors, 2) filter performance and 3) coagulant requirements. The laboratory study focused on the oxidation-reduction reactions between two oxidants (chlorine dioxide and permanganate) and two reduced substances, manganese(II) and organic carbon.

The data in Table 3 show that the water quality of Abel Lake varies seasonally, with increased contaminant concentrations during overturn. (In this study the word contaminant refers to any material that is objectionable in drinking water and in no way is meant to imply a non-anthropogenic origin.) Because there is seasonal fluxuation in water quality, the plant study was divided into two phases, one during the period of when the lake was thermally stratified and the other during the period when the lake was not stratified.

Table 3.
Seasonal changes in the raw water quality of Abel Lake

<i>Contaminant</i>	<i>Stratified</i>	<i>Not Stratified</i>
Soluble Mn (mg/L)	<0.010-0.014	0.22-0.41
Soluble Fe (mg/L)	0.08-0.23	0.16-0.83
DOC (mg/L)	2.6-3.9	5.5-9.5
THM formation potential (ug/L)	233-293	396-713
Turbidity (NTU)	1-3	5-30

Plant Study

This section considers the removal of Mn, Fe, DOC and THM formation potential (THMFP) during the treatment of the water in the water treatment plant. These data were considered in two ways, first the concentrations of these contaminants after each treatment step were observed to determine which steps were most effective in removing the contaminants and which steps were most affected by a change in preoxidant conditions. To do this, the contaminant concentrations were graphed as a function of the extent of treatment to develop what is termed here as removal patterns in the water treatment plant. Second, the data was examined in terms of percent removal so as to be able to determine which preoxidant condition performed the best for the removal of the various contaminants. In most cases the water was chlorinated just prior to filtration to prevent bacterial growth on the filters. This action may have enhanced the removal of iron or manganese. Chlorine was not added prior to filtration during the periods when chlorine dioxide was used as a preoxidant. As a precaution, the concentration of chlorine dioxide was monitored throughout the plant and was found to decrease upon addition to the raw water in the flash mixer from an initial dose of 2.0 to 3.0 mg/L to 0.2 to 0.5 mg/L. The concentration remained at this level through the remainder of the water treatment plant.

Removal Patterns

Manganese

Figure 17 shows that soluble manganese levels in the raw water were relatively low (≈ 0.01 mg/L) during the period of thermal stratification. During periods when raw water was preoxidized with permanganate (either as the sole oxidant or with chlorine dioxide), the soluble manganese concentrations increased in the clarifier and decreased upon passage through the filter. When permanganate was used alone, the soluble manganese concentration decreased in the clearwell.

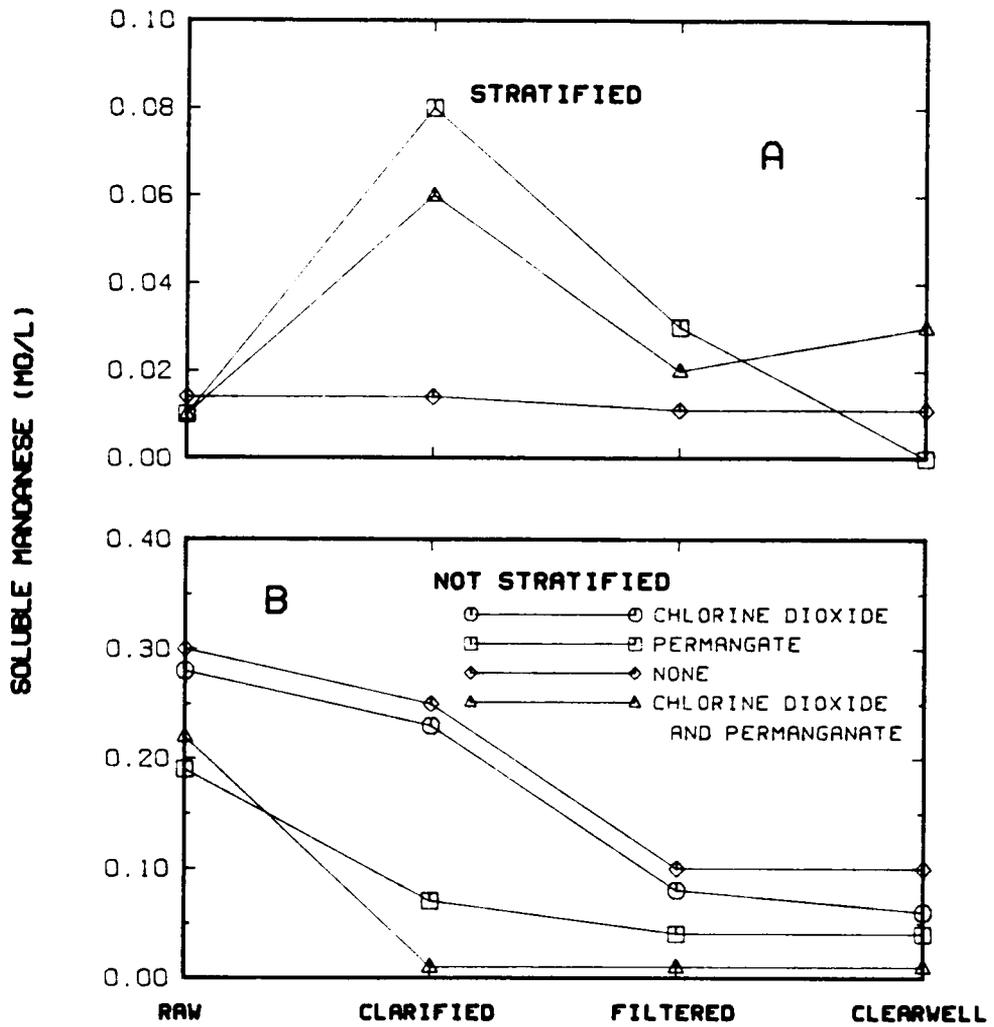


Figure 17. Effect of preoxidant choice on soluble manganese removal in the Abel Lake Water Treatment Plant.

However, when permanganate was used with chlorine dioxide, the soluble manganese concentration did not decrease in the clearwell. Soluble manganese concentrations did not decrease significantly through the treatment process when no preoxidant was used. During the period that chlorine dioxide was applied alone, the soluble manganese concentration in the raw water was below detection limits. Thus, no data were presented for this case.

During the fall circulation period, when the soluble manganese levels were much greater in the raw water, the manganese removal pattern was different than that observed while the lake was stratified. At all times, the manganese levels decreased through the plant. When permanganate was being added, most of the soluble manganese was removed by flocculation and settling. The pattern of manganese removal observed when chlorine dioxide was used as a preoxidant was the same as that observed when no preoxidant was used, that is in both cases, a small amount of soluble manganese was removed by flocculation and settling but most was removed by the filters.

Iron

Figure 18A shows that the concentrations of soluble iron in the raw water while the lake was stratified were less than 0.3 mg/L. The removal pattern through the treatment plant was the same regardless of which preoxidant was being applied. Most of the iron was removed by clarification, but some was also removed by the filter. During the period that the lake was not stratified, the soluble iron concentrations were elevated (Figure 18B). For each preoxidant condition, the soluble iron concentrations decreased markedly in the clarifier. No samples were taken for soluble iron analysis during overturn at times when no preoxidant was being used.

DOC

Figures 19A and 19B show that the pattern of organic carbon removal was similar regardless of the preoxidation condition. Organic carbon concentrations decreased in the clarifier and remained

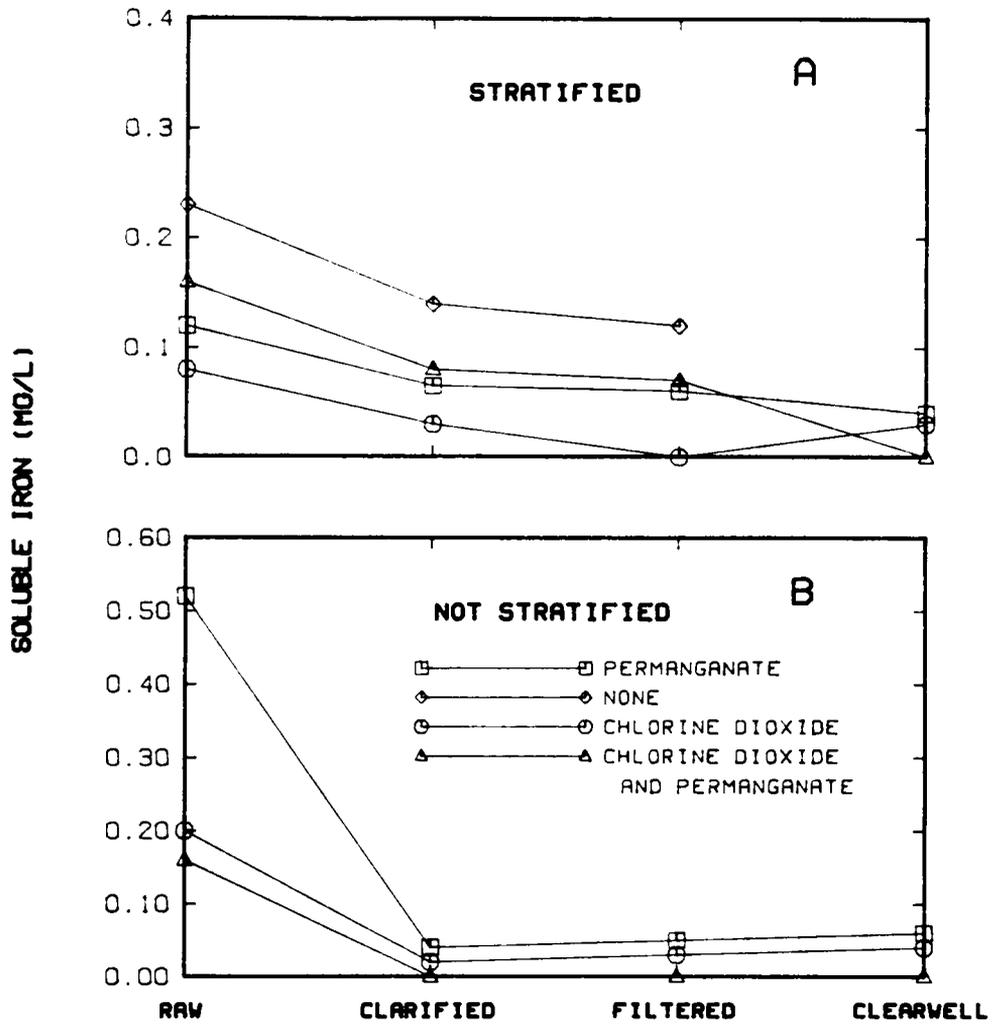


Figure 18. Effect of preoxidant choice on soluble iron removals in the Abel Lake Water Treatment Plant.

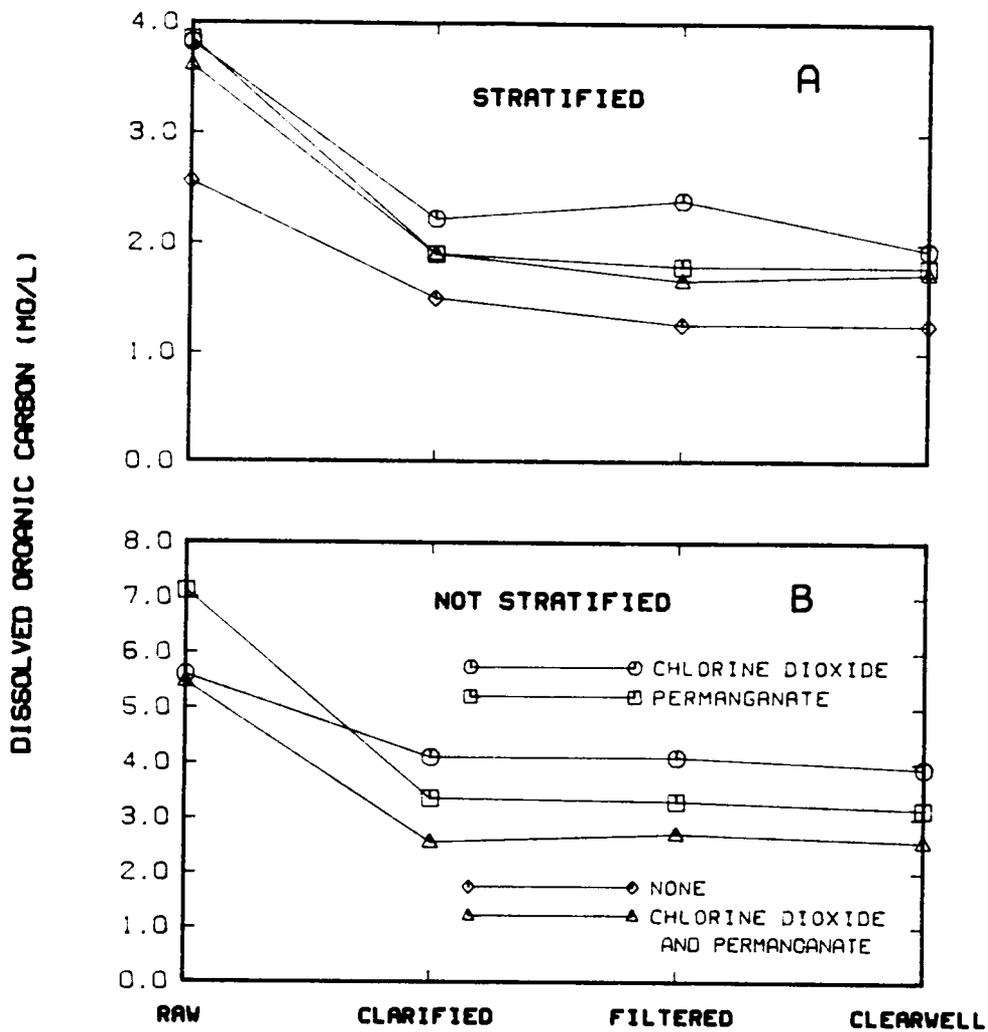


Figure 19. Effect of preoxidant choice on organic carbon removals in the Abel Lake Water Treatment Plant.

virtually constant through the remaining treatment processes. The increase in DOC observed in the clarifier during periods when no preoxidant was used was considered to be anomolous. The pattern of DOC removal when the lake was not stratified was identical to that observed while the lake was stratified.

THM-Precursors

In this dissertation, THMFP is assumed to represent a measure of the concentration of the organic THM-precursors in the water. During periods while the lake was stratified and while it was not, the patterns of THM-precursor removal were similar regardless of preoxidation conditions. Figures 20A and 20B show that THM-precursor (precursor) concentrations decreased during flocculation and settling steps and then remained constant through the remainder of the plant.

Percent Removals of Mn, Fe, DOC and THM-formation Potential

Table 4 summarizes the treatment plant efficiencies in removing reduced manganese and iron, DOC and THMFP under the various preoxidant conditions. The removals under the various preoxidant conditions while the lake was stratificatied and while the lake was not stratified were presented separately. The percent removals were determined by dividing the difference between concentrations in the raw and treated water by the initial concentrations. The data presented in Table 4 represent the average of the results of four sampling periods. The raw data used for these calculations is listed in Appendix B. Because of the daily variability of the raw water source and the treatment conditions, the percent removals were rounded to the nearest multiple of five.

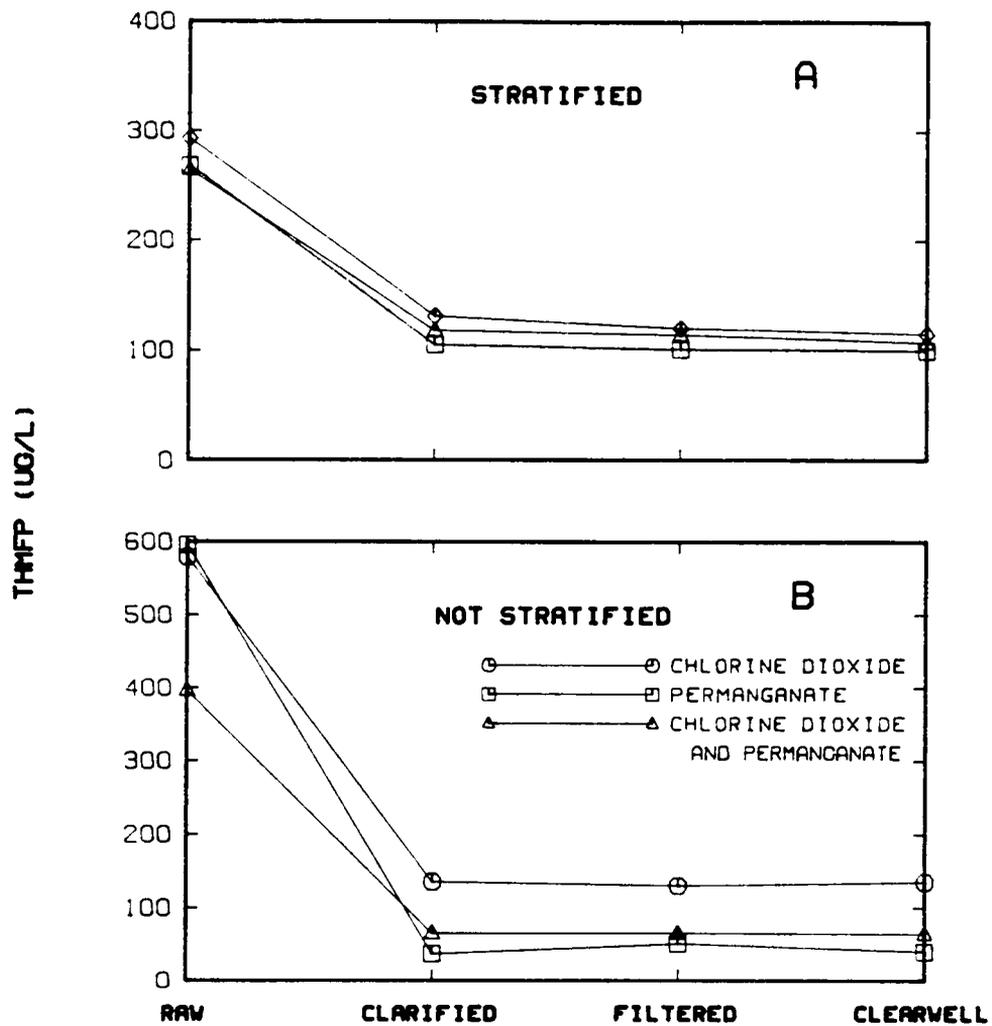


Figure 20. Effect of preoxidant choice on THM-precursor removals in the Abel Lake Water Treatment Plant.

Table 4.
Effect of preoxidant choice on the removals of Fe(II), Mn(II), DOC and THM-Precursors by treatment at the Abel Lake WTP.

Raw Water Constituent	Percent Reduction for Pretreatment Shown							
	While Lake was Stratified				While Lake was Not Stratified			
	ClO ₂	KMnO ₄	Both Preox.	No Preox.	ClO ₂	KMnO ₄	Both Preox.	No Preox.
Soluble Mn	ND ¹	BD ²	100 percent increase	20	80 ³	80	95	70 ³
Soluble Fe	65	70	>99	50	80	90	>99	ND
DOC	50	55	50	50	30	55	55	ND
THM-precursors	65	55	60	60	75	95	85	ND
¹ ND = no data ² BD = manganese concentration reduced from 0.01 mg/L to below detection limit (0.01 mg/L) ³ 50 percent was removed by chlorination/filtration								

Manganese Removal

Soluble manganese removal ranged from removal to levels below detection (permanganate) to an increase in concentration of 100 percent (permanganate and chlorine dioxide together) over the raw water concentration. This wide range was probably a result of the low initial soluble manganese concentrations (i.e., a small change in the treated soluble manganese concentration caused a large percent difference). While the lake was not stratified, the percent removals of soluble manganese ranged from 70 percent when no preoxidant was used to 95 percent when chlorine dioxide and permanganate were applied at the same time. Permanganate and chlorine dioxide both removed 80 percent of the soluble manganese.

Iron Removal

While the lake was stratified, soluble iron removals ranged from 50 percent when no preoxidant was supplied to greater than 99 percent when ClO_2 and KMnO_4 were used in combination. When permanganate was the sole preoxidant and when chlorine dioxide was the sole oxidant 65 percent of the iron was removed, which was intermediate to the two extremes.

While the lake was not stratified, iron removals ranged from 80 percent (when chlorine dioxide was added) to greater than 99 percent (when chlorine dioxide and permanganate were added in combination). When no preoxidant was applied, iron determinations were not performed. Preoxidation with permanganate affected 90 percent soluble iron removal which was intermediate to the iron removals was achieved by chlorine dioxide or the combined use of chlorine dioxide and permanganate.

Organic Carbon Removal

While the lake was stratified, the removal of DOC ranged from 45 percent when chlorine dioxide was applied to 50 percent when permanganate was dosed. A decrease of 50 percent was achieved during periods when no preoxidant was dosed and during periods when chlorine dioxide and permanganate were both added to the water. While the lake was not stratified, the range in DOC removal was 25 percent when chlorine dioxide was applied to 65 percent when no preoxidant was dosed. The water treatment plant removed 50 percent of the DOC during periods when only permanganate was added and when permanganate and chlorine dioxide were being added simultaneously.

THM-Precursor Removal

While the lake was stratified, THM-precursor removals were greater than the removals of DOC, ranging from a high of 65 percent for chlorine dioxide to 60 percent for the three other conditions of preoxidation. During the period when the lake was not stratified, the THM-precursors were removed even more efficiently, ranging from 80 percent when chlorine dioxide was applied to 90 percent when permanganate was applied. Dosing these two preoxidants in combination resulted in a THM-precursor removal of 90 percent. No data were available for periods when no preoxidant was used.

Filter Operation

The plant records were reviewed to determine the effect of each preoxidant condition on the filter-operation times (time of filter operation between backwashes). Figure 21 shows the length of time between backwashes at the plant for several years since its construction, including the years this study was conducted. The cyclical pattern of filter performance was probably a result of seasonal

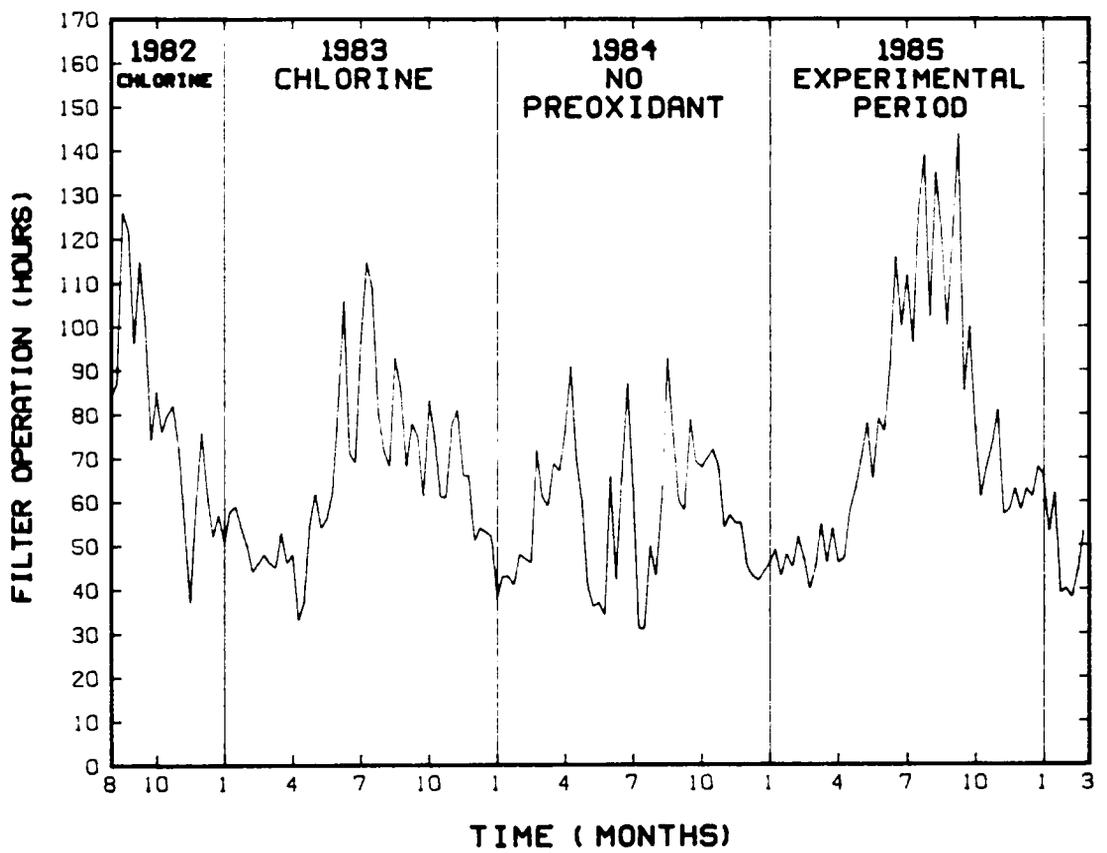


Figure 21. Time line of filter operation time between backwashes for the Abel Lake Water Treatment Plant.

changes in the raw water source. Filter operation times typically increased during stratification (during the summer months) and then decreased during the period when the lake was not stratified (mid-November through April). During the summer of 1984, when no preoxidant was used, the filter operation times did not experience a seasonal increase as in the other summers when a preoxidant was used. Filter operation times during the summer months of the study period were longer than during any previous period. It was not possible to tell from Figure 21 which preoxidant condition (chlorine dioxide, permanganate, or the combination) was responsible for the increased filter- operation times.

The data in Table 5 show the average filter-operation time between backwashes at the plant under the five preoxidant conditions. The data collected when the lake was stratified and those collected when it was not were statistically analyzed as two distinct groups to determine if the differences in the filter operation times observed during periods of for the five preoxidant conditions were statistically significant. Initially, a two-way analysis of variance (ANOVA) was performed at the 95 percent confidence level. The results of this test indicated that the difference in the mean values of filter operation time for each preoxidant was statistically significant. However, this test only tested the whether or not the preoxidation condition had a significant effect on the filter operation times. It did not test whether specific filter operation times were statistically different from others. Multiple t-tests were performed to determine which of the individual differences in the mean filter operation times were significant at the 95 percent level. The tests used were the LSD, Duncan's and Scheffe's tests (97). Of these, Scheffe's test was the most rigorous and was less apt to find data sets statistically different. The other tests (LSD and Duncan's) were less rigorous and, therefore, more readily found data sets to be statistically different. The results of the statistical analysis are presented in Table 5.

The most conservative test (Scheffe's) indicated that during stratification the filter operation data could be considered as two groups. Group one, with shorter filter operation times, included treatment during periods when no preoxidant was used. Group two included significantly longer filter operation times than did group one and represented plant operation during periods that a preoxidant was used. The more liberal tests (LSD and Duncan) indicated that the five filter oper-

Table 5.
Results of ANOVA for filter operation times observed during different preoxidant conditions.

<i>LAKE STRATIFIED</i>					
Preoxidant Condition and mean filter operation time (hours)					
<i>T-TEST</i>	no oxidant 60 ± 10 ¹	chlorine 80 ± 7	permanganate 84 ± 9	chlorine dioxide 100 ± 9	chlor. diox. & permanganate 100 ± 15
Scheffe	-----group 1-----	-----group 2-----			
LSD	-----group 1-----	-----group 2-----		-----group 3-----	
Duncan	-----group 1-----	-----group 2-----		-----group 3-----	
<i>LAKE NOT STRATIFIED</i>					
Preoxidant Condition and mean filter operation time (hours)					
<i>T-TEST</i>	permanganate 46 ± 4 ¹	no oxidant 51 ± 3	chlorine dioxide 52 ± 3	chlorine 64 ± 4	
Scheffe	-----group 1-----				-----group 2-----
LSD	-----group 1-----				-----group 2-----
Duncan	-----group 1-----				-----group 2-----
¹ 95 percent confidence limits					
<i>Preoxidant conditions with a common group number do not have statistically different filter operation times.</i>					

ation times, associated with the five preoxidant choices, could be classified into three groups. The first group included the filter operation times observed when no preoxidant was being used. These were shorter than those obtained when a preoxidant was used (groups two and three). The second group contained filter operation times observed when chlorine was dosed and when permanganate was dosed. The use of these preoxidants resulted in filter operation times intermediate to those in groups one and two. The third group contained chlorine dioxide, when dosed by itself and when dosed in combination with permanganate. Preoxidation with these two oxidant conditions yielded the longest filter operation times.

When the lake was not stratified, the mean filter operation times did not vary as widely as when the lake was stratified. The mean filter operation times observed during the application of each preoxidant condition were more tightly grouped, and the 95 percent confidence bands for each of the means were smaller. The analysis of variance test revealed that the means were statistically different so multiple t-tests were again performed, and the results are shown in Table 5. The results of the three tests were all identical and showed that the data could be separated into two groups. The first group contained the shorter filter operation times which occurred during treatment with permanganate, no preoxidant, or chlorine dioxide. The filter operation times of the second group were statistically greater and included filter operation times when chlorine and the combination of chlorine dioxide and permanganate were dosed.

Figures 22 and 23 show the relationship between the turbidity of the waters being applied to the filters (applied turbidity) and the filter-operation time of the filters. To help make the graphs less cluttered, the data was divided into two parts, those which occurred while the lake was stratified and those which occurred while it was not. Also, the data points were not connected by lines. In both cases (stratified and not stratified) an inverse relationship existed between the applied turbidity and filter-operation time. During the period of lake stratification, the function is curvilinear, and while the lake was not stratified it is linear. For a given applied turbidity, filter-operation time were longer when a preoxidant was used than when the water was not preoxidized. This was especially true while the lake remained stratified. It should be noted that this relationship is purely observational and that a cause and effect relationship is not valid unless a mechanism is known.

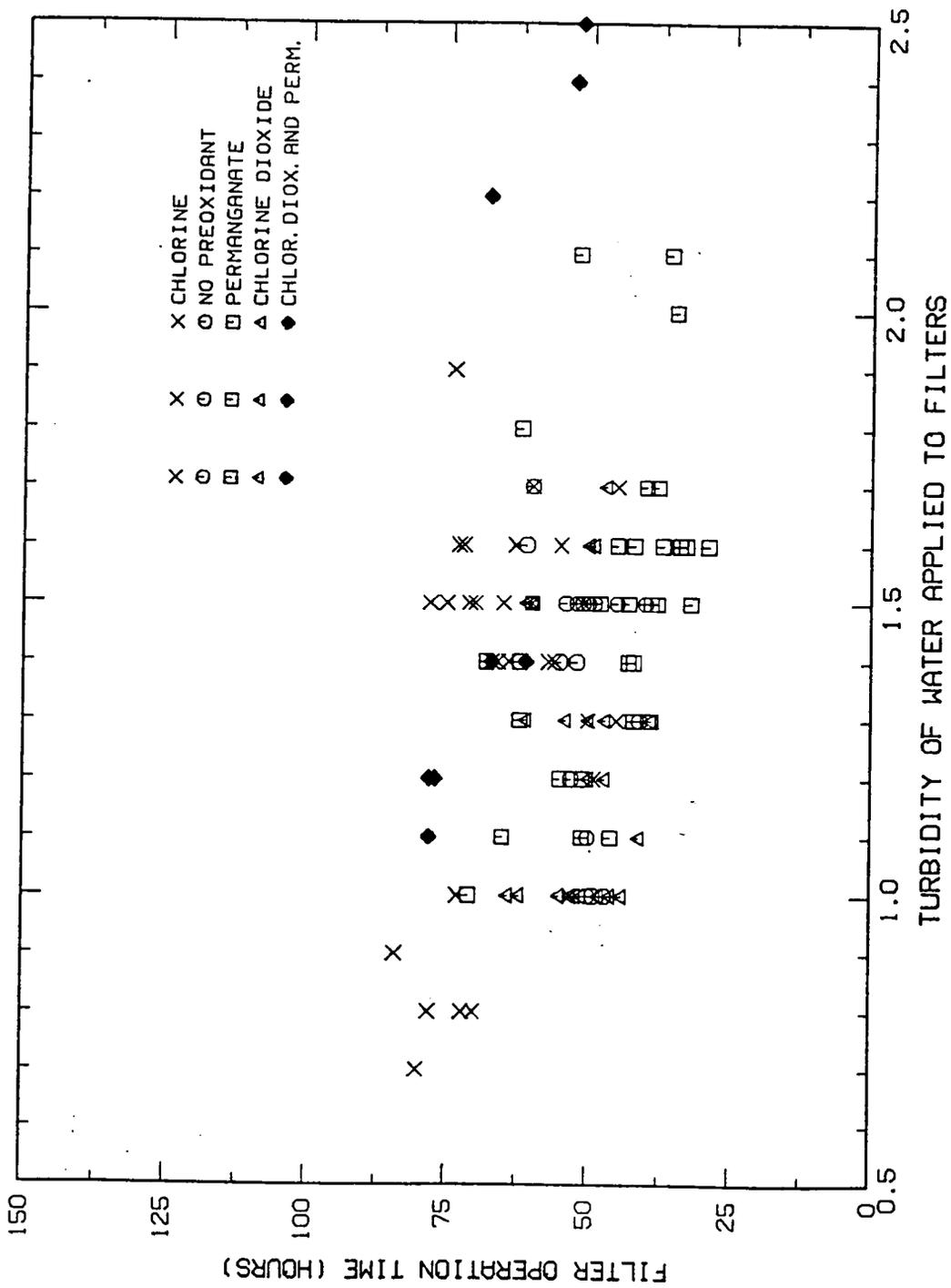


Figure 22. Turbidity of water applied to the filter versus filter operation times while Abel Lake was stratified.

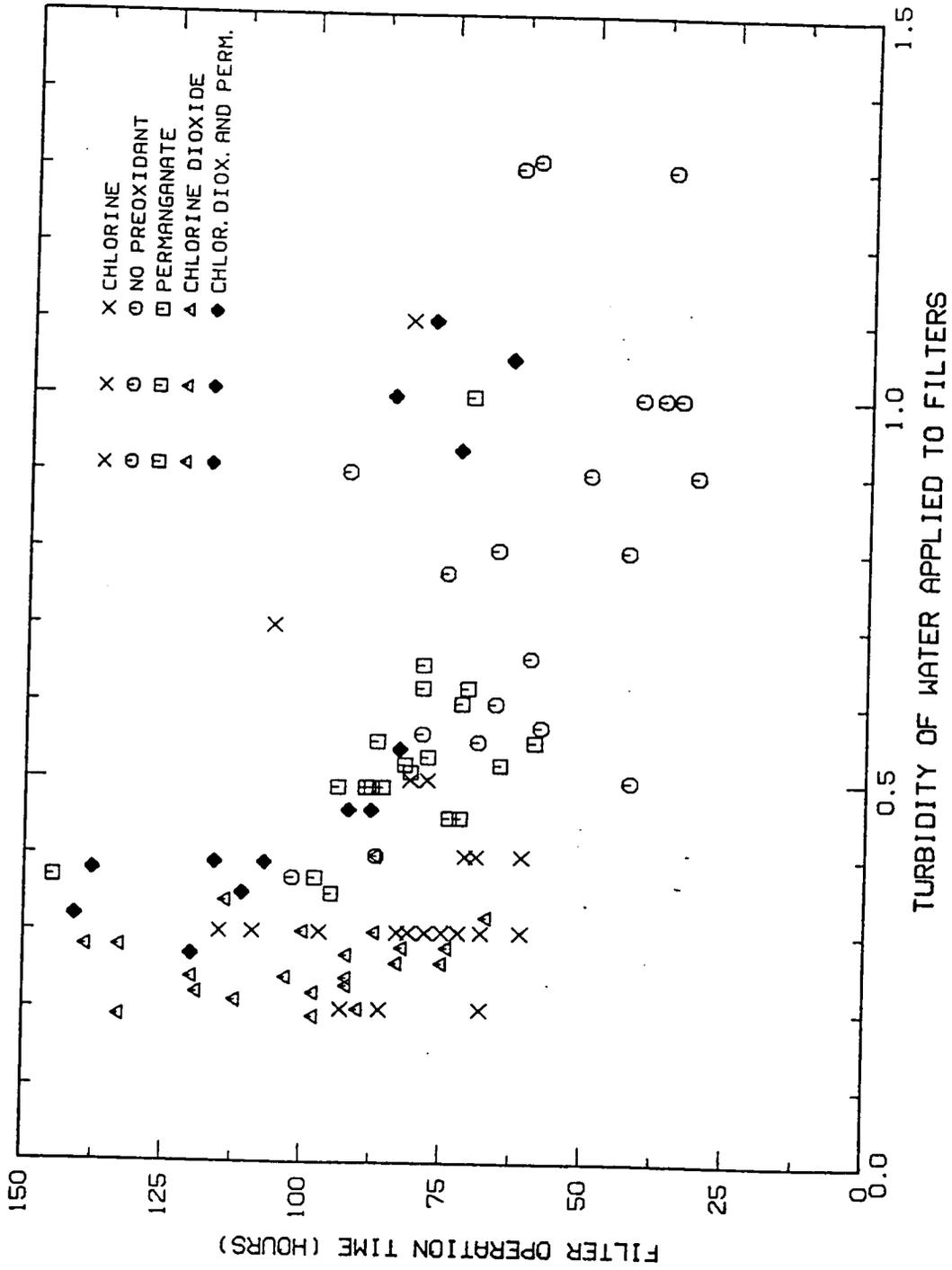


Figure 23. Turbidity of water applied to the filter versus the filter operation times while Abel Lake was not stratified.

During the period when the lake was not stratified (Figure 23), the applied turbidity had less of an effect on the filter-operation time than it did during the period of lake stratification (Figure 22). The preoxidant condition did not seem to affect the applied turbidity. That is, the preoxidant conditions were all equally represented along the x-axis. Preoxidation with chlorine was associated with longer than average filter-operation times.

Effect of Oxidants on Coagulant Requirements

Aluminum sulfate (alum) $[Al_2(SO_4)_3 \cdot 18H_2O]$ was the coagulant at all times. During plant operation, the optimum dose was determined by monitoring the effluent turbidity from a pilot filter. The alum concentration that resulted in the lowest effluent turbidity was then applied to the flash mix basin. The plant operator then made final adjustments to the alum dose after observing the floc size in the flocculators and its settling characteristics in the clarifier. Figure 24 shows that the alum dose requirements did not fluxuate seasonally as much as did the filter operation times. The alum dose during the experimental period was moderate to low and did not fluxuate as widely as it did during the previous years, but whether this condition was caused by any of the preoxidants being studied or by unusually consistent raw water quality is not known.

To evaluate the effect of the different oxidants on alum-dose requirement at the water treatment plant, the average alum doses during the applications of the different preoxidant conditions were determined during the periods when the lake was stratified and when it was not. To determine if the differences between the mean alum doses were statistically significant at the 95 percent confidence level, two ANOVA procedures were performed, one on the data representing water from the lake while it was stratified and the other from the lake while it was not stratified. In both cases, the ANOVA revealed that the choice of oxidant affected changes in the optimum alum doses. Multiple t-tests were performed to determine which data sets were not statistically different and, thus, could be grouped together.

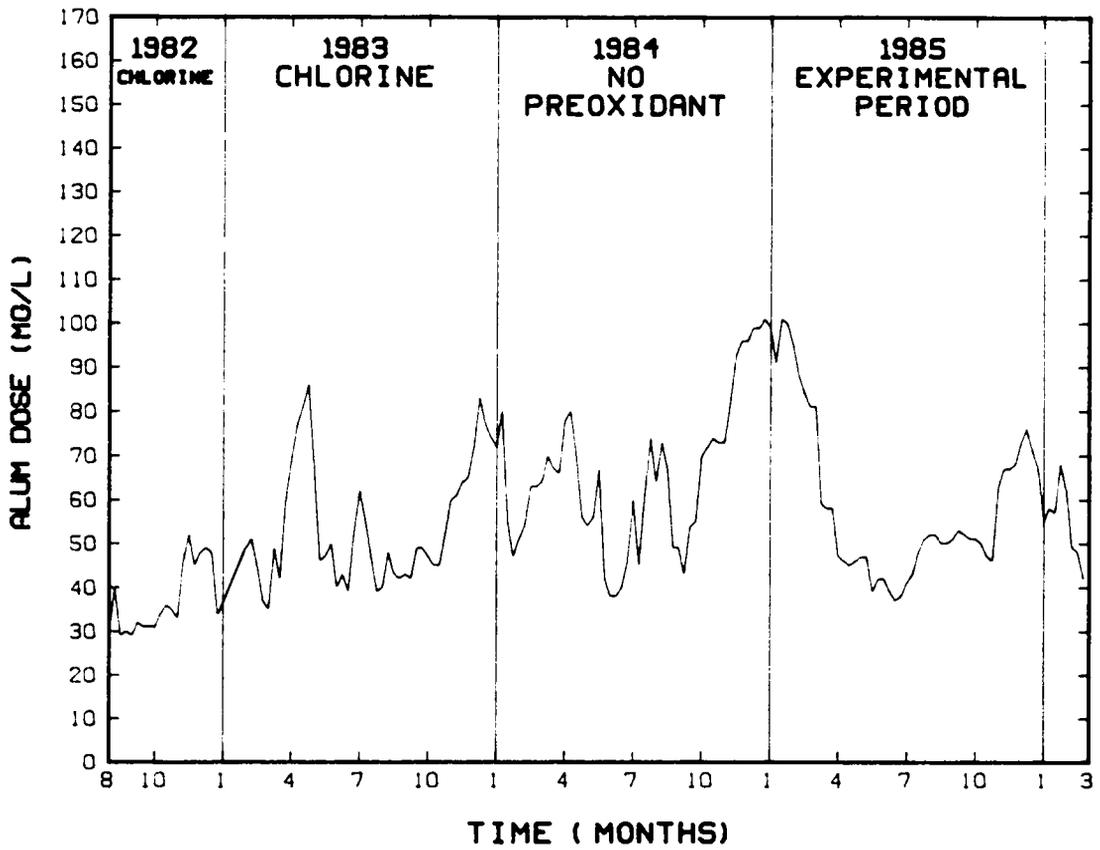


Figure 24. Time line of alum dose for the Abel Lake Water Treatment Plant.

The average alum requirements categorized by oxidant and the results of the multiple t-tests are presented in Table 6. The alum requirements during periods of lake stratification, shown at the top of Table 6 were reviewed first. The lowest alum doses were required when chlorine was used as an oxidant (41 mg/L) and the greatest alum doses were required when no preoxidant was used. The most conservative of the t-tests showed that the data could be separated into two significantly different groups. Group one included the alum requirements during periods when the following preoxidants were in use: chlorine dioxide alone, chlorine dioxide and permanganate together and permanganate alone. Group two contained only alum requirements during the period when chlorine was applied. The lowest optimum alum dose occurred during these periods. The LSD test (somewhat more liberal than Scheffe's test) classified the data into three groups. The first group included those periods associated with the highest alum requirements. The following preoxidation conditions prevailed: no preoxidant, chlorine dioxide alone, and chlorine dioxide and permanganate together. The second group contained some alum doses that were also in the first group. The preoxidant condition that produced alum doses common to groups one and two was the combined use of chlorine dioxide and permanganate together. In addition to the common alum dose, group two contained the alum dose required when permanganate was used by itself. The use of the preoxidants in group two resulted in alum requirements (46 and 47 mg/L) that were intermediate to those in groups one (47 to 50 mg/L) and three (41 mg/L). The third group contained the lowest alum requirement which occurred while chlorine was the preoxidant. Duncan's multiple t-test also separated the oxidants into three groups and only differed from the LSD test in that the second group contained the alum dose that was required when chlorine dioxide was dosed. In all three multiple t-tests, the amount of alum required when chlorine was used as a preoxidant was statistically less than that required for any other preoxidant condition.

While the lake was not stratified, the effects of dosing chlorine dioxide and permanganate in combination were not evaluated to the extent the other preoxidant conditions because of problems with odors. (The taste-and-odor data are reviewed in the next section.) Because too few data were collected for this preoxidant condition, it was not included in the statistical analysis. The multiple t-tests were the same as those performed on the alum dose data obtained while the lake was stratified. The optimum alum doses and the results of the multiple t-tests were presented on the

Table 6.
Results of ANOVA for optimum alum doses observed during different preoxidant conditions.

LAKE STRATIFIED					
Aluminum Sulfate dose [Al ₂ (SO ₄) ₃ •18H ₂ O] (mg/L)					
T-TEST	no oxidant 50 ± 1 ¹	chlorine dioxide 49 ± 3	chlor. diox. & permanganate 47 ± 2	permanganate 46 ± 2	chlorine 41 ± 2
Scheffe	-----group 1-----		-----group 2-----		
LSD	-----group 1-----		-----group 2-----	-----group 3-----	
Duncan	-----group 1-----		-----group 2-----	-----group 3-----	
LAKE NOT STRATIFIED					
Aluminum Sulfate dose [Al ₂ (SO ₄) ₃ •18H ₂ O] (mg/L)					
T-TEST	chlorine 65 ± 3 ¹	no preoxidant 63 ± 6	permanganate 56 ± 4	chlorine dioxide 47 ± 2	
Scheffe	-----group 1-----		-----group 2-----	-----group 3-----	
LSD	-----group 1-----		-----group 2-----	-----group 3-----	
Duncan	-----group 1-----		-----group 2-----	-----group 3-----	
¹ 95 percent confidence limits					
<i>Preoxidant conditions with a common group number do not have statistically different optimum alum doses.</i>					

bottom half of Table 6. The ANOVA test indicated that the differences between four data sets (representing the four preoxidant conditions) were not a result of natural variations in means that belong to the same population of data. The most conservative multiple t-test, Scheffe's test, indicated that the data could be divided into three groups. The use of the first group of preoxidant conditions, which included chlorine and no preoxidant, was associated with the highest alum requirement. Preoxidation with the oxidant in the second group (chlorine dioxide) was associated with the lowest alum requirements. Preoxidation with permanganate and no preoxidation at all were associated with the intermediate alum requirements in group three. The more liberal t-tests, LSD and Duncan's also divided the data into three groups, but excluded no preoxidant from the second group. In all three tests, the optimum alum dose required while chlorine dioxide was the preoxidant was statistically less than that required while other preoxidants were used.

Taste-and-odor Complaints

Consumer-complaint records of taste and odors were initiated by plant personnel at the beginning of this study. During the 164-day experimental period while the lake remained stratified, 33 complaints were registered. Most complaints were of chlorinous or kerosene-like odors, though there were a few complaints of bad tastes as well. Twenty-seven of these (82 percent) occurred while chlorine dioxide or chlorine dioxide in combination with permanganate was used as the preoxidant. Five complaints occurred during periods when permanganate was the preoxidant, and one complaint was registered during the nine days that no preoxidant was used. Consumer complaint records were not kept during the time that chlorine was used as a preoxidant. The complaints recorded for each preoxidant were listed in Table 7. To facilitate comparisons of the oxidants, which may have been in use for different lengths of time, the complaints were expressed as complaints per month (number of complaints recorded for an oxidant divided by the number of days that oxidant was in use, times 30 days per month) The number of complaints ranged from three per month during the periods both when no preoxidant was used and when permanganate was used

Table 7.
Taste-and-odor complaints recorded by Abel Lake WTP personnel during five preoxidant conditions

<i>Preoxidant</i>	Taste-and-odor complaints while lake was stratified			Taste-and-odor complaints while lake was not stratified		
	Days Used	Total Complaints	Complaints per Month	Days Used	Total Complaints	Complaints per Month
None	9	1	3	0	0	0
Cl ₂	0	-	-	38	0	0
KMnO ₄	49	5	3	57	1	1
ClO ₂	56	13	7	28	3	3
KMnO ₄ &ClO ₂	50	14	9	6	2	10

to nine complaints per month during the period when chlorine dioxide and permanganate were used in combination.

The phase of the study conducted while the lake was not stratified lasted 129 days and was characterized by six complaints. The number of complaints registered ranged from zero for the 38 days that chlorine was used as a preoxidant to three complaints during the 28 days that chlorine dioxide was used. The combination of chlorine dioxide and permanganate was used for only six days and generated two complaints (10 complaints per month). These two complaints were described as both "chlorinous" and "kerosene" odors and were strong enough to render the water unpotable for the complainants, who persuaded the operator to terminate the combined use of chlorine dioxide and permanganate.

Jar-Test Studies

The jar-test studies evaluated the effects of both alum dose and oxidant dose on the removal of DOC, THMFP, Fe and Mn. The jar-test studies were divided into two phases. This first phase of jar-tests included those experiments in which the alum dose was varied and the second phase included those in which both the oxidant type and the oxidant dose was varied.

Evaluation of Jar-test Procedures

Before the results of the jar tests were interpreted, the reproducibility of data generated by this test procedure was examined, and comparisons to plant performance were made. The data in Table 8 show the results of several jar-tests, many of which were performed on different dates. The DOC, and the manganese data were reproducible, however, the iron data and especially the THMFP data

Table 8.
 Variability of data resulting from the jar-test procedure used in this study to mimic treatment at the Abel Lake WTP.

Concentrations After Treatment					
DATE	Alum mg/L	DOC mg/L	THMFP ug/L	Fe mg/L	Mn mg/L
SURFACE WATER					
7/09/85	20	2.9	255	0.02	0.01
7/09/85	20	3.0	184	0.03	0.01
7/10/85	20	3.1	185	0.03	0.01
7/31/85	20	3.3	138	0.06	0.01
7/09/85	40	2.4	156	0.05	0.01
7/09/85	40	2.2	179	0.02	<0.01
7/09/85	40	2.5	ND	0.04	0.01
7/09/85	60	3.4	ND	0.05	0.03
7/09/85	60	2.1	ND	0.02	0.01
7/10/85	60	2.6	203	0.02	0.01
7/31/85	60	2.4	110	0.03	0.01
SURFACE WATER MIXED WITH HYPOLIMNETIC WATER					
9/17/85	50	2.4	107	<0.02	0.39
9/17/85	50	2.4	111	<0.02	0.36
9/17/85	50	2.3	116	<0.02	0.38
9/17/85	50	2.3	84	<0.02	0.38
ND= No Data					

showed unexpected variability. Some variations due to natural variations in the raw water quality from one date to the next was expected, but the THMFP data was reproducible to within only 15 to 30 percent for jar tests performed on the same day under identical conditions.

Table 9 shows comparison of data obtained using the jar test procedure described in the Methods chapter to those obtained when water was withdrawn from various points in the water treatment plant as shown. The variability of the data from the jar-tests was greater than that of the data from the water treatment plant, but, in general, the jar tests were found to be good predictors of plant performance. The manganese concentrations were at or below detection limits in all cases and, thus, showed little variability.

Effect of Oxidants on the Optimum Alum Dose for Organics Removal

The effect of the oxidant conditions on the optimum alum dose for DOC removal was evaluated in this section (Figure 25). (The effect of the oxidants on the *removal* of DOC THM-precursors and manganese is presented later in this chapter.) These experiments were performed in duplicate on water from the surface of Able Lake while it was stratified. The curves shown represent the results of second order regressions which yielded a better fit than did linear regressions. The optimum alum dose was defined as the lowest concentration of alum that yielded the best removal of DOC. This was determined with the data in Figure 25 by sighting the minimum on the curve and following the curve towards the ordinate until the slope started to increase. This analysis yielded the following results. With no preoxidant present, the optimum alum dose was 35 to 40 mg/L. [In all cases the alum concentration was expressed as $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$.] When chlorine dioxide was present, the optimum alum dose decreased to 25 to 30 mg/L, but DOC removal suffered. (More about this in this chapter). Permanganate and chlorine increased the optimum alum dose to 45 to 50 mg/L and 50 to 55 mg/L, respectively. The optimum alum doses for the two cases in which a combination of preoxidants was used, permanganate with chlorine dioxide and permanganate with chlorine, were 50 to 55 and 45 to 50 mg/L, respectively.

Table 9.
Comparison of the removals of DOC, THMFP, Mn(II), and Fe(II) observed in jar tests to those observed in the WTP

Alum dose was 53 mg/L in all cases and no oxidant was used					
<i>SOURCE</i>	<i>DOC</i> mg/L	<i>THMFP</i> mg/L	<i>Fe</i> ug/L	<i>Mn</i> mg/L	<i>Yield</i> ug/mg
Jar-test	3.0	95	0.02	0.01	30
Jar-test	2.3	90	0.05	<0.01	40
Rapid mix	2.3	85	0.02	0.01	35
Flocculator-1	2.3	85	0.09	0.01	35
Flocculator-2	2.2	100	0.03	<0.01	45
Flocculator-3	2.2	115	0.02	<0.01	50

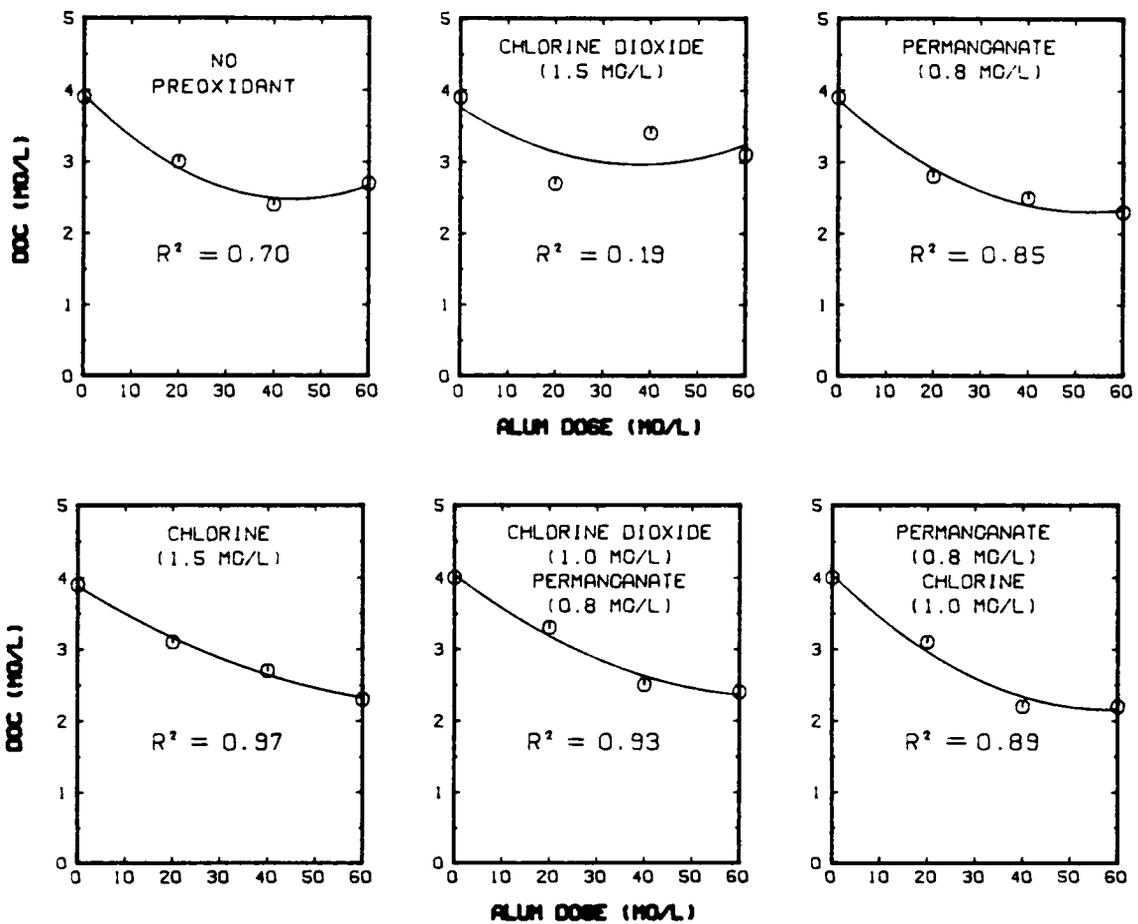


Figure 25. Effect of oxidants on alum dose for optimum organic carbon removal from Abel Lake surface water while lake is stratified.

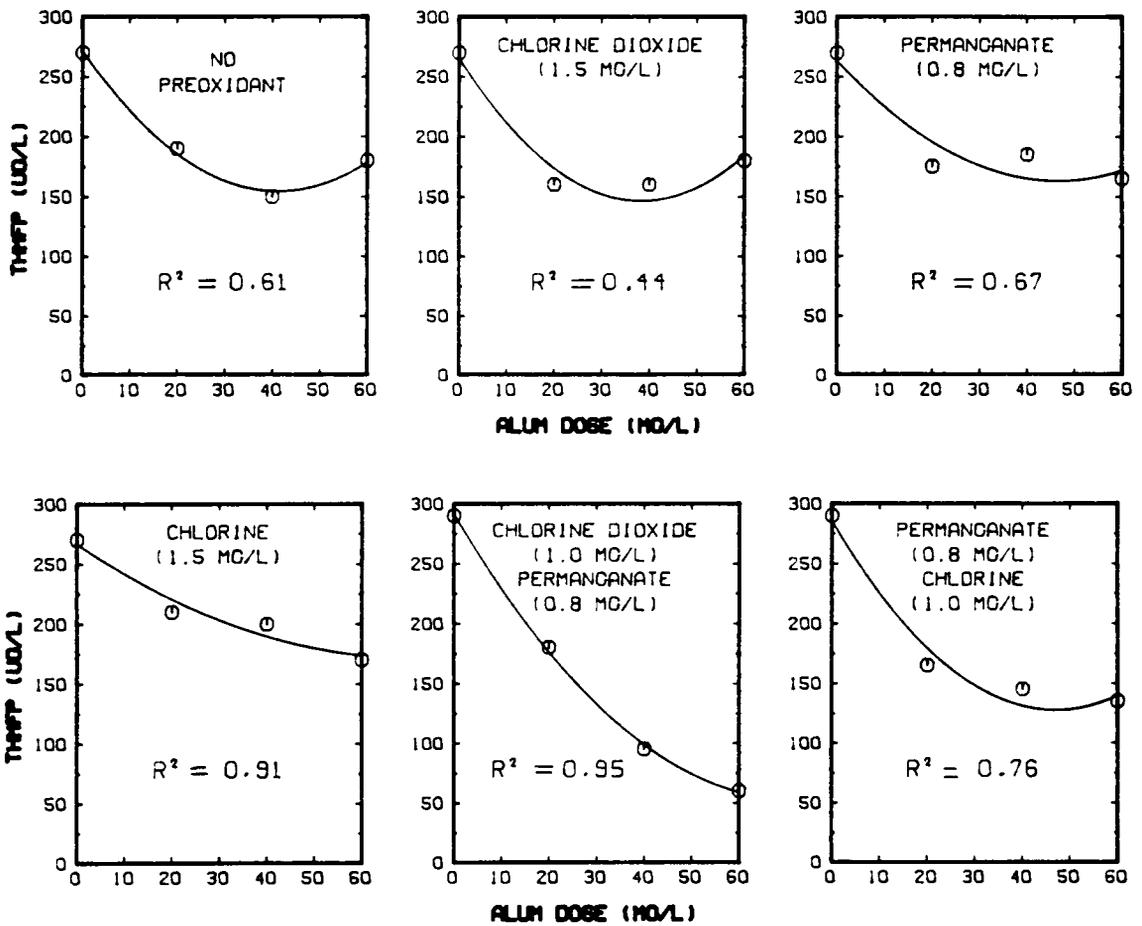


Figure 26. Effect of oxidants on the alum dose for optimum precursor removal from Abel Lake surface water while lake is stratified.

Figure 26 shows the effect of the oxidants on the optimum alum dose for THM-precursor removal. Second-order regressions were fitted to the data, and the same procedure was followed to determine the optimum alum dose. With no preoxidant present, the optimum alum dose was 35 to 40 mg/L. Chlorine dioxide slightly decreased the optimum alum dose to 30 to 35 mg/L, and permanganate alone and permanganate with chlorine slightly increased the optimum alum dose to 40 to 45 mg/L. When chlorine or chlorine dioxide with permanganate were added, the optimum alum dose increased to about 60 mg/L.

Effect of Oxidants on Removals of DOC, THM-precursors and Manganese(II)

Laboratory studies (jar-tests) were conducted to evaluate the removal of DOC, THM-precursors and manganese(II) from two different types of water that simulated conditions that would occur in the plant both while the lake was stratified and while the lake was not stratified. The water typical of the lake while it was not stratified had higher concentrations of manganese(II) (0.40 mg/L). In all jar tests, the alum dose was between 40 and 50 mg/L (depending on the plant's dose during the day of the jar test). In the following figures, a dose of "0" refers to water that was coagulated with alum only, not the raw water DOC. The oxidant concentrations were expressed as milliequivalents per liter (meq/L), assuming a transfer of one equivalent per mole for chlorine dioxide and 3.5 equivalents per mole for permanganate so that they could be compared. (The normality of permanganate was based on the results obtained in the section on the interference of permanganate on chlorine dioxide determination.)

DOC removal

The removal of DOC was considered first. Coagulation decreased the DOC concentration from 3.9 mg/L to 2.5 mg/L (Figure 27A). Increasing the concentrations of either permanganate and

chlorine dioxide together, or permanganate alone did not effect DOC removal. In contrast, when chlorine dioxide was used by itself, DOC removal was hindered. Chlorine dioxide also hindered DOC removal in the studies on optimum alum doses presented previously in this chapter (Figure 25).

The DOC removal from the mixture of surface and bottom waters, which contained higher concentration of manganese(II), was not influenced by the presence of an oxidant (Figure 27B). Unlike its effect on DOC removal in the surface water, chlorine dioxide did not inhibit the removal of DOC in the mixed waters. Thus, in the presence of high manganese(II) concentrations, the choice of preoxidant and the concentration used had little effect on the DOC removal.

THM-precursor removal

The removal of THM-precursors from Abel Lake water was also examined and these data are shown in Figures 28A and 28B. Coagulation of the surface waters not dosed with an oxidant decreased the THM formation potential from 270 ug/L to 170 ug/L. At oxidant concentrations less than 1×10^{-2} meq/L, the THMFP of the solutions treated with chlorine dioxide increased and that of the solutions treated with either permanganate alone or in combination with 2.4×10^{-2} meq/L chlorine dioxide decreased. Increased concentrations of chlorine dioxide caused the THMFP to decrease to as low as 100 ug/L. Permanganate by itself also decreased the THMFP of the water steadily, but not as dramatically as did the chlorine dioxide. The THMFP in the solutions containing both permanganate and chlorine dioxide decreased rapidly with the addition of the initial oxidant dose, then remained constant with increased permanganate concentrations.

The THMFP of the mixture of surface and bottom waters decreased from 240 ug/L to about 100 ug/L upon coagulation (Figure 28B). The oxidants (chlorine dioxide, permanganate, or combinations of chlorine dioxide and permanganate) were not as effective in the removal of THM-precursors in these waters as they were in the surface water. In each instance, the lowest oxidant dose did not change the THMFP of the water. Increased concentrations of permanganate

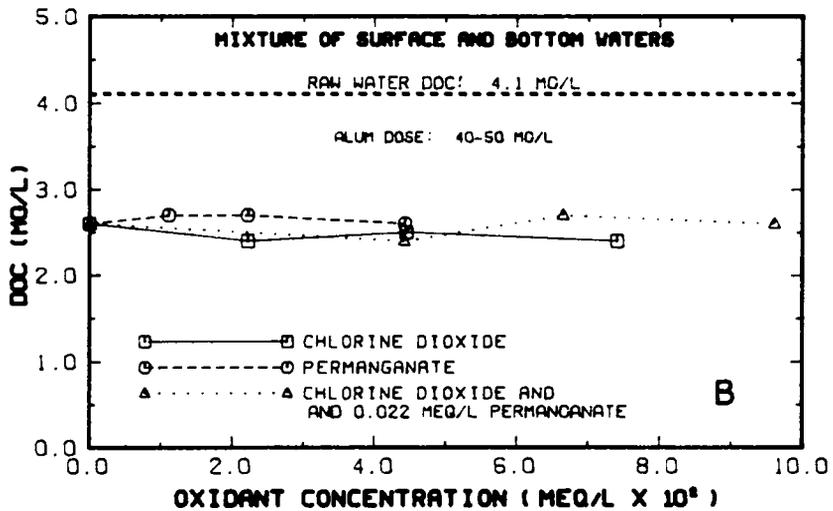
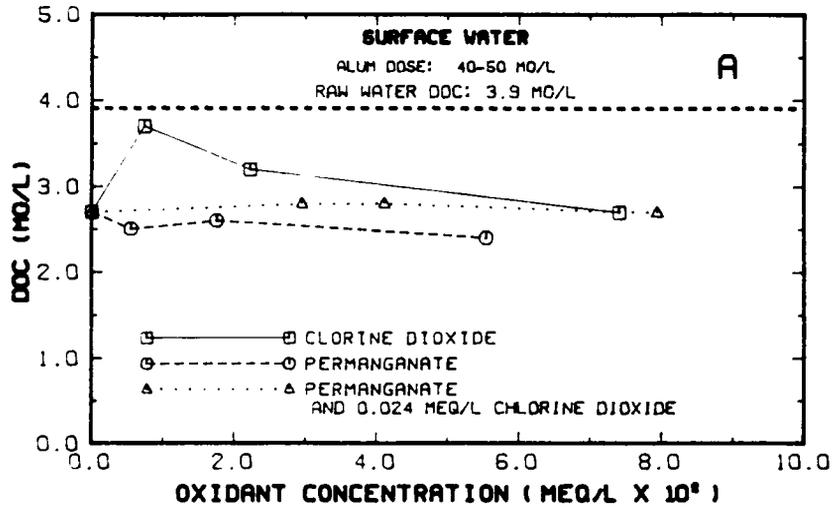


Figure 27. Effect of oxidant choice on organic carbon removal from Abel Lake waters dosed simultaneously with alum and oxidants shown. Reaction times in jar-test is one hour.

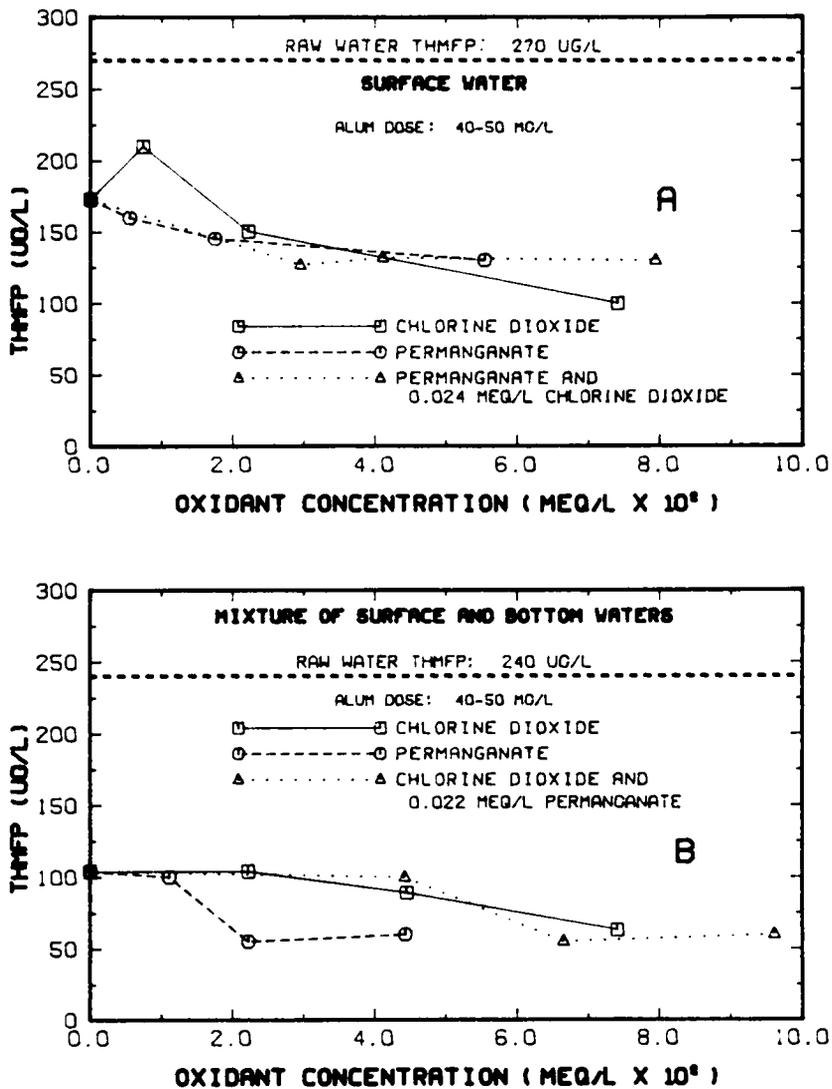


Figure 28. Effect of oxidant choice on precursor removal in Abel Lake waters dosed simultaneously with alum and oxidants shown. Reaction time in jar-test is one hour.

caused the THM precursor concentration to decrease abruptly, then remain constant. Increasing the chlorine dioxide concentration to levels greater than 2×10^{-2} meq/L (1.3 mg/L) caused the THM-precursor concentrations to steadily decrease to 65 ug/L. When 2.2×10^{-2} meq/L permanganate (1 mg/L) was added in combination with chlorine dioxide, the THM-precursor concentration decreased sharply then remained constant at 50 ug/L as the chlorine dioxide concentration was increased to 7.4×10^{-2} meq/L (5 mg/L).

Yield

Figure 29A shows that coagulation decreased the yield of THMs per DOC in the surface waters from 70 ug/L to about 65 ug/L. Increased concentrations of chlorine dioxide caused the yield to decrease steadily to under 40 ug/mg. Permanganate, when dosed by itself, slightly increased the THMFP, especially at the lowest concentration tested (0.7×10^{-2} meq/L or 0.3 mg/L). When permanganate was used in conjunction with chlorine dioxide, the initial dose of oxidants decreased the yield to about 45 ug/mg, and subsequent increases in the permanganate concentration did not decrease the yield below this level.

The yield of THMs per DOC in the mixture of surface and bottom waters was decreased by coagulation from 60 ug/mg to 43 ug/mg (Figure 29B). The lowest dose of chlorine dioxide caused a slight increase in the yield, and subsequent increases in chlorine dioxide concentration caused the yield to decrease to 25 ug/mg. When 2.2×10^{-2} meq/L (1 mg/L) of permanganate was in solution with chlorine dioxide, the yield decreased slightly with the initial dose, then decreased abruptly and remained constant at about 25 ug/mg. Permanganate, when dosed alone at 1.1 meq/L (0.5 mg/L), caused the yield to decrease to 30 ug/mg. At a permanganate dose of 4.4×10^{-2} meq/L (2 mg/L) the yield increased to 50 ug/mg.

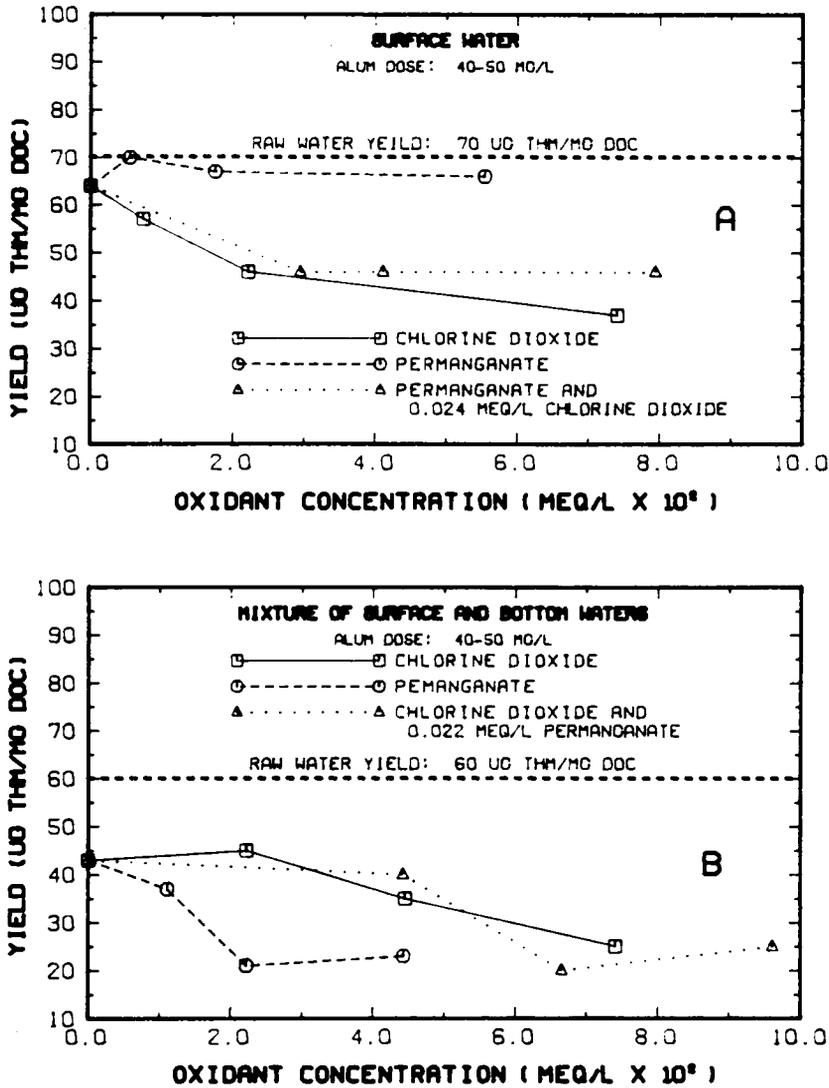


Figure 29. Effect of oxidant choice on yield of THMs per DOC (ug/mg) in two waters dosed simultaneously with alum and oxidants shown. Reaction time in jar-test is one hour.

Manganese(II) Removal

Soluble manganese concentrations in the surface water of Abel Lake during stratification were too low to be of concern; therefore manganese removal from these waters was not evaluated. Thus, only the manganese removals from the mixture of epilimnetic and hypolimnetic water is shown in Figure 30. Coagulation without an oxidant was ineffective for manganese removal. In general, increasing the oxidant concentration increased the manganese(II) removal efficiency, and the effectiveness of manganese(II) removal varied with each oxidant. The best removal was achieved by chlorine dioxide which removed virtually all of the manganese with a dose of 4.4×10^{-2} meq/L (3 mg/L).

The next best manganese(II) removal was achieved when permanganate was used by itself. In this case it was necessary to differentiate between the concentrations of permanganate and manganese(II), both soluble forms of manganese. Because the analytical techniques for this procedure were not developed until later in this study, the concentration of permanganate was accounted for mathematically by assuming that 1) the permanganate reacted only with manganese(II), 2) manganese(II) was oxidized only by permanganate and 3) no manganese(II) or permanganate was retained by the glass-fiber filter. Assumption two is valid but assumptions one and three probably cause the concentrations of manganese(II) to be slightly overestimated. Thus, removal of manganese(II) by permanganate was probably close to that achieved by chlorine dioxide.

When chlorine dioxide was added in combination with permanganate, soluble manganese concentrations remained quite high. Most likely, the oxidation potential of this solution was greater than that in the solutions containing either permanganate alone or chlorine dioxide alone. This condition would normally result in more complete manganese(II) oxidation. It is the author's belief that much of the soluble manganese in this solution was in the form of permanganate, not manganese(II). It was not possible to mathematically determine that portion of the soluble manganese that was in the form of manganese(II) when chlorine dioxide was present because of the probability of chlorine dioxide oxidizing some of the manganese(II) (violating assumption two

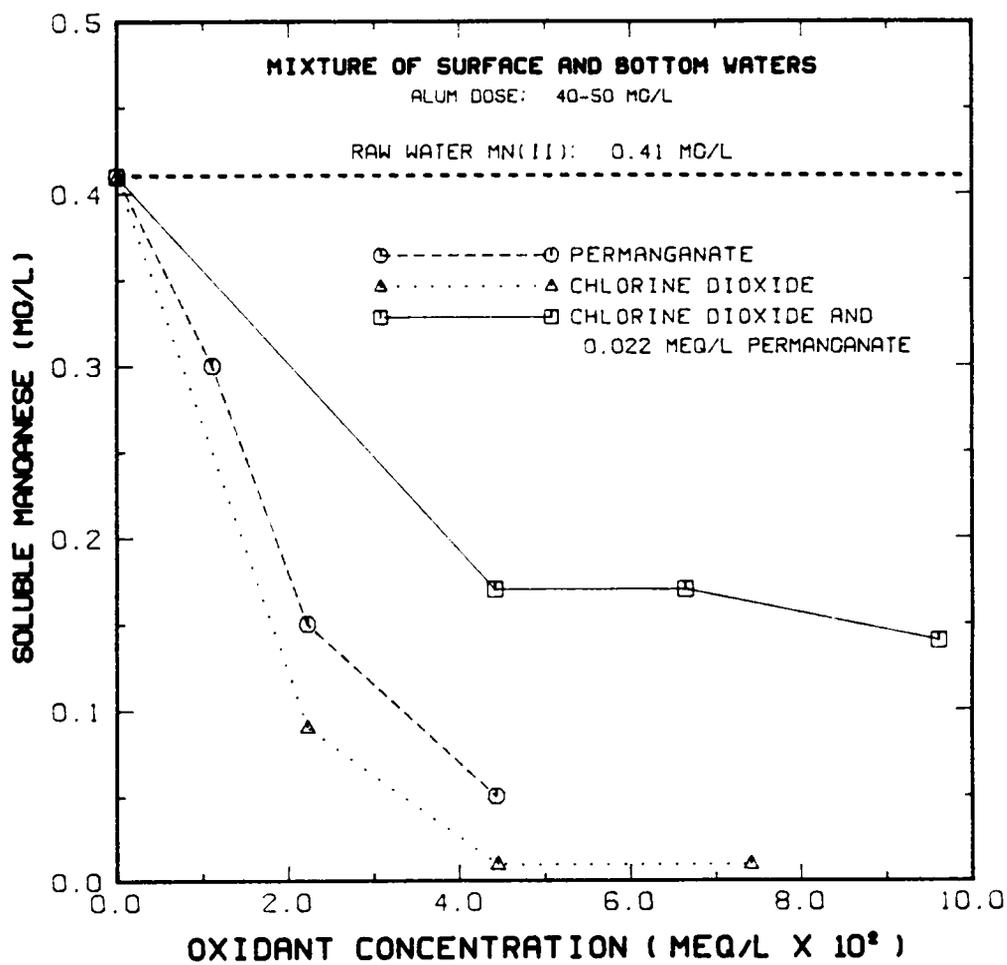


Figure 30. Effect of oxidant choice on manganese removal in waters dosed simultaneously with alum and the oxidants shown. Reaction time in jar-test is one hour.

above). Thus, these data were suspect and the merits of using permanganate with chlorine dioxide for manganese(II) oxidation were further explored in the next section.

The results of the plant-scale study served as a spring-board for the remainder of this dissertation by suggesting the following hypotheses:

- Chlorine dioxide has a greater affinity for DOC than does permanganate. At increased concentrations of DOC, permanganate is more effective in oxidizing manganese(II) than is chlorine dioxide.
- Chlorine dioxide removes THM-precursors by oxidizing, or deactivating them. Permanganate removes THM-precursors by making them more amenable to coagulation.
- Chlorine dioxide hinders the removal of organic materials by fragmenting them into smaller organic units.

Before the first hypothesis could be tested, it was first necessary to develop a method to determine the concentrations of manganese(VII), manganese(II), and particulate manganese when they were all in solution. In addition, the interference of oxidized forms of manganese in the determination of chlorine dioxide, and chlorite had to be quantified. The next section describes the development of these techniques and the results obtained.

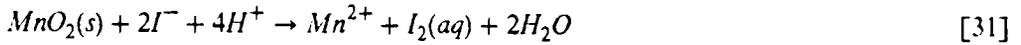
Laboratory Studies

Manganese: Interference in Determination of Oxy-Chlorine Species and Species Determinations

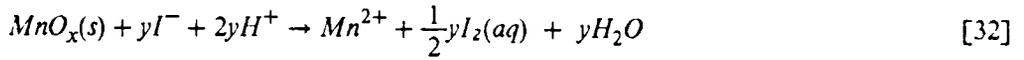
Aieta *et al.* (50) noted that manganese oxides [$\text{MnO}_x(\text{s})$] have the potential to interfere in both steps of the titration procedure that are performed at pH 2 (Figure 13). This section describes the pro-

cedure used to quantify this interference and how the results were employed to correct the chlorine dioxide and chlorite data for the presence of manganese. In addition, the methods developed for the determination of manganese(II), permanganate, and particulate manganese [$MnO_x(s)$] are presented.

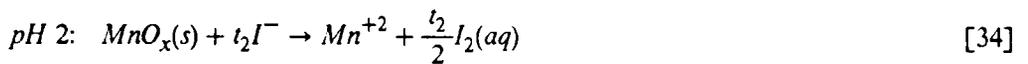
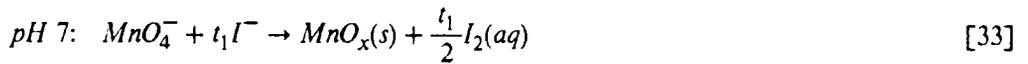
The following reaction shows the nature of manganese dioxide [$MnO_2(s)$] interference during the steps of the titration procedure performed at pH 2. Titrations at this pH are designated as steps B and D in Figure 13 (50).



Particulate manganese encountered in water treatment does not have a well defined oxidation state (1). A more general equation, representing the reaction between $MnO_x(s)$ and I^- , is as follows:



where y represents the number of equivalents transferred per mole of $MnO_x(s)$ upon reaction with I^- . In addition, permanganate would interfere in the two stages of the titration procedure performed at pH 7 and pH 2 as follows:



The product of permanganate reduction at pH 7 is unknown and is symbolized in equation [33] as $MnO_x(s)$. The values for t_1 and t_2 represent the total number of electrons transferred. It is expected that permanganate would accept a total of 5 electrons per molecule (i.e., $t_1 + t_2 = 5$). Thus, equations [24] - [27] can be corrected for the presence of manganese as follows:



$$B = \frac{4}{5}ClO_2 + ClO_2^- + f_2KMnO_4 + MnO_x(s) \quad [36]$$

$$C = Cl_2 + f_1KMnO_4 \quad [37]$$

$$D = ClO_2^- + f_2KMnO_4 + MnO_x(s) \quad [38]$$

where f_1 and f_2 represent the fraction of the total normality expressed at each step of the titration procedure (i.e., $f_1 = \frac{t_1}{5}$ and $f_2 = \frac{t_2}{5}$).

Aieta *et al.* (50) offered the following equations for the calculation of the various oxy-chlorine species:

$$ClO_2 \text{ (mg/L)} = \left(\frac{5}{4}\right) \times (B - D) \times N \times 13,490 \text{ mg/eq} \quad [39]$$

$$ClO_2^- \text{ (mg/L)} = D \times N \times 16,863 \text{ mg/eq} \quad [40]$$

$$Cl_2 \text{ (mg/L)} = \left[A - \frac{(B - D)}{4}\right] \times N \times 35,450 \text{ mg/eq} \quad [41]$$

where A, B, C and D represent the volume of titrant required per volume of sample for each step in Figure 13 and N is the normality of the titrant in eq/L.

From equations [39] to [41], the interference from manganese oxides can be further evaluated. By equation [39], the ClO_2 concentration is obtained by subtracting equation [38] (step D) from equation [36] (step B) as indicated in the following equation:

$$B - D = ClO_2 + ClO_2^- + f_2KMnO_4 + yMnO_x(s) - [ClO_2^- + f_2KMnO_4 + yMnO_x(s)]$$

$$B - D = ClO_2 \quad [42]$$

As is seen in equation [42], the manganese terms cancel and the chlorine dioxide determinations will not be affected. The equation for ClO_2^- [40] can be manipulated in a similar manner to yield:

$$D = ClO_2^- + f_2 KMnO_4 + MnO_x(s) \quad [43]$$

There is no subtraction of manganese terms as in equation [43], so $MnO_x(s)$ and $KMnO_4$ will cause chlorite determinations to be overestimated. A similar analysis of equation [41] reveals that chlorine determinations would remain unaltered in the presence of manganese oxide.

Because the amperometric titrations are based on electron transfer, the beginning and ending oxidation states must be known in order to quantify manganese interference. The number of equivalents transferred per mole of permanganate in the titration procedure is not known. The number of electrons transferred upon the reduction of $MnO_x(s)$ cannot be determined until their initial oxidation states are known. The oxidation state of $MnO_x(s)$ is not well defined; Stumm and Morgan (12) reported a range in x , in $MnO_x(s)$, of 1.3 to 1.8 over a range of pH and oxidation conditions. Before the interference of $MnO_x(s)$ species in the chlorine dioxide test can be adequately quantified, the values for f_1 , f_2 and y must be determined.

Quantification of Interference

This section determines the oxidation states of manganese at the beginning and the end points of titration. Several known concentrations of both permanganate and manganese oxide were titrated in accordance with the steps outlined in Figure 13. Two $MnO_x(s)$ suspensions, that were prepared under different chemical conditions, were titrated. One $MnO_x(s)$ suspension was prepared by oxidizing about 70 mg/L manganese(II) in an oxygen atmosphere with excess $KMnO_4$ (≈ 150 mg/L as Mn) at a pH of 11 to 13. After a period of 24 hours, the remaining $KMnO_4$ was removed by introducing hydrogen peroxide (H_2O_2) to the solution. The other suspension was prepared by oxidizing low (≈ 0.15 mg/L) manganese(II) concentrations with smaller quantities of $KMnO_4$ (≈ 0.35 mg/L) at a slightly acidic pH (6.3). These conditions would be common in a water treatment plant concerned with avoiding trihalomethane formation. The particulate manganese concentrations of both suspensions were determined in a two-step procedure. First, total manganese was determined by reducing all the manganese to the manganese(II) state with hydroxyl amine sulfate

prior to analysis by AAS. Secondly, the suspension was filtered through a 2.1 nM ultrafilter to remove particulate manganese prior to the addition of hydroxyl amine sulfate and analysis by AAS. The difference in concentration between these two solutions was the concentration of particulate manganese. The manganese concentration after filtration was typically less than than one percent of the total manganese concentration.

Upon titration, the number of electron equivalents transferred per mole of oxidized manganese was calculated as follows:

$$v = \frac{NV}{M} \quad [44]$$

where:

v = equivalents transferred/mole,

N = normality of the titrant (eq/L),

V = Volume of titrant (L), and

M = moles of manganese oxide present.

Eight different solution concentrations were titrated. The results of titrating the 0.940 mg/L KMnO_4 solution, presented in Table 10, show that permanganate interfered in both step A and step B of the titration procedure (Figure 13). As is seen, the solution was titrated eight times using the procedure outlined in steps A (pH 7) and B (pH 2) of Figure 13. Permanganate transferred more electrons at pH 7 than at pH 2. Also, the 95 percent confidence intervals were greater for the separate titrations than was the 95 percent confidence interval for the total. That is, there was more variation in the separate titrations than in the total. If a smaller volume of titrant were required to reach the endpoint at pH 7, a larger volume of titrant was required to reach the endpoint at pH 2, so that the total volume showed less variation than did the two steps (pH 2 and pH 7). The greater variations in eq/mole transferred when categorized by pH than when totalled implied that the endpoint of the pH 7 titration (or beginning of the pH 2 titration, since these were performed in series, these two are equivalent) was variable. The variability in intermediate oxidation states of the

Table 10.
Permanganate equivalents transferred to iodide at pH 7 and pH 2 for a 0.940 mg/L KMnO₄ solution.

	A	B	A + B
Trial	eq/mole at pH 7	eq/mole at pH 2	eq/mole total
1	3.65	1.80	5.45
2	3.89	1.56	5.45
3	3.98	1.33	5.31
4	4.17	1.47	5.64
5	3.89	1.47	5.36
6	4.08	1.47	5.55
7	3.84	1.47	5.31
8	3.98	1.71	5.69
mean	3.94	1.54	5.47
std. deviation	0.16	0.15	0.15

Table 11.
Permanganate equivalents transferred to iodide at pH 7 and pH 2.

	A	B	A + B
Permanganate (mg/L as KMnO ₄)	eq/mole at pH 7	eq/mole at pH 2	eq/mole Total
0.236	3.8 ± 0.6 ¹	1.5 ± 0.6	5.3 ± 0.3
0.473	3.6 ± 0.2	1.7 ± 0.3	5.3 ± 0.1
0.940	3.9 ± 0.1	1.5 ± 0.1	5.5 ± 0.1
0.945	3.5 ± 0.1	1.7 ± 0.1	5.2 ± 0.2
1.89	3.3 ± 0.1	1.7 ± 0.1	5.0 ± 0.1
3.31	3.0 ± 0.2	1.9 ± 0.1	4.9 ± 0.1
5.00	3.3 ± 0.5	2.0 ± 0.5	5.3 ± 0.2
7.81	3.6 ± 0.02	1.4 ± 0.1	5.0 ± 0.1
Means	3.5 ± 0.5	1.7 ± 0.4	5.2 ± 0.3
¹ 95 percent confidence limits			

manganese after reaction at pH 7 is also evident for the other solution concentrations presented next.

Table 11 shows the results of all eight titrations. Each solution was titrated at least four times, and the 95 percent confidence intervals for each titration were presented. The results of the inference at pH 7 is presented first, followed by the results of the interference at pH 2 and the total interference.

A casual glance at the data may indicate that the number of equivalents transferred per mole at pH 7 has a relationship to the initial KMnO_4 solution, but linear regression revealed a very weak relationship ($r^2 \approx 0.1$). The interference averaged 3.5 ± 0.5 equivalents per mole when the solution pH was 7 (steps A and C). This normality indicated that the average oxidation state of manganese was 3.5 at the end of the pH 7 titration.

The interference that occurred at a solution pH of 2 was 1.7 ± 0.4 equivalents per mole (eq/mole) of $\text{MnO}_x(\text{s})$. At pH 2, the variability was greater (on a percentage basis) than it was at pH 7.

The total number of equivalents transferred when permanganate was reduced to manganese(II) is theoretically 5.0 eq/mole. The number of eq/mole transferred from the titrations at pH 7 and at pH 2 totalled 5.2 ± 0.3 eq/mole resulted. This experimental value (5.2) was within four percent of the theoretical value (5.0), an error deemed acceptable considering that this procedure was developed to measure oxy-chlorine species, not KMnO_4 . The variability from each step of the titration procedure is less if the data are first summed because the oxidation state of the manganese after titration at pH 7 is more variable than the initial oxidation state of permanganate or the oxidation state after titration at pH 2 manganese(II).

Effect of Manganese Oxides on Determination of Chlorine Species

The $\text{MnO}_x(\text{s})$ suspensions prepared as described previously in this section were titrated according to the ClO_2 , ClO_2^- , and Cl_2 analysis procedure described previously in Methods [reference (50)

and Figure 13]. The data in Table 12 show that at pH 7 the manganese in these suspensions did not react with I^- , but at pH 2 it did. The number of electrons transferred was different for the two suspensions. The $MnO_x(s)$ suspension prepared under rigorous conditions had a higher oxidation state (≈ 4) than did the $MnO_x(s)$ suspension created under less rigorous or "plant" conditions (defined previously) which had an oxidation state of 3.5 to 3.6. The range in oxidation states of the $MnO_x(s)$ created under plant conditions were at the upper end of the range reported by Stumm and Morgan (12) of 2.6 to 3.6. The oxidation state of the solution created under rigorous conditions was somewhat greater than the maximum found by Stumm and Morgan (12).

Error in Calculating Concentrations

The information in Tables 11 and 12 was used to calculate the error caused by the presence of permanganate during the titration procedure. These data are presented in Table 13. Permanganate caused the overestimation of chlorite and chlorine concentrations by 0.52 mg ClO_2^- /mg manganese(VII) and 2.26 mg Cl_2 /mg manganese(VII), respectively. These values can be used to correct the ClO_2^- and Cl_2 data from jar tests and water treatment plants where permanganate and ClO_2 are both present. The ClO_2^- concentrations reported in the laboratory study of this paper were corrected for the interference from permanganate. A discussion of the impact of permanganate interference on water treatment plants follows.

Typically, the concentration of ClO_2 is monitored throughout the water treatment plant. When permanganate is also present, the measured concentrations of ClO_2^- and Cl_2 will be greater than their actual concentrations. The magnitude of the error can be estimated by measuring the permanganate concentration and calculating the amount of interference using the values presented in Table 13. The approximate permanganate concentration required to use these interference values can be determined by a amperometric titration technique presented later in this chapter. Because permanganate is typically dosed to yield negligible concentrations in the clarifier of a water treatment plant, most of the interference would probably occur in the water from the flash mix basin

Table 12.
Manganese oxide equivalents transferred to iodide at pH 7 and pH 2.

Oxidation Conditions	MnO _x (s) mg/L as Mn	Equivalents transferred per Mole		Original Oxidation State
		pH 7	pH 2	
pH 12, excess KMnO ₄ O ₂ atmosphere	0.52	0	1.6 ¹	3.6
	0.57	0	1.5	3.5
pH 7, ambient atmosphere stoichiometric KMnO ₄ dose	2.17	0	2.0 ± 0.04	4.0
	2.40	0	2.1 ± 0.00	4.1
	4.07	0	2.1 ± 0.04	4.1
	5.84	0	1.7 ± 0.32	3.7

¹One titration performed

Table 13.
Overestimation of oxy-chlorine species when permanganate is present

Species	Correction in final concentration
ClO ₂	NE
ClO ₂ ⁻	0.52 mg ClO ₂ ⁻ /mg Mn(VII)
Cl ₂	2.26 mg Cl ₂ /mg Mn(VII)
ClO ₃ ⁻	NE
NE = No Effect	

or the flocculators. Errant ClO_2^- and Cl_2 determinations from these waters may lead to concern regarding the yield and efficiency of the ClO_2 generation process.

As mentioned previously, calculating the interference caused by the oxidized forms of manganese is not possible unless the initial oxidation state is known. The following equation describes the relationship between the oxidation state of manganese oxide, its concentration and the overestimation of the chlorite concentration.

$$E = Q(S - 2)(0.3) \quad [45]$$

where:

E = the overtitration error caused by manganese oxide (mg/L as ClO_2^-),

Q = the concentration of manganese oxide (mg/L as Mn), and

S = the initial oxidation state of manganese oxide.

This formula was used in Figure 31 to show how the interference due to $\text{MnO}_x(\text{s})$ would be affected by changes in the oxidation state of manganese. The interferences caused by particulate manganese formed in this study, and the particulate manganese formed by the oxygenation of manganese(II) at various pH conditions (12) are highlighted.

In many water treatment plants, and in the laboratory phase of this study, permanganate coexists with $\text{MnO}_x(\text{s})$, and the interferences of both must be accounted for. For example, if 0.2 mg/L manganese(VII) and 0.4 mg/L $\text{MnO}_x(\text{s})$ as manganese are present, the interferences from both forms of manganese in the ClO_2 titration can be calculated separately, then summed. The data in Table 13 were used to calculate the interferences from permanganate as 0.1 mg/L ClO_2^- and 0.45 mg/L Cl_2 . The interference caused by $\text{MnO}_x(\text{s})$, with an oxidation state of 3.5, is 0.18 mg/L ClO_2^- . The total interference from permanganate and $\text{MnO}_x(\text{s})$ in this example would then cause an overestimation of ClO_2^- by 0.28 mg/L and of Cl_2 by 0.45 mg/L. Thus, oxidized forms of manganese [$\text{MnO}_x(\text{s})$ and permanganate] can cause significant interferences in the determinations of chlorite and chlorine. Particulate manganese occurs in a range of oxidation states and, unless the

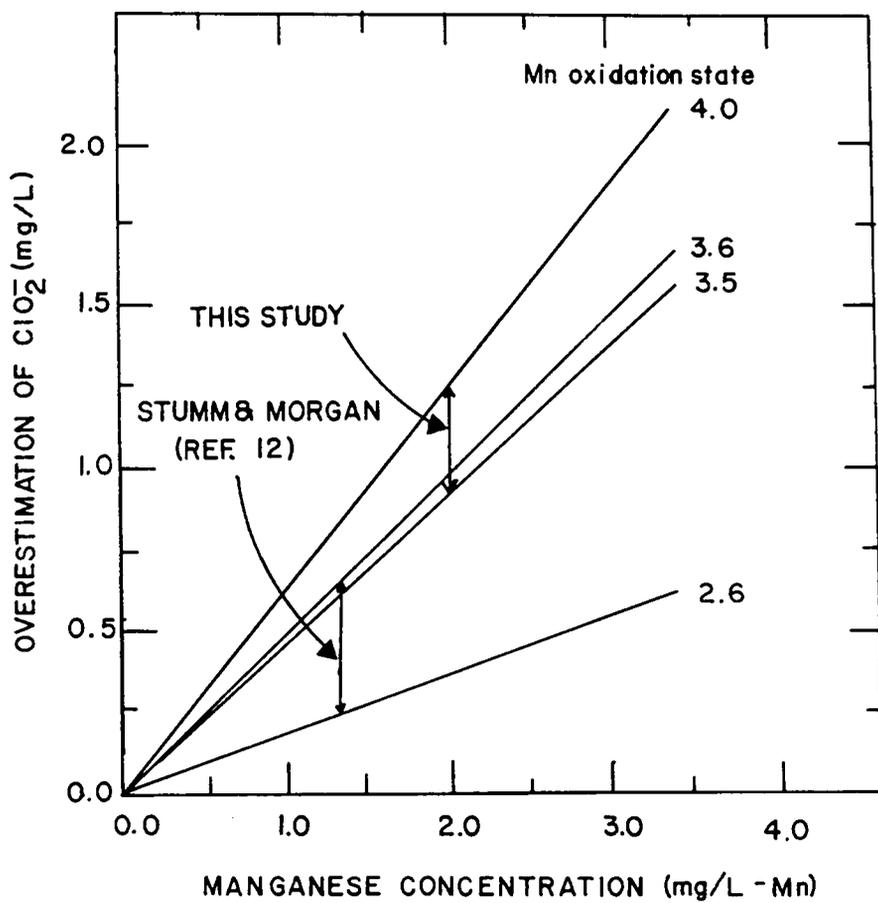


Figure 31. Effect of oxidation state of manganese oxides on the interference in chlorite determinations.

precise oxidation state is known, only an approximation of the interference can be determined. Figure 31 is presented to aid in making such an approximation.

Determinations of Manganese(VII), MnO_x(s), and Manganese(II)

Often when permanganate, MnO_x(s), manganese(II), ClO₂ and ClO₂⁻ are in solution together, it is neither possible nor desirable to make simplifying assumptions regarding the concentrations of manganese(II), MnO_x(s) or permanganate. The interference of manganese under these circumstances could be calculated only if the quantity of each manganese species present were known. This section describes a procedure that utilizes commonly available laboratory equipment to closely approximate the concentrations of permanganate, MnO_x(s), and manganese(II).

Methods of Manganese Determination

First, three methods of manganese determination will be reviewed, then, second, the analytical procedure itself will be presented. The first technique for the determination of manganese was based on the results of the amperometric titration reported in the first section of this dissertation. At pH 7, permanganate transfers 3.5 eq/mole (Table 3). MnO_x(s) does not interfere at pH 7, so amperometric titration does not require that MnO_x(s) be removed. The following equation can be used to calculate the concentration of permanganate present from the amount of titrant required.

$$M = \frac{NV}{v} \quad [46]$$

or

$$C = \frac{NV_1G}{vV_2} \quad [47]$$

where:

- M = molarity of permanganate solution,
C = concentration of permanganate solution (mg/L as Mn),
N = normality of titrant (eq/L),
G = gram molecular weight of manganese (54.94×10^3 mg/mole),
 V_1 = volume of titrant (L),
 v = equivalents transferred per mole (3.5), and
 V_2 = volume of sample (L).

The advantage of this technique is that it employs an amperometric titrator which is available to investigators and operators working with water treatment and does not require daily calibration. The disadvantages of this technique are 1) it will not work in the presence of chlorine and 2) it requires a substantial sample volume (typically 100 to 200 mL). This last point is especially important because if permanganate is in solution, a portion of it would be expected to pass when the samples are filtered to exclude particulate manganese. Thus, to measure permanganate by amperometric titration, 100 to 200 mL of sample would have to be filtered. Filtration of a $\text{MnO}_x(\text{s})$ suspension through filters with pore sizes small enough to exclude colloidal particles can be prohibitively slow. An alternate, more practical, method would be to analyze the permanganate colorimetrically, which requires the filtration of only 30 to 50 mL. The colorimetric method is discussed next.

The colorimetric determination of aqueous permanganate is based on its distinctive color. A spectrophotometric scan of a permanganate solution (Figure 32) shows two distinct absorbance peaks, at wavelengths of 525 and 546 nm. A Klett-Summerson photoelectric colorimeter (Klett Manufacturing Co., New York) fitted with a 520 ± 20 nm filter and a cuvette with a four-cm path length was used to measure the absorbance of permanganate solutions as described in section 319 B, paragraphs 4d and 4e of *Standard Methods* (84). If the solution had additional color due to either the presence of humic substances or turbidity, a reducing agent (such as hydroxyl amine sulfate) can be added to the solution. The permanganate color will fade, leaving the background color and turbidity. The difference between the initial reading and the final reading is an expression of the light absorbed only by permanganate, and this number can be applied to a standard curve

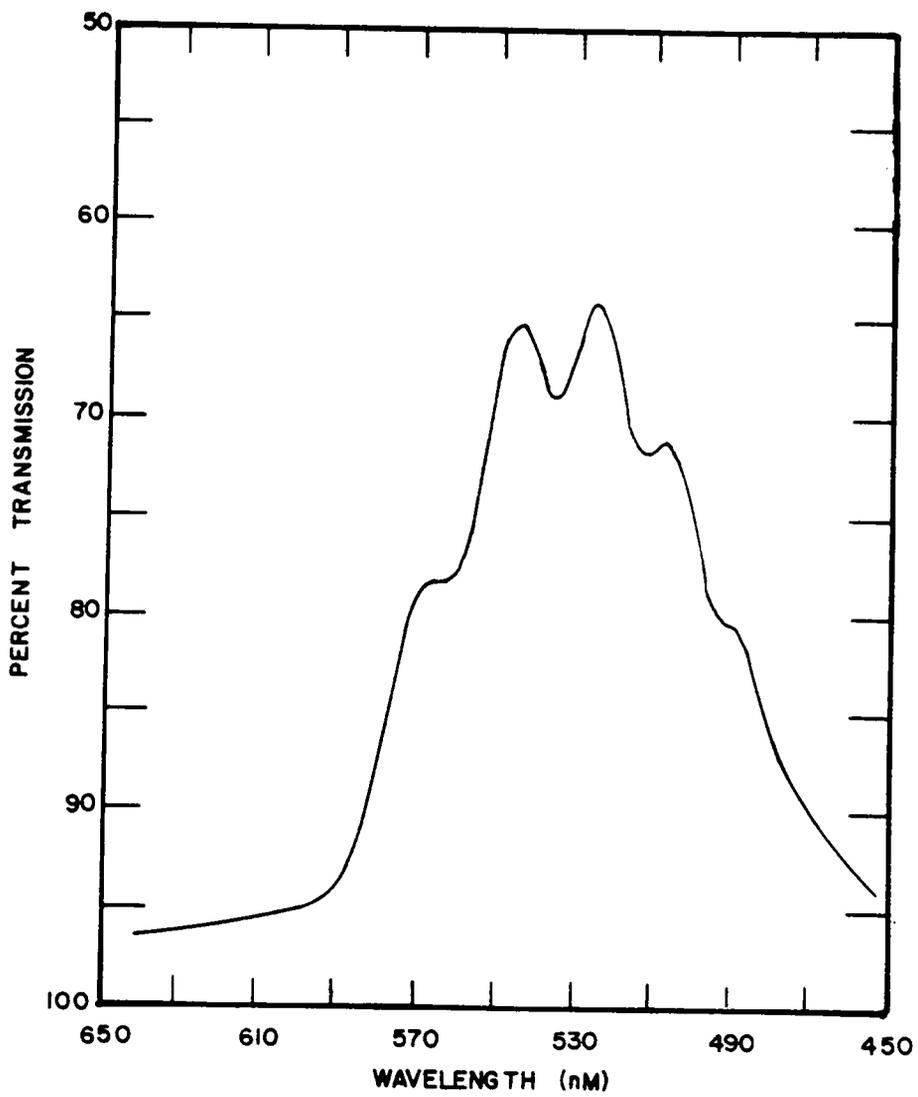


Figure 32. Spectrophotometric scan of permanganate solution.

to find the permanganate concentration. The colorimetric method has the advantage of requiring a relatively small sample size (10 to 50 mL) depending on the size of the cuvette.

The colorimetric method has two disadvantages: 1) a standard curve must be developed daily and 2) particulate manganese interferes with permanganate determinations. Figure 33 shows a spectrophotometric scan of a solution containing both permanganate and particulate manganese. A peak still appears at 525 nM, but permanganate's contribution to this peak cannot be separated from that of particulate manganese with single wavelength techniques. The addition of a reducing agent, such as hydroxyl amine sulfate or hydrogen peroxide, reduced light absorption by both permanganate and particulate manganese (bottom of Figure 33). Thus, permanganate determinations cannot be performed on solutions containing particulate manganese using colorimetry.

The third technique, flame atomic absorption spectrophotometry, is so well documented that it only bears mentioning here. The advantage of this instrumental analysis is that it requires a small sample size (≈ 10 mL). A disadvantage is that it does not distinguish among forms of manganese. In all cases, a strong reducing agent, hydroxyl amine sulfate, was added to the samples prior to manganese determinations by AAS to maintain manganese in the Mn^{2+} state.

Determination of Manganese Species in Solutions Containing Manganese(II), $MnOx(s)$, and Permanganate

Many oxidation states of manganese are possible, but environmental engineers usually consider permanganate, $MnO_4(s)$ and manganese(II). Of these forms, particulate manganese is the most poorly defined because it can be composed of manganese in various oxidation states. In water treatment, particulate manganese is usually considered as a single species by environmental engineers because it is the removable end-product of manganese(II) oxidation.

Figure 34 shows a schematic of the manganese-analysis procedure developed for this project. First, an aliquot of sample is filtered through either a membrane filter (200 nm pore diameter) or a mo-

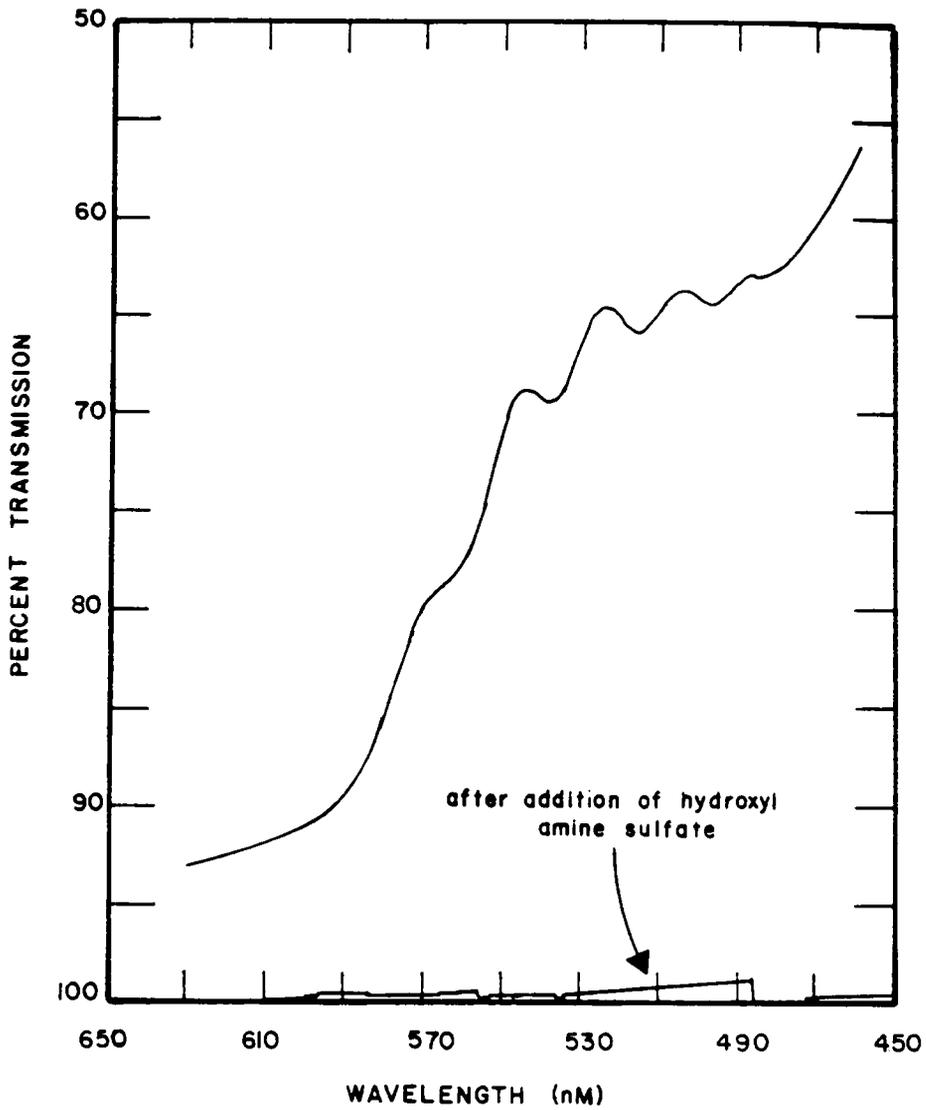
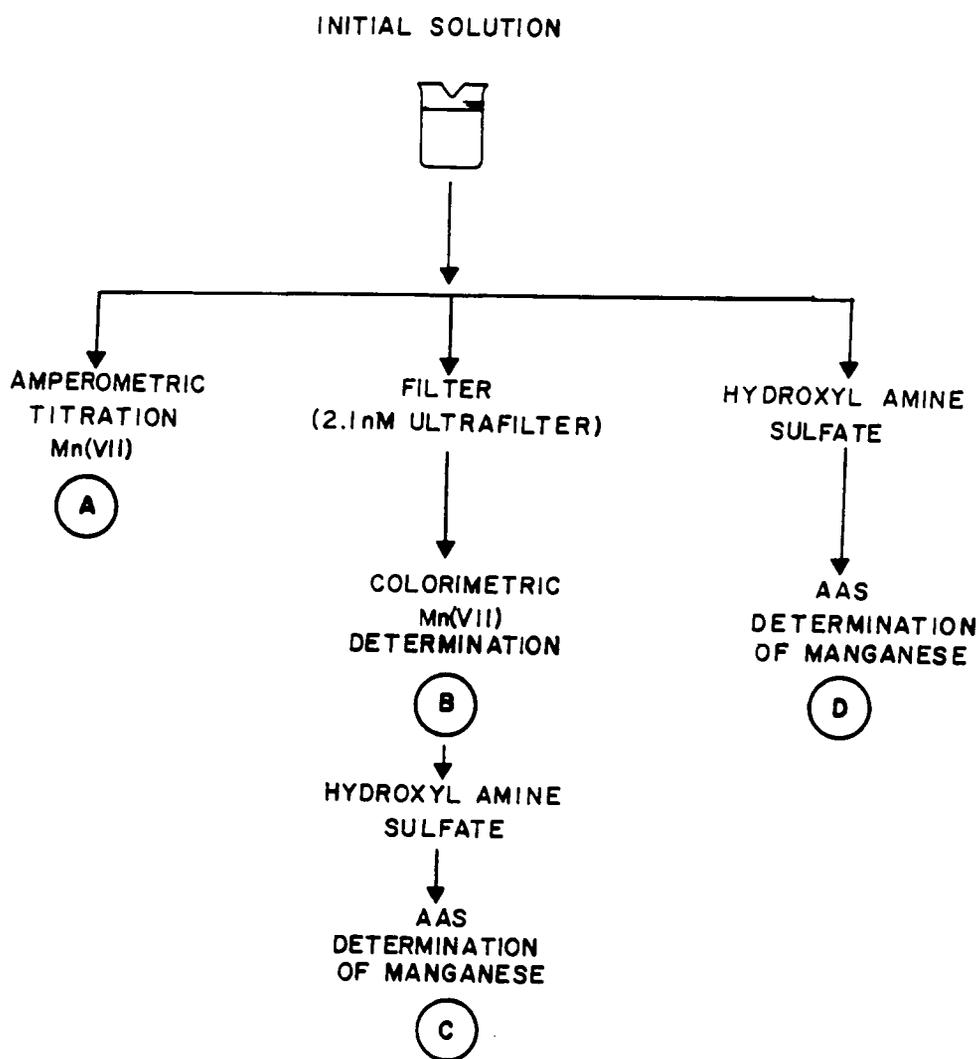


Figure 33. Scan of permanganate solution with particulate manganese before and after addition of hydroxyl amine sulfate.



$\text{Mn(VII)} = \text{A}$
 $\text{Mn(II)} = \text{C} - \text{B}$
 $\text{Mn(IV)} = \text{D} - \text{A} - (\text{C} - \text{B})$

Figure 34. Schematic of procedure used for determination of manganese(II), particulate manganese and permanganate.

lecular sieve (Amicon) (2.1 nm pore diameter) to exclude the particulate manganese. Permanganate in the filtrate is determined colorimetrically (step A). Colloids range from 1 to 200 nm in diameter, so they are able to pass through the membrane filter. Those colloids with diameters less than 2.1 nm can also pass through the molecular sieve. The extent of error posed by the passage of manganese colloids was quantified by passing aliquots of the two $\text{MnO}_x(\text{s})$ suspensions through various filters (Table 14). As is seen, when manganese(II) was oxidized under rigorous conditions, the particulate manganese was retained by the 200 nm pore diameter filter. Under less rigorous conditions typical of many water treatment plants, the particles were able to pass through the 200 nm filter but not the molecular sieve. (Only five percent passed through the 2.1 nm pore diameter molecular sieve.) The results indicate that the molecular sieve is the better choice for excluding particulate manganese. The data in Table 14 also show that the chemical conditions present while manganese(II) is oxidized affected the particle size. Manganese particles created under rigorous conditions were larger than those created under less rigorous conditions.

Many water treatment plants use a coagulant such as aluminum sulfate [$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$] to remove suspended particles. Aluminum sulfate hydrolyzes in water to form a fluffy floc that enmeshes particulate manganese. It may be possible to use a larger filter (e.g., a glass-fiber filter or 450 nm filter) when alum floc is present in solution, as is the case in water treatment plants practicing flocculation.

After the colorimetric determination, a total manganese determination by AAS was performed on the filtrate (step B). A second aliquot was analyzed for permanganate by amperometric titration (step C). The permanganate concentration in both the filtered and unfiltered samples had to be determined because not all of the permanganate in solution passed through the filter. In a final step, an aliquot of the original solution was dosed with hydroxyl amine sulfate and then analyzed for total manganese by AAS (step D).

As is seen in Figure 34, the concentrations of the three forms of manganese were calculated by three equations. Permanganate concentration was determined directly, manganese(II) was calculated as the difference between the total soluble manganese and the permanganate concentrations (B-A),

Table 14.
Colloidal manganese retention by filters with decreasing pore sizes

Oxidation Conditions	Initial Mn (mg/L by AAS)	Filter type (pore size, nM)	Filtrate Mn mg/L by AAS)
pH 12, O ₂ atmosphere excess KMnO ₄	0.62, 0.62	glass fiber (300) ¹	0.61, 0.61
	0.62, 0.62	membrane (200)	0.05, 0.09
	0.62, 0.62	molecular sieve (2.1)	0.04, <0.01
pH 7, ambient O ₂ stoichiometric KMnO ₄	0.70, 0.70	membrane (200)	0.65, 0.70
	0.70, 0.70	molecular sieve (2.1)	0.02, 0.02
¹ Sized by retention of air borne particles			

and particulate manganese concentration was obtained by subtracting both the permanganate and manganese(II) concentrations from the total manganese concentration in the original solution $[D-(B-A)-C]$.

Probable Sources of Error

The following criticisms illustrate the limitations of this technique and the most likely sources of error:

- Manganese(VII) and manganese(II) were assumed to be the only soluble forms of manganese. Under conditions typical during potable water treatment, it is unlikely that manganese(V) or manganese(VI) would be present, so this is a reasonable assumption.
- Soluble manganese is determined by excluding particulate manganese with a filter that permits the passage of some particle in the colloid range (1.0 to 2.1 nm). This study presents evidence that the size of the manganese colloids depends on the conditions of the solution in which they are formed. When large particles are formed, this error is likely to be quite small, but when the particles are relatively small, the error may be significant.
- The terminal valence state of the permanganate during the pH 7 titration step may be a function of pH. Thus, a good pH 7 buffer such as a phosphate buffer (84) is recommended in place of a weak buffer of the type commonly used to calibrate pH meters.
- If both permanganate and reduced manganese are present during filtration, some reduced manganese may be oxidized on the surface of the membrane filter or molecular sieve and cause an underestimation of the true reduced manganese concentration.
- Reduced manganese may be complexed by large organic molecules, which may subsequently be retained by the molecular sieve and result in an underestimation of the true reduced manganese concentrations.

Effect of DOC on Manganese(II) Oxidation

The results of the second set of jar-tests show the effects of first, chlorine dioxide on the maintenance of permanganate in the Mn^{+7} state, and second, organic carbon on the oxidation of manganese. As described in the Methods chapter, jar tests were performed on three solutions that varied only in their DOC concentrations. The solution with 2.1 mg/L DOC was prepared by adding ions to from deionized New River water, the solution with 3.0 to 3.7 mg/L DOC originated from Abel lake and was left untreated, and the water with 4.4 to 5.2 mg/L DOC was prepared by adding fulvic acids to the Abel Lake water.

The results of the first experiment (with permanganate alone) are presented in Figure 35. At all three concentrations of DOC, the concentrations of permanganate and manganese(II) decreased and the concentration of particulate manganese increased with time. Increases in the DOC concentration caused the rate of manganese(II) oxidation to decrease, and the rate (and extent) of permanganate reduction to increase. More will be said about reaction rates later in the kinetic analysis that follows.

When chlorine dioxide was added (Figure 36) the manganese(II) concentrations decreased in the the two solutions containing lower concentrations (2.1 mg/L and 3.0 mg/L) of DOC. In the solution containing 5.2 mg/L DOC, manganese(II) was not oxidized appreciably. Thus, increasing the DOC concentration decreased the extent of manganese(II) oxidation by chlorine dioxide. Figure 37 shows that the concentration of chlorine dioxide decreased with time in all three solutions and formed primarily chlorite as the reduction product. The greatest reduction in chlorine dioxide was observed in the solution containing the highest concentration of DOC (5.2 mg/L). This was not a result of volatilization because the jars were capped.

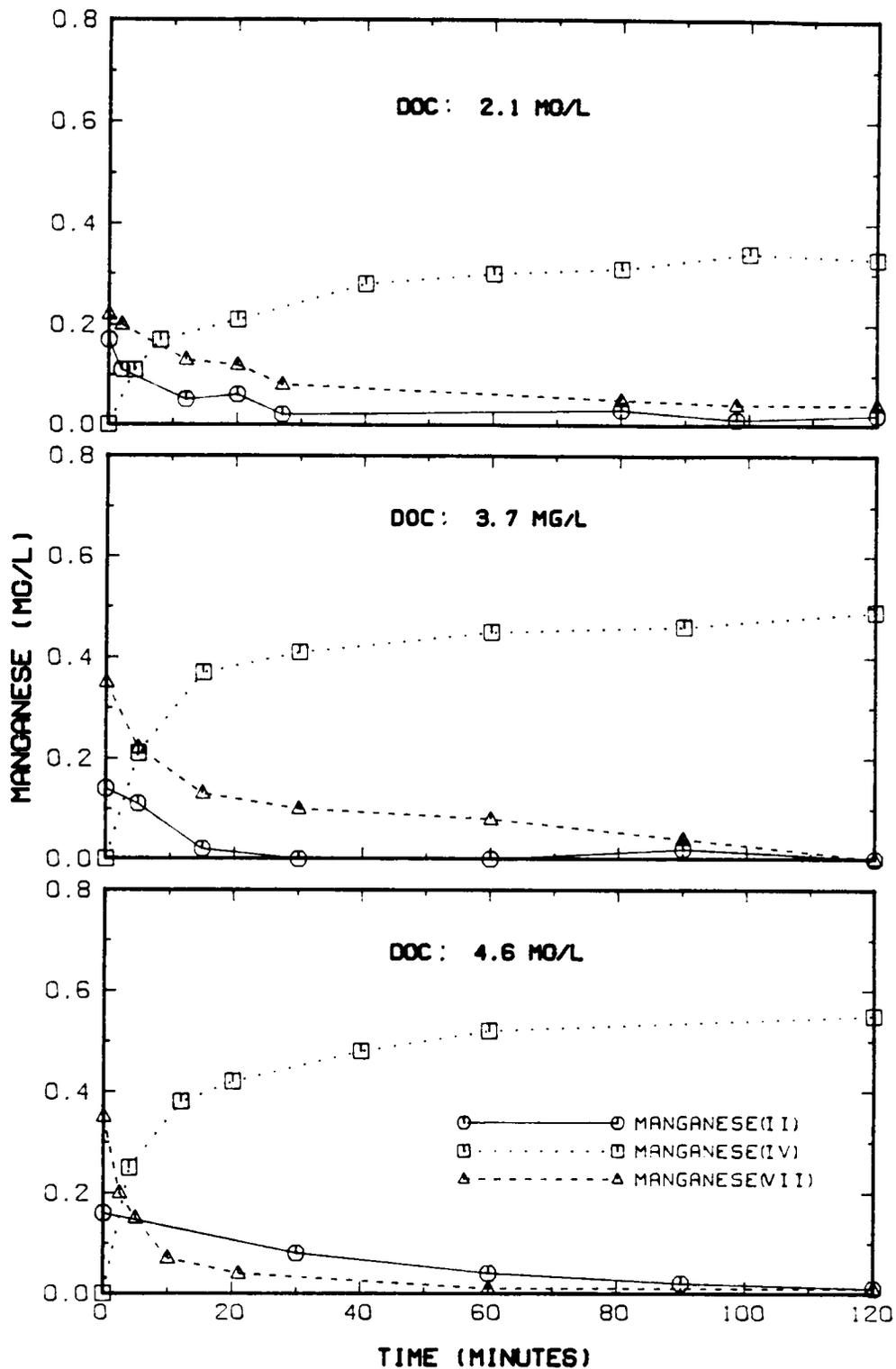


Figure 35. Manganese species in three waters dosed with manganese(II) and ≈ 1 mg/L potassium permanganate at pH 6.3.

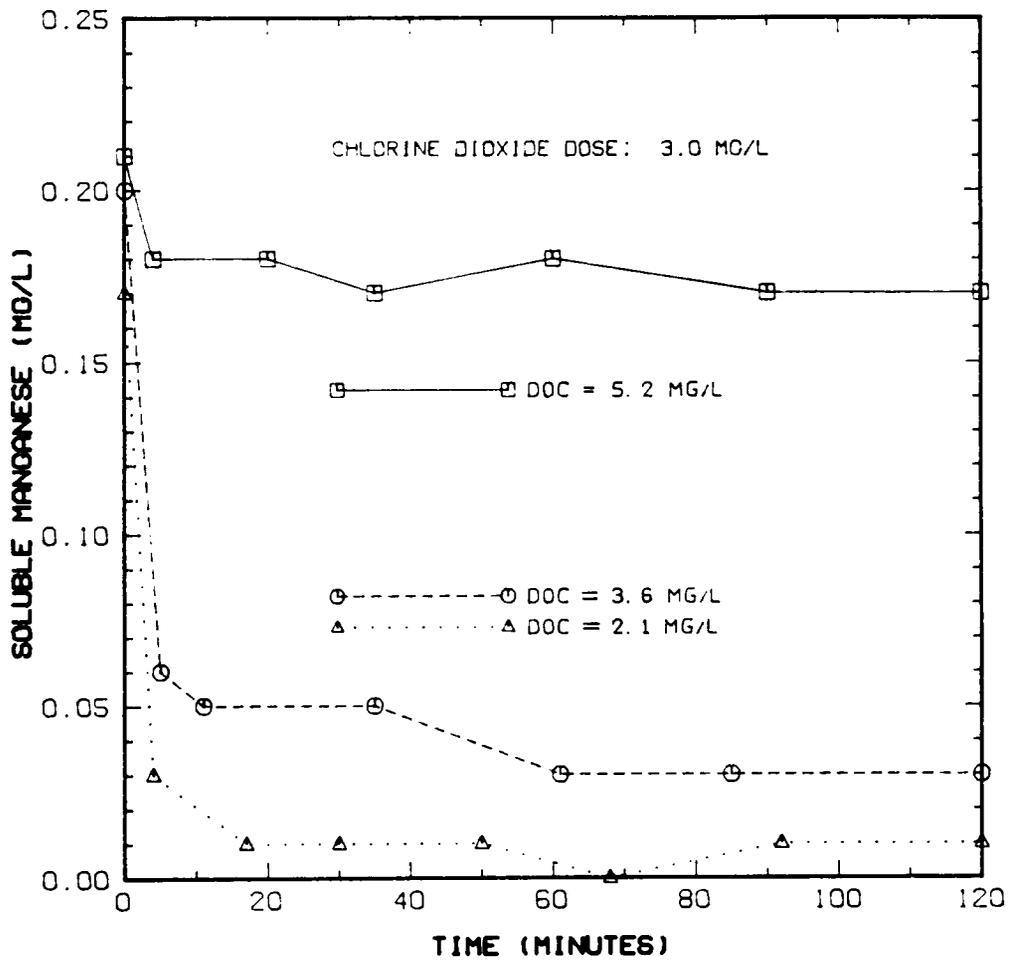


Figure 36. Manganese species in three waters dosed with manganese(II) and ≈ 3 mg/L chlorine dioxide at pH 6.3.

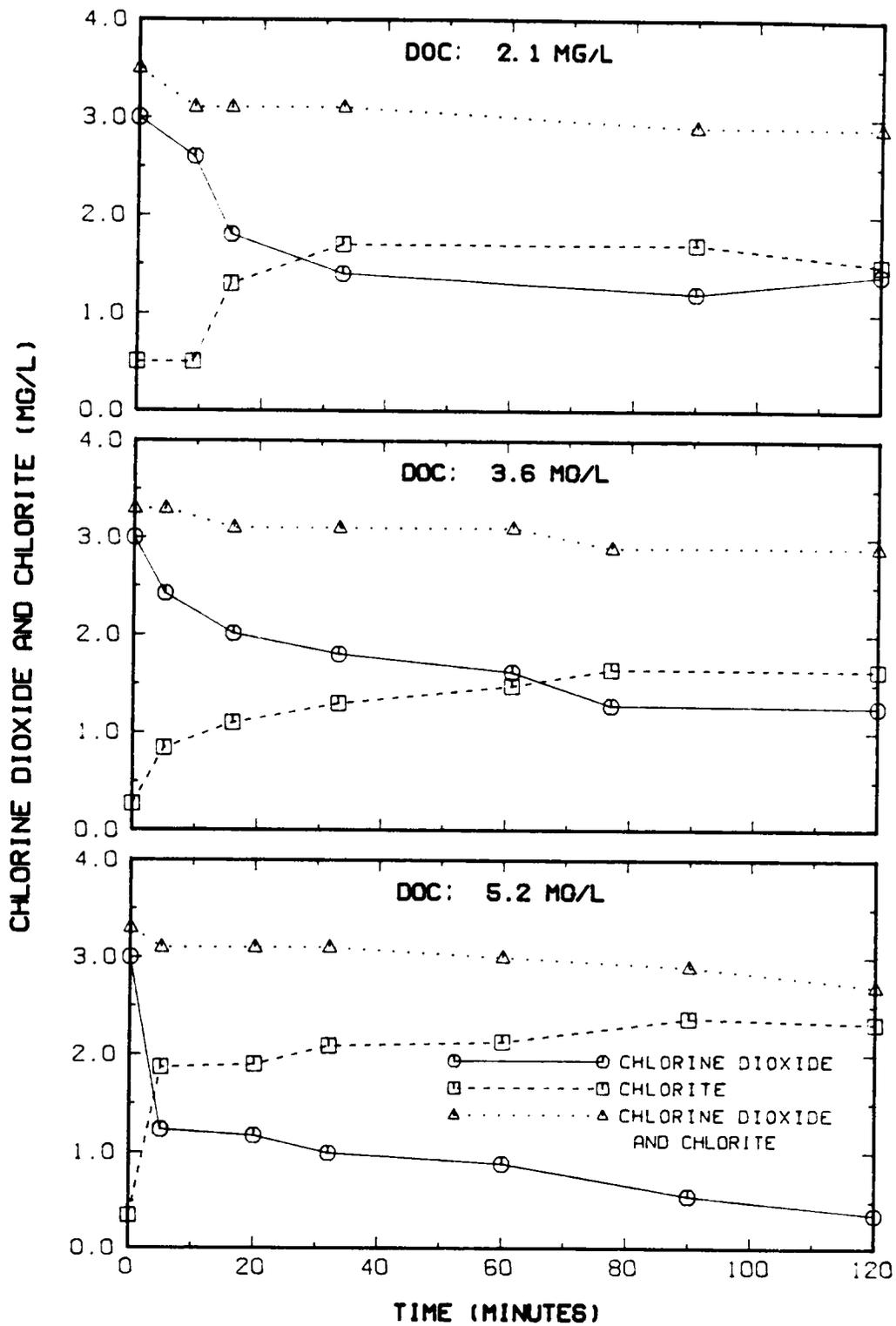


Figure 37. Chlorine dioxide and chlorite in three waters dosed with manganese(II) and chlorine dioxide at pH 6.3.

Interaction Between Chlorine Dioxide and Permanganate

The final series of reactions involved the application of chlorine dioxide and permanganate simultaneously. Again, the effect of three levels of DOC (2.1 mg/L, 3.0 mg/L, and 4.4 mg/L) on manganese(II) oxidation was investigated. Also, the effect of combining the oxidants on the concentrations of permanganate and chlorine dioxide was evaluated. Figure 38 shows that, as in the previous experiments, manganese(II) concentrations decreased in all three solutions, although this occurred much more slowly at a DOC concentration of 4.4 mg/L than it did in the other solutions that contained less DOC. Unlike the jar-tests evaluating permanganate alone, the permanganate concentration did not decrease appreciably in the two solutions containing lower concentrations of DOC (2.1 mg/L and 3.0 mg/L). Figure 39 shows that the concentrations of chlorine dioxide decreased more rapidly when it was used in conjunction with permanganate, especially at the high DOC concentration, than it did when it was used as the sole oxidant. In addition, less chlorite formed when permanganate was present, especially at the lowest DOC concentration examined (2.1 mg/L).

Kinetic Coefficients

Kinetic coefficients were developed to define manganese(II) oxidation rates and to determine the effect of increasing the DOC concentration on these reaction rates. Also, the rate of oxidant reductions was documented. Two reaction orders, first and second order, were evaluated using graphical techniques. The straight line equations and their derivation follow:

first order:

$$\frac{d[A]}{dt} = -k[A_o] \quad [48]$$

integrated form of first order:

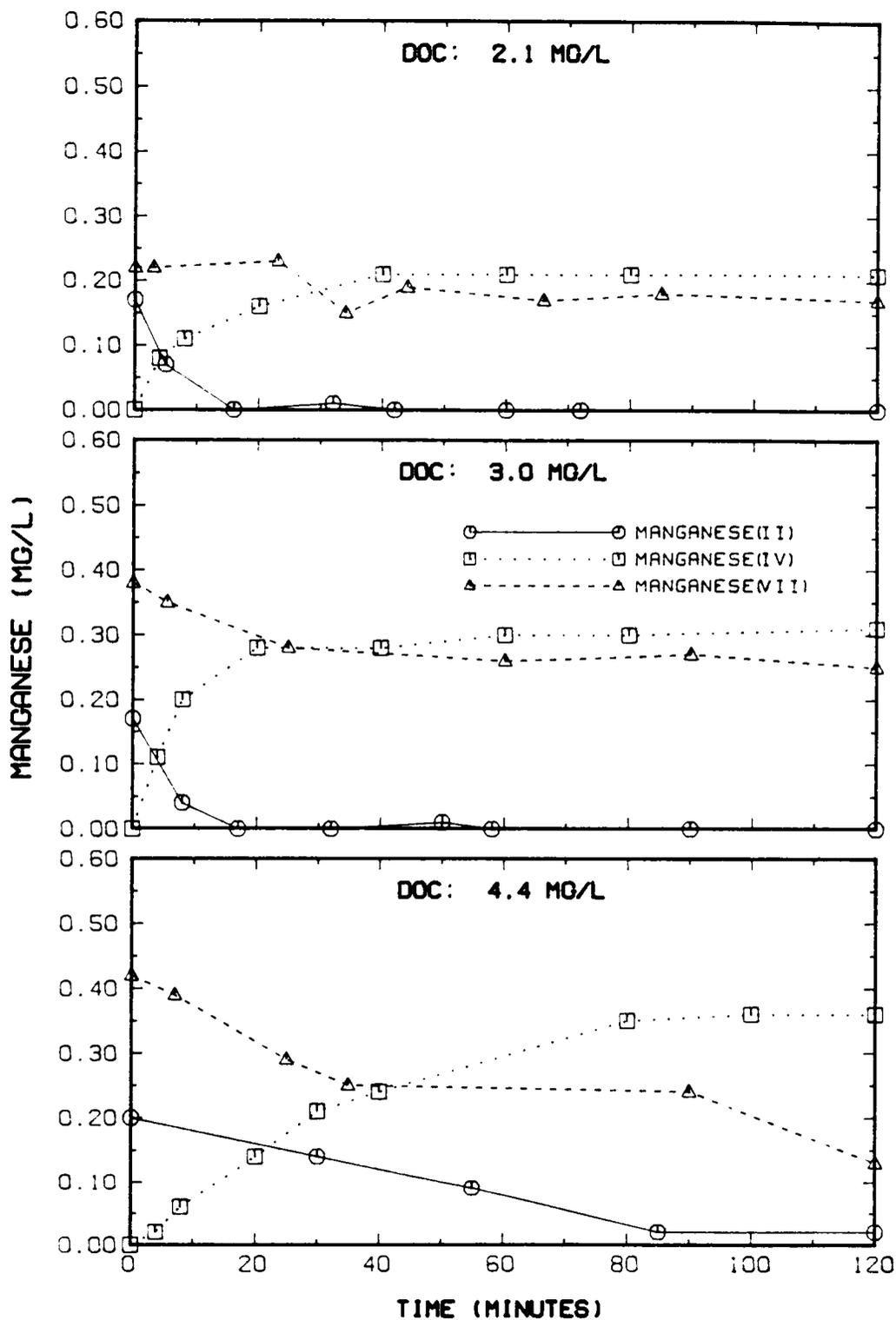


Figure 38. Manganese species in three waters dosed with manganese(II), permanganate and ≈ 3 mg/L chlorine dioxide at pH 6.3.

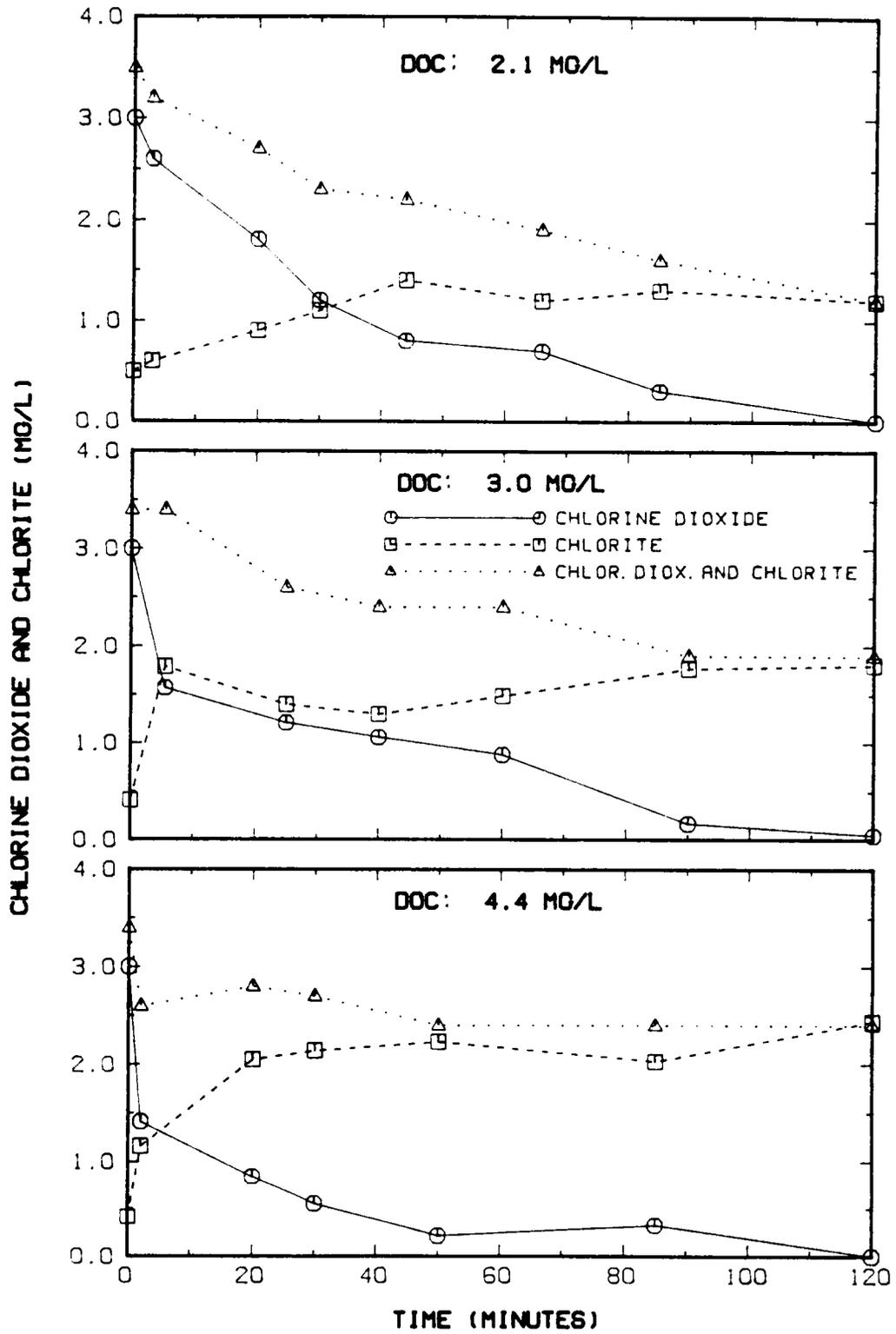


Figure 39. Oxy-chlorine species in three waters dosed with permanganate, manganese(II) and chlorine dioxide at pH 6.3.

$$\ln[A] = \ln[A_o] - kt \quad [49]$$

second order:

$$\frac{d[A]}{dt} = -k[A_o]^2 \quad [50]$$

integrated form of second order:

$$\frac{1}{[A]} = \frac{1}{[A_o]} + kt \quad [51]$$

where:

$[A_o]$ = the initial concentration of the chemical species being modeled,

$[A]$ = the concentration of the chemical species at time = t ,

t = time, and

k = the rate constant.

The closeness of fit to either a first- or second-order model was determined by linear regression. The oxidant (permanganate or chlorine dioxide) concentrations and manganese(II) concentrations (presented in Figures 35 and 37 through 39) were plotted using both equations [49] and [51] and the line with the highest coefficient of determination (r^2) was assumed to better represent the appropriate rate order. The units for the kinetic coefficients of first-order reductions were minutes⁻¹ and those of second-order reactions were minutes⁻¹ M⁻¹. Because the units differ, the kinetic coefficients of one order were not directly compared to those of the other order.

Table 15 lists the coefficients of determination (r^2) and kinetic coefficients for the oxidation of manganese(II) by permanganate alone, chlorine dioxide alone, and permanganate and chlorine dioxide together. The reaction between permanganate and manganese(II) was reviewed first. Manganese(II) exhibited first-order decay when oxidized by KMnO₄. The coefficients of determination were high (0.99 and 1.00) for the first-order reactions in the two solutions with 3.7 mg/L and 4.7 mg/L DOC and intermediate (0.87) for the first-order reactions in the solution containing 2.1

Table 15.
Determination of rate orders and kinetic coefficients for the oxidation of manganese(II).

Coefficients of determination (r^2) and kinetic coefficients (k) for manganese(II) oxidation at three DOC concentrations							
		2.1 mg/L		3.0 - 3.7 mg/L		4.4 - 5.2 mg/L	
OXIDANT	ORDER	r^2	k*	r^2	k	r^2	k
KMnO ₄	first	0.87	0.07	0.99	0.11	1.00	0.02
	second	0.75	72,000	0.89	153,000	0.87	41,000
ClO ₂	first	0.83	0.15	0.81	0.12	0.93	0.02
	second	0.99	459,000	0.87	73,000	0.95	1,600
ClO ₂ &KMnO ₄	first	0.97	0.08	1.00	0.18	0.91	0.02
	second	0.90	152,000	0.93	200,000	0.85	24,000

*The units for first- and second-order k values are minutes⁻¹ and minutes⁻¹M⁻¹ respectively

mg/L DOC. The rate coefficient was the highest ($k = 0.11 \text{ minute}^{-1}$) for manganese oxidation with 3.7 mg/L DOC in solution and lowest (0.02 minute^{-1}) for that with 4.6 mg/L DOC in solution.

When oxidized by chlorine dioxide, manganese(II) concentrations decreased at a rate best described by second-order kinetics. This model fit quite well; the coefficients of determination ranged from 0.87 for manganese(II) oxidation in the solution containing 3.0 mg/L DOC to 0.99 for that in the solution containing 2.1 mg/L DOC. A comparison of the kinetic coefficients among the solutions in which manganese(II) was oxidized by ClO_2 , reveal a strong trend. The rate of manganese(II) oxidation decreased as the DOC concentration of the solutions increased.

When chlorine dioxide and permanganate were used in combination, reductions in manganese(II) concentrations were best described by first-order kinetics. The coefficients of determination were again quite high and ranged from 0.91 to 1.00. The rates were comparable to those exhibited by the reaction between permanganate and manganese(II). The fastest rate of manganese oxidation (and the fastest rate observed in this study) (0.18 minute^{-1}) occurred in the solution containing 3.0 mg/L DOC, and the slowest rate occurred in the solution containing 4.4 mg/L (0.02 minute^{-1})

The rates of oxidant reduction were determined in the manner identical to that used for the calculation of manganese(II) oxidation rates. The results of these kinetic analyses are presented in Table 16. Permanganate reduction in the three solutions in which it was the sole oxidant followed second-order kinetics for two cases and followed both first- and second-order kinetics in the third case (DOC of 2.1 mg/L). The rate of permanganate depletion increased from $11,400 \text{ minute}^{-1} \text{M}^{-1}$ to $90,000 \text{ minutes}^{-1}$ as the DOC concentration increased.

Chlorine dioxide concentrations decreased according to second-order kinetics in the three solutions in which it was the sole oxidant. The rate of chlorine dioxide depletion among these three solutions was the greatest (1,300 moles/minute) when the DOC was 5.2 mg/L and the least (300 moles/minute) in solutions containing 3.6 mg/L DOC.

The reduction of permanganate in the solutions containing both chlorine dioxide and permanganate did not closely follow either of the kinetic models. The coefficients of determination were slightly

Table 16.
Determination of rate orders and kinetic coefficients for the reduction of chlorine dioxide and permanganate.

		Coefficients of determination (r^2) and kinetic coefficients (k) for oxidant reductions at three DOC concentrations					
		2.1 mg/L		3.0 - 3.7 mg/L		4.4 - 5.2 mg/L	
OXIDANT	ORDER	r^2	k*	r^2	k	r^2	k
ClO ₂ & KMnO ₄ Used Separately							
KMnO ₄	first	0.98	0.02	0.55	0.02	0.89	0.05
	second	0.98	11,400	0.96	26,000	0.99	90,000
ClO ₂	first	0.90	0.02	0.82	0.01	0.90	0.02
	second	0.96	600	0.88	300	0.94	1,300
ClO ₂ & KMnO ₄ Used Together							
KMnO ₄	first	0.79	0.002	0.84	0.006	0.71	0.004
	second	0.79	600	0.87	1,100	0.75	800
ClO ₂	first	0.99	0.03	0.93	0.03	0.99	0.05
	second	0.93	1,400	0.71	9,000	0.90	6,000
*The units for first- and second-order k values are minutes ⁻¹ and minutes ⁻¹ M ⁻¹ respectively							

better for the second-order model and ranged from 0.75 for the reaction that occurred in the solution containing 4.4 mg/L DOC to 0.87 for the reaction that occurred in the presence of 3.0 mg/L DOC. The rates of permanganate reduction were much lower in the presence of chlorine dioxide than when permanganate was dosed by itself.

When in solution with permanganate, chlorine dioxide reduction followed first-order kinetics; the coefficients of determination ranged from 0.93 to 0.99. These rate coefficients cannot be compared to those encountered in the solutions in which chlorine dioxide was the sole oxidant because of the difference in the rate order.

Because the k and r^2 values derived from the analyses of first- and second-order relationships cannot be compared, the half-lives of the various species [(manganese(II), permanganate, and ClO_2] were compared. The following equations show the relationship between half-life and k for first- and second-order reactions.

first-order:

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} \quad [52]$$

second-order:

$$t_{\frac{1}{2}} = \frac{1}{k[A_0]} \quad [53]$$

The half-lives were calculated with either equation [52] or equation [53] depending on the reaction order that yielded the greatest coefficient of determination in Tables 15 and 16. They are listed in Table 17 and show the following results. The fastest oxidation of manganese occurred with chlorine dioxide in the solution low in DOC, and the slowest oxidation occurred when chlorine dioxide was used as the oxidant and the DOC was high. At the lowest DOC concentrations, manganese(II) oxidation was slower when permanganate was the oxidant than it was when chlorine dioxide was the oxidant, and the rates were about the same at the intermediate DOC concentration. At the highest DOC concentrations used in this experiment, permanganate oxidized manganese(II) more

Table 17.
Half lives of chlorine dioxide, manganese(VII), and manganese(II) calculated from kinetic coefficients

Half-lives of reactants in solutions with three DOC concentrations									
	2.1 mg/L			3.0 - 3.7 mg/L			4.4 - 5.2 mg/L		
	Half lives (minutes)			Half lives (minutes)			Half lives (minutes)		
<i>oxidant</i>	Mn(II)	Mn(VII)	ClO ₂	Mn(II)	Mn(VII)	ClO ₂	Mn(II)	Mn(VII)	ClO ₂
KMnO ₄	11	22	NA	6	6	NA	30	2	NA
ClO ₂	0.7	NA	37	4	NA	78	160	NA	18
KMnO ₄ & ClO ₂	8	413	23	4	130	22	30	160	13

quickly than did chlorine dioxide. Manganese(II) half-lives in the solutions treated with a combination of chlorine dioxide and permanganate were intermediate to those observed when permanganate was used by itself.

The half-lives of permanganate were consistently shorter than those of chlorine dioxide when the oxidants were used separately. When the oxidants were dosed simultaneously used together this relationship was reversed. The half-life of permanganate increased more than the half-life of chlorine dioxide decrease.

Organic Size Determinations

In this section, molecular sizes of naturally occurring organic materials were investigated. The precision and usefulness of the data from ultrafiltration was first evaluated. Second, the molecular sizes of the naturally occurring organic materials in Abel Lake were determined. Finally, the effect of the oxidants on the size distribution was presented.

Evaluation of ultrafilter performance

The precision of the ultrafilters was measured by introducing surface surface water from Abel Lake and monitoring the flow rate and the DOC concentration of the permeate. Also, the extent of adsorption of organic carbon to the filters was measured. Five membranes with a 500 dalton molecular weight cutoff, three with a 1K dalton molecular weight cutoff, two with a 5K molecular weight cutoff and only one with a 10K and 30K dalton the molecular weight cutoffs were evaluated.

The data in Table 18 show the flow rate through the membrane filters used for the molecular-size studies. Flow rates were greater through membranes having greater exclusion limits. The filter with the 500 dalton exclusion-limit (500 dalton filter) had the slowest flow rate (19 mL/hr) and the 30K dalton filter had the fastest flow rate (754 mL/hr). The flow rates for filters of the same pore size

Table 18.
Variations in flow rate and permeate DOC concentration for the ultrafilters used in this study.

Nominal Molecular Weight Exclusion Limit (daltons)	Filter Number	Volume interval (mL)	Flow Rate (mL/h)	Permeate DOC Concentration (mg/L)
500	1	0 - 10	19	0.56
500	1	20 - 30	26	0.72
500	5	30 - 40	25	0.86
500	5	60 - 70	24	0.64
500	4	110 - 120	33	0.76
1K	1	0 - 10	38	1.28
1K	3	10 - 20	32	1.29
5K	1	10 - 20	75	1.84
5K	1	25 - 35	81	2.41
5K	1	40 - 50	67	2.06
5K	2	10 - 20	150	1.92
5K	2	30 - 45	156	2.40
5K	2	60 - 70	155	2.18
5K	2	80 - 120	150	2.30
10K	1	0 - 20	285	2.56
10K	1	20 - 40	297	3.23
30K	1	0 - 40	754	3.31

were relatively consistent with one exception. The flow rates through the two 5K dalton filters were remarkably different (74 mL/h and 155 mL/h), but the permeate DOC concentration did not increase accordingly. The concentration of DOC in the permeate from the 500 dalton exclusion-limit membrane shows a slight correspondence to the flow rate. Also, there was little relationship between the total volume of permeate that had passed the filter and the flow rate. That is, passing a solution through the filter membranes did not clog the membrane pores.

For ultrafiltration data to be meaningful, the retained DOC should be excluded by the membrane (i.e. too large to pass the pores of the filter) not by adsorption to the membrane. The data in Table 19 show a comparison between the mass of DOC in both the retentate and the permeate and that originally introduced to the ultracell. The differences between the masses of DOC introduced and that recovered was assumed to represent the percent of adsorbed DOC and ranged from -5 to +8 percent. There were no trends relating to the filter pore size and losses or gains in DOC. In most cases, more DOC was recovered than was introduced (as evidenced by positive percent differences on the table). Most likely, the unaccounted for DOC resulted from either contamination of the sample after collection or errors in the DOC determinations.

The exclusion of molecules must be precise, to some degree, for ultrafiltration data to be meaningful. The data presented in Figure 40 show the results of filtering several aliquots (six to ten) of water from the surface of Abel Lake through ultrafilters of the same size (the same ultrafilter for the results of the 10K-dalton exclusion limit) and recording the DOC concentration of the permeate as a function of the volume fraction of the permeate. A volume fraction was defined as the volume of permeate divided by the total initial volume in the cell. Figure 40, shows that the permeate DOC concentration seemed to be more consistent in the volume fraction range of 0.3 to 0.6 than in the initial and final volume fractions. Also, the concentration of the permeate steadily increased as the volume fraction increased. These results suggested that maximum precision could be obtained by collecting a consistent volume fraction each time a sample was filtered.

The reason for this dependence of permeate DOC concentration on volume fraction was unknown, but two theories were investigated. First, molecules of organic carbon may have initially sorbed to

Table 19.
Comparison of DOC introduced to ultracells to that recovered after filtration.

A	B	C	D	E	F	
Nominal MW exclusion limit (daltons)	Filter number	Initial DOC in cell (ug)	DOC in permeate (ug)	DOC retained (ug)	Total DOC recovered (ug)	Percent difference columns C & F
500	1	176	27	141	168	-5
500	2	176	29	153	182	3
500	4	351	80	296	376	7
500	5	176	28	144	172	-2
1K	1	176	51	122	173	-2
1K*	1	176	72	105	177	1
5K	1	176	83	88	171	-2
5K	1	176	88	89	177	1
5K	2	176	90	81	171	-3
5K	2	176	95	80	175	-0.3
10K	1	176	116	72	188	7
10K	1	176	126	62	188	7
10K	1	176	112	78	190	8
30K	1	176	128	49	177	1
30K	1	176	127	59	186	6

*Ultracell not stirred

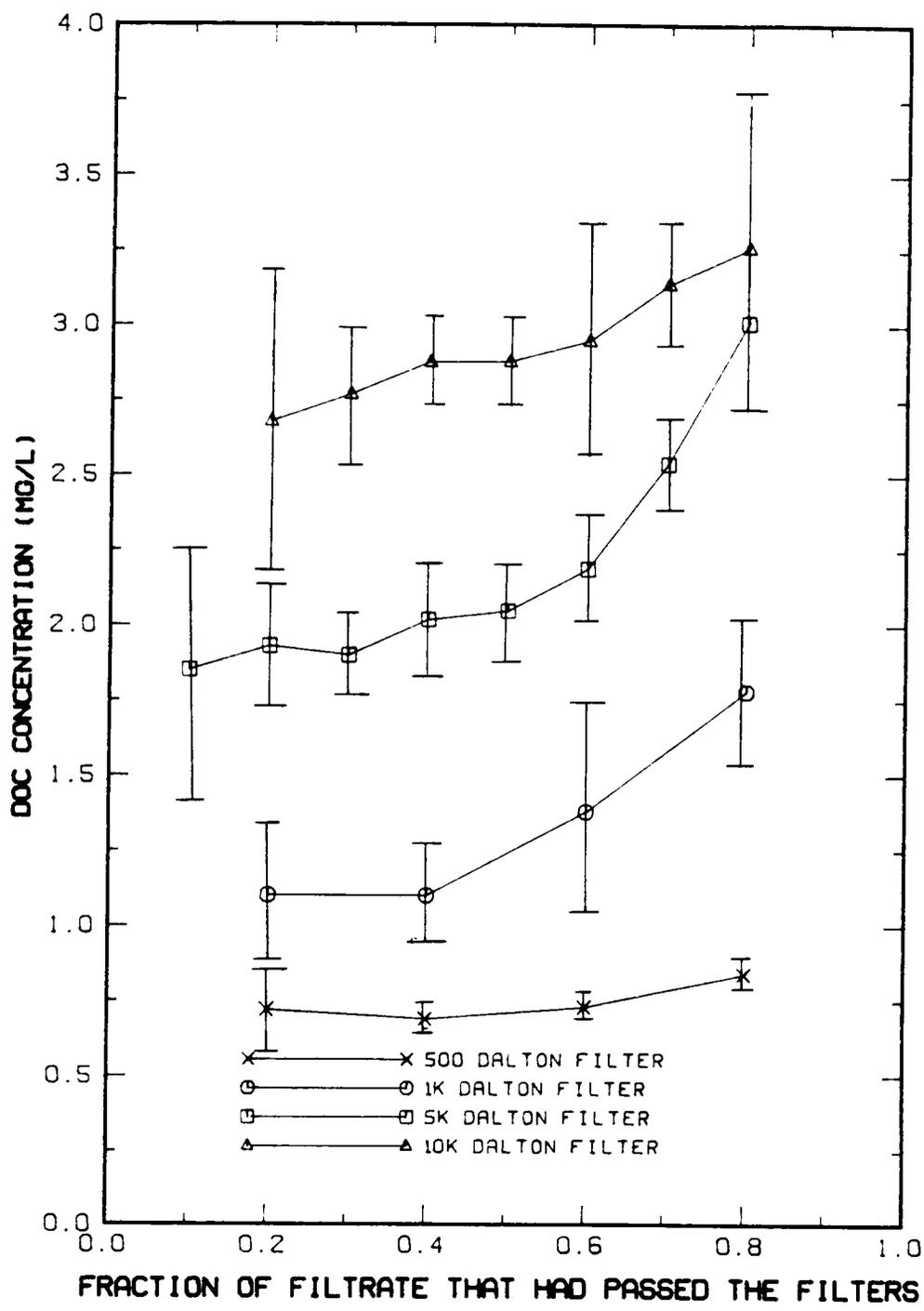


Figure 40. Permeate DOC concentration versus permeate volume for Abel Lake waters filtered through four different membrane sizes. Error bands are 95 percent confidence intervals

the membrane until all the adsorption sites were occupied, at which time they were free to pass the filter. Second, the permeate concentration may be dependant on the retentate concentration, which increases in concentration with increasing permeate volume. The data in Figures 41A and 41B address these two theories. Figure 41A shows the relationship between the volume fraction and permeate DOC concentration for two solutions that varied only in their initial volumes. If the organic carbon were adsorbing to sites on the ultrafilter, these sites would be expected to be occupied after the same volume of permeate passed in each case. Because the permeate DOC concentrations did not increase at simultaneous permeate volumes, it was reasoned that sorbtion sites were not being saturated at the same rate. Because there was no reason for sorbtion to occur faster in one case than in the other the hypothesis of organic molecules breaking through when all the sites were occupied was discounted. The bottom graph shows the close dependance the permeate DOC of both solutions had on the retentate DOC. Thus, as the retentate DOC concentration increased, more organic materials were able to pass the membrane.

Precision of the Rosin-Rammler analysis

The results of filtering 11 replicates of water from Abel Lake through the ultrafilters (with molecular weight exclusion limits of 500, 1K, 5K, 10K, and 30K) and analyzing them by the Rosin-Rammler method are presented in Table 20. These data represented the DOC concentrations from the permeate in volume fractions 0.3 - 0.6 (as was suggested to be the best procedure based on the results shown in Figure 40). Because the coefficients of determination were generally greater than 0.92, the Rosin Rammler model appeared to describe the data quite well. The mean and standard deviation for X_0 were 5,900 and 611. The mean value for n was 0.59 with a standard deviation of 0.07. These standard deviations were considered to be acceptable and an indication that the model was not overly sensitive to the experimental error encountered in sampling and DOC determination.

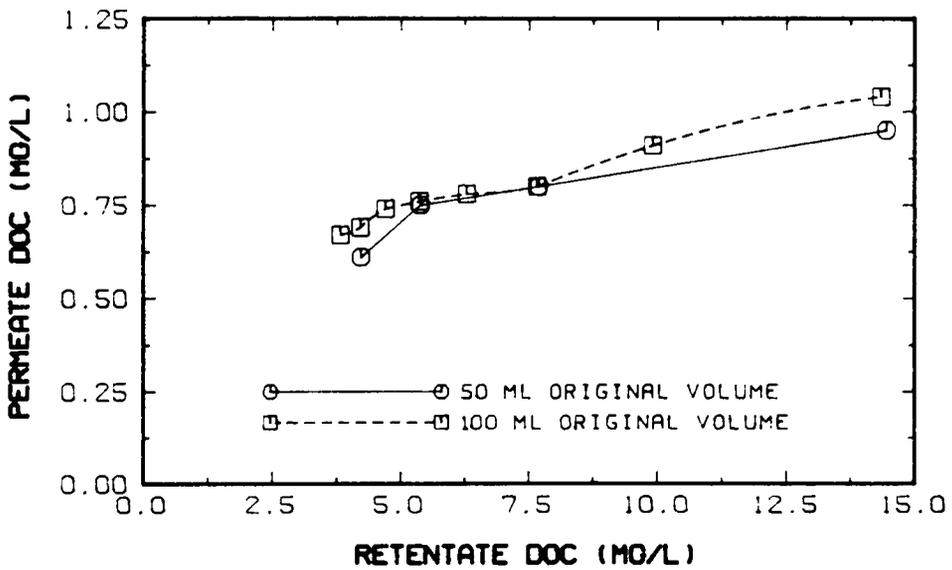
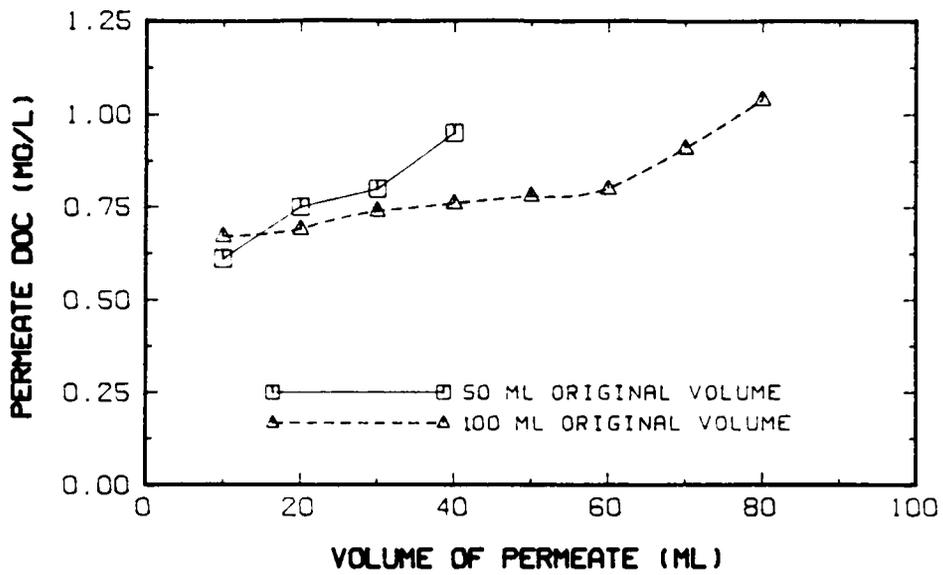


Figure 41. Effects of increasing both permeate volume (top) and retentate DOC concentration (bottom) on permeate DOC concentration.

Table 20.
Variation in n and X_0 resulting from Rosin Rammler analyses of molecular-size data obtained from Abel Lake water

Trial	r^2	n	X_0 (daltons)
1	0.98	0.66	6,100
2	0.92	0.47	7,000
3	0.96	0.70	5,100
4	0.97	0.54	6,700
5	1.00	0.64	5,500
6	0.94	0.64	5,200
7	0.84	0.52	6,000
8	0.96	0.58	5,900
9	0.97	0.59	5,400
10	0.96	0.53	6,400
11	0.99	0.66	5,700
mean	0.95	0.59	5,900
standard deviation	0.04	0.07	611

Variations in size of naturally occurring organic matter

In this section the sizes of naturally occurring organic materials from the top and bottom of Abel Lake and the lake's inlet both while the lake was stratified and while it was not. An analysis of covariance (ANCOVA) (101) was performed to determine if the differences observed for X_0 and n were statistically significant. In each case the 90 percent confidence level was used. The data for DOC in Abel Lake water are presented in Tables 21 and 22. For the DOC data from Abel Lake water while the lake was stratified (Table 21), there were no significant differences in the values of either X_0 or n . The characteristic sizes (X_0) for the organic compounds ranged from 5,000 to 5,400 daltons and the range for n was 0.62 to 0.75. As is seen, the coefficients of determination (r^2) were near one, indicating that the Rosin Rammler model fit the data well. The values for X_0 were higher for THM-precursor than they were for the parent population of organic molecules (DOC) the characteristic size (X_0) of the THM-precursors did not vary significantly from the top to the bottom of the lake, or in the inlet. The values for the width of the distribution of molecular sizes of the precursors (n) in the surface water was low, indicating that these precursors were more widely distributed in size than were the precursors in the inlet or bottom waters.

The molecular sizes were also investigated while the waters were not stratified in March and the same three sites were sampled (inlet, surface, and bottom waters). These data are presented in Table 22. The differences in the characteristic size distribution were not significant, but the differences in value of X_0 and n for the THM-precursors were significant. The precursors were much larger than were the general organic carbon molecules, as they were when the lake was mixing. Among the three sites, the precursors in the inlet were the smallest and those in the surface water were the largest. The width of the precursor size distribution in the surface water was greater than that of the precursor size distribution in either the inlet or bottom waters.

Effects of oxidants on THM yield and size of organic molecules

Table 21.
Results of Rosin Rammler analyses performed on the molecular-size data from Abel Lake water while the lake was stratified.

Source	Values of r^2 , X_0 , and n for DOC			Values of r^2 , X_0 , and n for THMs formed by chlorinating DOC		
	r^2	X_0 (daltons)	n	r^2	X_0 (daltons)	n
Inlet	0.97	5,100	0.62	1.00	11,900	0.55
Surface	0.99	5,000	0.66	0.94	14,300	0.38
Bottom	0.87	5,400	0.75	0.90	13,600	0.59

Table 22.
Results of Rosin Rammler analyses performed on the molecular-size data from Abel Lake while it was not stratified.

Source	Values of r^2 , X_0 , and n for DOC			Values of r^2 , X_0 , and n for THMs formed by chlorinating DOC		
	r^2	X_0 (daltons)	n	r^2	X_0 (daltons)	n
Inlet	0.97	6,100	0.54	0.99	6,200	0.72
Surface	0.95	5,500	0.71	0.99	12,800	0.63
Bottom	0.94	5,200	0.70	0.96	8,100	0.80

In this section, the THM yield and size of the organic molecules were investigated before and after exposure to an oxidant. The effects of the oxidants were evaluated both when a coagulant was absent (Table 23) and when one was present (Table 24). As the data in Table 23 show, when a coagulant was not present the yields ranged from 20 ug/mg to 79 ug/mg. The THM yields were highest in the water before treatment and the lowest in the water treated with chlorine dioxide. The THM yields from the DOC in the water treated with permanganate were slightly less than those before treatment. Ultrafiltration allowed the comparison of yields from different sizes. The yields from the permeates of filters with different nominal molecular weight cutoffs were not yields from a specific size range of organic matter, but the permeate from the next larger filter did contain the larger organic molecules that were excluded by the membranes with smaller pore sizes. For example, the permeate of the 5K-dalton exclusion membrane contained organic materials that also passed the 1K-dalton exclusion membrane plus some that did not pass. Thus, the difference in yields between the DOC in the permeates from these two membranes was attributable to the larger organic materials that were able to pass the 5K-dalton exclusion membrane, but were excluded by the 1K-dalton exclusion membrane. In general, chlorine dioxide and especially, permanganate decreased the yield of the smaller sizes of organic molecules more than they decreased that of larger organic materials. In the raw water, there was a slight trend of increasing yield with increasing molecular size.

In most water treatment plants, a coagulant such as aluminum sulfate is added at the same time that the oxidants are added. The data in Table 24 show the results of introducing a coagulant and an oxidant at the same time on the yield from permeates of different sized filters. The range of the yields (24 ug/mg - 76 ug/mg) was about the same as it was for the solutions treated without a coagulant. Among the bulk solutions, the untreated water exhibited the greatest yield (62 ug/mg). Coagulation without an oxidant decreased the yield only slightly to 60 ug/mg. Chlorine dioxide decreased the yield to 35 ug/mg, and permanganate was less effective (52 ug/mg). In this experiment, the water was also treated with a combination of chlorine dioxide and permanganate which decreased the yield by an amount intermediate to the decreases observed when the water was dosed with chlorine dioxide and permanganate by themselves. The extent of the decreases can be compared to those observed for the solutions not treated with a coagulant (Table 23). Chlorine dioxide

Table 23.
Effect of molecular-size on the yield of THMs per DOC (ug/mg) in Abel Lake waters treated with oxidants only

Ultrafilter MW exclusion limit	Yield of THMs per DOC from Abel Lake water treated as shown		
	Raw water	ClO ₂ (1.5mg/L)	KMnO ₄ (1.0mg/L)
500	75	25	48
1K	58	20	45
5K	51	23	42
10K	59	32	55
30K	65	47	63
Bulk	79	38	78

Table 24.
Effect of molecular size on the yield of THMs per DOC (ug/mg) in Abel Lake waters treated with both coagulant and oxidant.

ultrafilter MW exclusion limit	Yields of THMs per DOC (ug/mg) from waters treated as shown				
	No coagulant	All coagulated with 20 mg/L alum			
	Raw water	Alum only	ClO ₂ (1.5mg/L)	KMnO ₄ (1.0mg/L)	ClO ₂ (1.0 mg/L) KMnO ₄ (0.5mg/L)
500	64	34	25	53	31
1K	62	62	33	61	43
5K	70	60	24	58	46
10K	75	67	32	65	44
30K	76	83	37	66	42
Bulk	62	60	35	52	44

was slightly more effective when a coagulant was not introduced; the yield decreased 52 percent in this latter case versus a 44 percent decrease when a coagulant was used. Permanganate was more effective in reducing the yield when used with a coagulant than when it was used alone (16 percent and 1 percent decreases respectively).

The data in Table 25 show the effects that chlorine dioxide and permanganate had on the molecular size. The differences in X_0 were statistically significant. Permanganate and especially chlorine dioxide caused substantial decreases in the size of the organic molecules. The size of THM-precursors was also significantly changed by the oxidants. Chlorine dioxide decreased the size of the THM precursors whereas permanganate slightly increased the size of the precursors. The differences in the width of the organic molecule size distribution were not significant.

The data in Table 26 show the effects of the oxidants on the size distribution of the organic molecules when aluminum sulfate was present as a coagulant. The differences in size were significant, but the differences in the width of the size distributions were not. The dissolved organic compounds remaining after coagulation were much smaller than those in the bulk solution (X_0 decreased from 7,600 to 3,000). The presence of oxidants during coagulation slightly affected the sizes of the organic materials. Chlorine dioxide further decreased the size of the organic molecules, but only slightly. When permanganate was dosed with the coagulant, the organic molecules increased in size. Treatment with both of the oxidants did not change the size of the organic molecules.

In the untreated water, THM-precursors were smaller than were the general organic molecules. Coagulation with alum resulted in a shift in molecular size to smaller DOC (X_0 decreased from 3,8000 daltons to 2,400 daltons). The addition of oxidants to solution during coagulation had varying effects. When chlorine dioxide was present (alone or with permanganate) during coagulation, the THM-precursors that remained in solution were larger than those that remained in the solution after coagulated when no oxidant was present. When permanganate was present, coagulation resulted in smaller THM-precursors than when permanganate was not present. The width of the size distributions (n) did not change significantly.

Table 25.
Results of Rosin Rammler analyses performed on the molecular-size data from Abel Lake waters treated as shown

Treatment	Values of r^2 , X_0 , and n for DOC			Values of r^2 , X_0 , and n for THMs formed by chlorinating DOC		
	r^2	X_0 (daltons)	n	r^2	X_0 (daltons)	n
Raw Water	0.92	6,700	0.66	0.97	16,000	0.30
1.5 mg/L ClO_2 (0.022 meq/L)	0.94	2,700	0.48	0.96	7,800	0.56
1.0 mg/L KMnO_4 (0.022 meq/L)	0.96	4,600	0.49	0.99	20,000	0.46

Table 26.
Results of Rosin Rammler analyses performed on the molecular-size data from Abel Lake waters treated with alum and oxidants

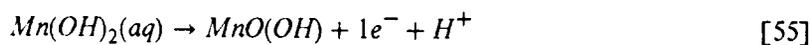
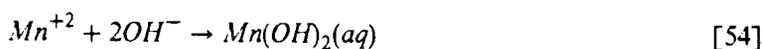
Treatment	Values of r^2 , X_0 , and n for DOC			Values of r^2 , X_0 , and n for THMs formed by chlorinating DOC		
	r^2	X_0 (daltons)	n	r^2	X_0 (daltons)	n
Raw Water	0.96	7,600	0.47	0.99	3,800	0.68
40 mg/L alum	0.86	3,000	0.55	0.88	2,400	1.00
1.5 mg/L ClO_2 (0.022 meq/L)	0.88	2,500	0.49	0.72	4,200	0.62
1.0 mg/L KMnO_4 (0.022 meq/L)	0.88	4,000	0.55	0.90	1,900	1.19
1.0 mg/L ClO_2 & 0.5 mg/L KMnO_4	0.85	3,300	0.58	0.77	3,800	0.72

DISCUSSION

The organization of this chapter differs slightly from that of the Results chapter. Where appropriate, the results of the plant and laboratory studies have been combined so that the results of each can be compared and contrasted. The manganese chemistry involved in studying the interference of manganese with chlorite and chlorine determinations is discussed first. Next, the results from the plant-study, which have no laboratory-study analog (filter operation and taste-and-odor problems), are discussed. Following this, the performance of the preoxidants for DOC, THMFP, manganese and iron removals in the plant and laboratory studies will be examined and compared. Where possible, unifying mechanisms of removal are proposed in an effort to better describe the physical and chemical phenomena responsible for the removal of these constituents. Next, the interactions of chlorine dioxide and permanganate both with each other and with DOC are examined to gain a better understanding of the reasons for better or worse plant performance experienced when different oxidants were used. Finally, the method for determining the molecular size and the effects of the oxidants on the molecular size of the naturally occurring organic will be discussed.

Mechanism of Manganese(II) Oxidation

Before the nature of the interferences by manganese in the determinations of chlorite and chlorine is discussed, the nature of the manganese particles formed in the two MnO_x suspensions will be examined; manganese(II) oxidation will be reviewed first. The following mechanism, proposed by Kessick and Morgan (13), can be used to explain the variations in oxidation states of MnO_x particles formed under different conditions.



Equation [55] is the rate limiting step. The authors noted that thermodynamic data suggest the existence of only extremely low concentrations of $\text{Mn}(\text{OH})_2$ (aq) in free solution. A similar structure could conceivably be formed at higher concentrations in the double layer at the surface of an already formed particle. (Thus, the reaction shown in equation [55] probably occurs on the surface of an $\text{MnO}(\text{OH})$ particle.) Because $\text{MnO}(\text{OH})$ can be further oxidized to MnO_2 , and both are likely to occur in the same particle simultaneously, it may be more accurate to refer to this particle as an MnO_x particle. The oxidation state of the precipitate is determined by the rate of oxidation relative to the rate of accretion. If the rate of accretion exceeds the rate of oxidation, oxidized forms [e.g. $\text{Mn}(\text{II})$ and $\text{MnO}(\text{OH})$] can become sequestered in the particle. An oxide forming at a low pH and a high oxidation potential might be oxidized further than one forming at a high pH [providing a large supply of OH^- to form $\text{Mn}(\text{OH})_2$] and a low oxidation potential because the rate of oxidation would exceed the rate of accretion. In summary, a lower oxidation state is expected when the rate of accretion is faster than the rate of oxidation, and, in contrast, a higher oxidation state would be expected when the rate of oxidation is faster than the rate of accretion. The difference in the *oxidation state* of the two MnO_x suspensions formed in this study was probably caused by a difference in the ratio of particle formation rate and the manganese oxidation rate. The dif-

ference in the *particle size* between the two solutions was probably a function of the concentration of particles. At higher concentrations, the frequency of collisions between particles and, thus, the chances of particles combining increases.

Manganese Interference With Chlorite and Chlorine

Determinations

Two species of manganese were found to interfere with chlorite and chlorine determinations: permanganate and MnO_x . The interference from permanganate was more consistent than was the interference from MnO_x , but the standard deviations of permanganate interference in chlorite and chlorine determinations still indicated substantial error (± 15 percent). This error caused imprecision in 1) the quantification of permanganate interference with chlorite and chlorine determinations and 2) the determination of permanganate by sums of the separate titrations. Occasional drifts near the endpoint of the pH 7 titration were observed and provide further evidence of the instability of this endpoint. Approximately ten minutes after an initial endpoint was reached, a new equilibrium was reached causing the indicator needle to drift slightly.

It is hypothesized that a kinetically favored product, probably composed of several manganese species was initially formed, and after 10 minutes, a thermodynamic equilibrium was reached. The product formed from the reaction between permanganate and I^- at pH 7 was probably a combination of MnO_2 and $\text{MnO}(\text{OH})$. The data in Table 11 indicate that the reaction product had an oxidation state of 3.5, which would support this hypothesis. During the titrations, particulate forms of manganese [MnO_2 and $\text{MnO}(\text{OH})$] were not observed, but when a concentrated solution [3 g/L of permanganate and excess I^-] was prepared, the particles were readily observable. The formation of kinetically favored, quasi-stable MnO_x particles may help explain the reasons for the variability of the endpoint when permanganate was titrated at pH 7. Permanganate oxidizes I^- to

I_2 and in turn is reduced to an MnO_x colloid. Thus, it is proposed that a mechanism for permanganate reduction involving particle formation, analogous to the mechanism for the oxidation of manganese(II) presented previously, was responsible for the loosely defined endpoint. That is, the extent of reduction of the manganese is determined by both the rate of accretion and the rate of permanganate reduction. In turn, the rate of accretion depends on the rate at which the colloids contact one another (a function of concentration and degree of solution agitation); and the rate of permanganate reduction depends on the reaction rate between the I^- and permanganate (a function of solution concentration). As particles formed, manganese(IV) was trapped inside while the manganese on the outside of the particles was exposed to the I^- and may have been reduced to manganese(III). The faster the colloid formation, the greater the quantity of entrapped manganese(IV); and, conversely, the slower the colloid formation, the less entrapped manganese(IV). It is proposed that the competing rates of particle formation, and permanganate reduction were responsible for the formation of a quasi-stable reduction product. In those cases that the solution was allowed to further equilibrate, the manganese(IV) that was only partially secluded from the I^- was reduced to manganese(III) and caused the titrator's indicator needle to drift.

The loosely defined endpoint in the pH 7 titration caused the variation in the separate steps (pH 7 and pH 2) to be greater than the variation in the overall titration. That is, when the accretion rate greatly exceeded the reduction rate and the particles were not as fully reduced, the less titrant would be required in the pH 7 step of the titration, but greater quantities of titrant would be consumed in the pH 2 step of the titration. Based on the mechanism previously proposed for an imprecise endpoint at pH 7, the following are offered as suggestions for making the titration of permanganate as consistent as possible:

- The mixing speed must be consistent to promote a steady accretion rate.
- The ionic strength of the solutions being titrated must also be consistent to stabilize the accretion rate.
- The solution must be well-buffered to maintain constant surface charges which are affected by changes in pH.

- The concentration of the iodide and permanganate must be consistent from one titration to another so the accretion rate is the same each time.

The conditions used in this study, which resulted in a transfer of ≈ 3.5 eq/mole (Table 4), were as follows:

- The solution was vigorously stirred, always at a constant rate as preset by the titrator used (see Methods and Materials).
- The ionic strength was slightly variable from titration to titration, but fairly high as a result of the presence of pH 7 buffer and of 1 g of KI.
- The pH was always well buffered at pH 7.
- One gram of KI crystals was used.

As evidenced by the low correlation coefficient for the relationship between the permanganate concentration and the oxidation state of the manganese in the iodide solution at pH 7, ($r^2 = 0.1$) the range in concentration used in this study did not affect the oxidation state of the particulate manganese.

The chlorite determinations presented in this report were affected by the presence of both the reduction product of permanganate and I^- and MnO_x . As mentioned, the oxidation states of MnO_x particles are somewhat variable so the chlorite concentrations presented in this report are considered approximations.

Permanganate Determinations

The amperometric titration of permanganate was subject to two kinds of error, which, for the purposes of discussion, shall be called "pure error" and "interference error". Pure error describes the error caused by the loosely defined endpoint of titration at pH 7 as previously discussed. Interfer-

ence error describes the error posed by chlorine. That is, free chlorine (HOCl and OCl^-) oxidizes I^- at pH 7 and, thus, would interfere in the titration of permanganate. Normally, chlorine is not present in a solution of permanganate, but is commonly found in solutions of chlorine dioxide. Thus, when chlorine dioxide and permanganate were both present in solution, chlorine would also be expected. Care was taken in preparing and testing the ClO_2 stock solutions to ensure low HOCl concentrations. (Typical values of HOCl in the stock ClO_2 solution, presented in the Methods and Materials section, were about 3 to 8 percent of the ClO_2 concentration by weight.)

Permanganate concentrations measured by titration were verified by colorimetric means (step A in Figure 34) after filtration but prior to manganese determinations by AAS. Concentrations determined by colorimetric methods were expected to be slightly less than those determined by titration because permanganate is lost during filtration. If a permanganate concentration determined from step B (colorimetric) (Figure 34) was greater than that from step A (titrimetric), the datum was discarded. Typically, about five to ten percent of the data were discarded because the colorimetric determinations were greater than the titrimetric determinations.

The least reliable of the manganese data were the concentrations of MnO_x . As displayed in Figure 34, four separate manganese measurements were made to determine one MnO_x concentration. The measurements required were as follows:

- total manganese
- manganese(VII) in solution prior to filtration
- manganese(VII) in solution after filtration
- soluble manganese [permanganate and manganese(II)]

Thus, the determination of MnO_x concentration was subject to four sources of error.

Filter Operation and Optimum Alum Dose

The filter operation was affected by the turbidity of the water applied to the filters (commonly called applied turbidity) and preoxidation. It was difficult to separate the effects of the preoxidants from those of the applied turbidity. Figure 24 shows convincingly that in 1984, when no preoxidant was used, the filter operation times were shorter than they were during the other years, when a preoxidant was applied. The mechanism by which preoxidants decrease the filter operation time is not known and further study is recommended to define this mechanism.

Optimum alum dose is a term used to describe either the alum dose determined by the plant operator for optimum water treatment in the plant or that required to remove the most organic material in the laboratory jar-test. The application of a preoxidant always resulted in a lower optimum alum dose than that which resulted when no preoxidant was applied. As is shown in Table 27, the alum dose - preoxidant dose relationship during periods of stratification (May through October) seemed to be strong. However, during periods when the lake was not stratified (November through April) the relationship between alum dose and preoxidant dose weakened, especially for chlorine, which was dosed in the greatest concentrations and during the period of the greatest alum requirements.

The effect of chlorine on the optimum alum dose is not clear. While the lake was stratified the lowest optimum alum doses occurred during periods of chlorine application, and while the lake was not stratified the highest optimum alum doses occur during periods of chlorine application. The reason for the relatively high alum requirements during the time that chlorine was dosed and the lake was not stratified is largely unknown, but the following hypothesis is presented. First, a slight dose dependency was assumed. That is, chlorine was assumed to assist in the coagulation process only if it was present in concentrations greater than an undetermined threshold. During periods while the lake was not stratified, the increased concentration of many raw water constituents placed a greater demand on the chlorine, thus decreasing its availability to aid in coagulation. To properly describe the observed phenomena, the substance placing the demand on the chlorine

Table 27.
Effect of preoxidant dose on filter operation time and optimum alum dose

lake conditions	preoxidant	preoxidant dose		filter operation time (hours)	Optimum alum dose (mg/L)
		(mg/L)	(meq/L)		
Stratified	Cl ₂	3.0	8.5x10 ⁻²	80	41
	ClO ₂ & KMnO ₄	1.2 & 0.7	3.3x10 ⁻²	100	47
	ClO ₂	1.2	1.8x10 ⁻²	100	49
	KMnO ₄	0.7	1.6x10 ⁻²	84	46
	None	0	0	60	50
Not Stratified	Cl ₂	5.0	14.1x10 ⁻²	64	65
	ClO ₂ & KMnO ₄	1.0 & 1.5	4.8x10 ⁻²	65	ND
	KMnO ₄	1.5	3.3x10 ⁻²	46	56
	ClO ₂	1.0	1.5x10 ⁻²	52	47
	None	0	0	51	63
ND = no data					

should be largely unreactive toward both permanganate and chlorine dioxide because the effectiveness of the oxidants were not as diminished during periods while the lake was not stratified. Ammonia, which reacts with chlorine to form chloramines, and is relatively unreactive towards permanganate and chlorine dioxide, was initially suspected as the causative agent. The ammonia concentration during periods while the lake was not stratified (0.2 mg/L) (106) was great enough to decrease the free chlorine concentration to about three mg/L (8.5×10^{-2} meq/L).

The relationship of longer filter operation times and lower applied turbidities that occurred while the lake was stratified (Figure 22), implies that improvements in the coagulation and settling process would cause decreases in the applied turbidity and resulted in increased filter operation times. Thus, the preoxidants being applied during periods when the lowest alum dosages were required, would also be expected to be applied during the times when filter operation times were the longest. The data in Table 27 shows that this was not the case, so while preoxidation is thought to benefit both the coagulation process and filter operation, the mechanism and cause and effects relationships remain poorly understood.

Jar tests were performed to help determine the relative benefits of preoxidation of the coagulation process using surface water from Abel Lake during a period when the lake was stratified. The jar tests were performed as described in the "Methods and Materials" chapter. The floc size, rate of formation and rate of settling were observed. This paragraph discusses these observations. When no oxidant was present the floc was slower forming, smaller, and slower settling. Better floc formed when permanganate was dosed than formed when the other oxidants were dosed. The floc produced when permanganate was present had a brownish color that was probably a result of the incorporation of MnO_x particles, formed from the reduction of permanganate, into the alum floc. It is hypothesized that the MnO_x particles aided in the formation of a larger, more dense floc. At a solution pH of 6.3, the aluminum hydroxide floc would be expected to have a positive surface charge and the MnO_x particles would be expected to have a negative surface charge. The MnO_x particles may have helped to reduce the repulsive surface forces between the aluminum hydroxide colloids.

Chlorine dioxide and chlorine also increased floc size and settling rate, but not to the extent that permanganate did. The benefits (larger floc and faster settling) provided by chlorine dioxide were more noticeable at doses greater than 2 mg/L than at smaller doses. The benefits provided by chlorine were even more dose dependent. Below a dose of 5 mg/L (as Cl₂) chlorine did not affect floc formation. This observation may help explain the change in the decreased effectiveness of chlorine during periods when the lake was not stratified. The reduction of chlorine concentration resulting from an increased chlorine demand may have lowered the chlorine concentration below a threshold, and rendered it ineffective for aiding floc formation. The increased oxidant demand associated with periods when the lake was not stratified may have decreased the concentrations of both permanganate and chlorine dioxide, but, these preoxidants were able to aid the coagulation process at lower doses. In summary, the major effect on floc formation was observed when an oxidant was present. There may be some differences caused by changing the preoxidant, but these were confounded in the plant-scale study by variations in the applied turbidity.

Turbidity Removal versus Organics Removal

In routine plant operations, the optimum alum dose was determined by turbidity removal, but the alum dose can also be optimized on the basis on DOC and THM-precursor removal. It is important that the optimal alum dose for the removal of DOC and the amount of DOC removed be differentiated. Thus, it is possible to have a low optimum alum dose and a low DOC removal efficiency associated with the same preoxidant. The effect of the preoxidant conditions on the optimum alum doses for DOC and THM-precursor and turbidity removals is discussed in this section. The effect of the preoxidant on the removal efficiencies of the water constituents will be presented in the next section.

Jar tests were performed to compare the optimum alum dose based on turbidity removal (from the water treatment plant data) to that for the removal of DOC and THM-precursors. A comparison of the optimum alum doses from coagulation of surface water during periods of lake stratification

is presented in Table 28 in order of decreasing alum requirements for turbidity removal. The optimum alum doses for the removal of DOC were similar those for the removal of THM-precursors but differed from those for turbidity removal. The alum dose required for optimum turbidity reduction when no oxidant, ClO_2 or KMnO_2 were dosed was greater than that required for the optimum DOC and THM-precursor removal; however, when Cl_2 or KMnO_4 in combination with ClO_2 were dosed, the alum dose required for optimum turbidity removal was lower than that required for optimum DOC and THM-precursor removal. The differences in alum dose were from about 5 to 10 mg/L. Therefore, when the water treatment plant adjusted the alum dose to optimize turbidity removal, the DOC and THM-precursor removal may not have been optimized, but nearly so.

The data in Figures 25 and 26, presented previously, show that in some cases the DOC and THM-precursor removal efficiency decreased when the alum dose was increased past an optimum dose. The reason for decreased sorption with increased coagulant concentration is not clear but may depend on the surface area (of the aluminum hydroxide floc) available for the organic materials. Increased concentrations of alum resulted in increased rates of particle formation and larger aluminum hydroxide particles. At lower alum doses the particles may have taken longer to form and remained smaller for longer periods. When the floc particles remained small, forming what is termed pinpoint floc, the surface area available for sorption of organic materials was greater than when the floc particles were larger but fewer in number. Also, the smaller floc particles remained in suspension longer before settling. Thus, the optimum alum dose for the removal of organic materials was great enough to provide ample surface area but not so great as to rapidly form large floc particles with smaller net surface area.

Table 28.
Comparison of alum doses for optimum turbidity and organics removal from surface water while Abel Lake was stratified.

Preoxidant Condition	Optimum Alum Dose (mg/L as $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) for the Removal of Turbidity and Organic Materials		
	Plant-Scale	Laboratory-Scale	
	Turbidity Removal	DOC Removal	THM-Precursor Removal
No Preoxidant	50	35-40	35-40
Chlorine Dioxide	49	25-30	30-35
Permanganate & Chlorine Dioxide	47	50-55	60
Permanganate	46	45-50	40-45
Chlorine	41	50-55	60

Taste and odor complaints

The increased occurrence of odor complaints from customers during the periods when chlorine dioxide was applied was an unexpected problem (Table 7). Since the completion of this project, another utility has also recorded problems with tastes-and-odors concurrent with chlorine dioxide applications (110). The dominant odor reported by the consumers affected was a kerosene, or a hydrocarbon odor. In addition, the City of Edmonton Water Works has reported that while effective in controlling other odors, chlorine dioxide was ineffective against hydrocarbon odors (57). The researchers did not state whether they felt that the hydrocarbon odors were caused by chlorine dioxide or just not removed by chlorine dioxide.

It is not known why chlorine dioxide caused taste and odors in the water from Abel Lake, but the following observations are known: First, the odors associated with chlorine dioxide were much more prevalent during overturn. Second, the odors were not detectable when the water left the plant. Third, the chlorine dioxide was entirely reduced to the chlorite form by the time the water left the plant. Fourth, the dose of chlorine dioxide used during overturn was greater because the oxidant demand increased during overturn. Although there is no clear explanation for the tastes and odors at this time, the following possibilities should be considered in future research:

- The formation of chloramines following chlorination of the treated water.
- The production of odorous chemicals by reactions of naturally occurring organic substances and chlorine dioxide or chlorite.
- The creation of an environment favoring one or more microorganisms that can produce odors in the distribution system.

There is little evidence to support one possibility over the other at this time, but Hrudey (107) has reported finding aldehydes in water treated with chlorine dioxide, some of which produce burning, sharp, pungent sensations in test subjects (108).

DOC Removal

The DOC removal efficiencies in the water treatment plant while Abel lake was stratified (45 to 50 percent) were higher than could be achieved by treatment in the laboratory (30 to 36 percent). The difference was probably caused by either kinetic limitations in the jar-test procedure or by the differences in the mixing conditions. Water in the plant was coagulated for about 45 minutes, and in the jar tests, the water was coagulated for only about 20 minutes. Also, the mixing speed of the rapid mix and flocculators were not necessarily duplicated by the jar-test procedure. The times and mixing speeds used in the jar test were developed by trial and error by the coagulation officer at the water treatment plant to mimic plant performance. The procedure developed allowed the turbidity removal in the jar test to match that in the water treatment plant at common alum concentrations. However, this procedure did not adequately predict DOC removal in the water treatment plant. Further research is required to determine why DOC removal suffered in the jar-test procedure.

There is some evidence that chlorine dioxide decreased the DOC removal in both the plant-setting and the laboratory-setting (Table 9 and Figure 27A). The evidence of this trend was not universal; in the laboratory tests, DOC removal suffered when the surface water was treated and in the plant-scale experiment, DOC removal suffered only when the lake was not stratified and the plant's influent water was a mixture of surface and bottom waters. There is some evidence that the ClO_2 oxidized the organic materials, causing them to be fragmented to smaller organic units that are more difficult to remove by coagulation than are larger organic molecules (45). This hypothesis was confirmed, as will be discussed later in this chapter in the section entitled "Molecular size determination by Ultrafiltration".

Permanganate also oxidizes organic materials, but the DOC removal efficiency did not decrease in either the plant- or the laboratory-scale studies when permanganate was dosed (Table 9 and Figure 27A). In contrast to that observed with applications of chlorine dioxide, DOC removal efficiency improved when permanganate was dosed. The differences in the affect of these two oxidants on DOC removal may have been caused by different mechanisms by which they acted on the DOC.

The removal of organic molecules during coagulation primarily occurred by sorption. Permanganate, by virtue of its reduction product, (MnO_x) may have provided more surface area to which the organic materials could adsorb. Sorption to MnO_x floc has been reported to be the dominant mechanism in the removal of some taste-and-odor compounds (58) and, to some extent, THM-precursor removal (73), and could have helped to remove DOC during the coagulation and settling process.

In contrast to results observed during the plant-scale study, DOC removal from the mixture of surface and bottom waters in the laboratory-scale study was not affected by preoxidation. When chlorine dioxide was being applied at the water treatment plant, the DOC removal efficiency was only 26 percent (Table 4), and in the jar test, the DOC removal efficiency was about 35 percent (Figure 27B). (The alum dose was not adjusted on the basis of DOC removal in the plant.) These data suggest that during the plant-scale study, chlorine dioxide was reacting with the organic matter and in the laboratory-scale study, it was not. The cause of the different reactivities towards DOC may be that the relative concentrations of the reducing agents [DOC and manganese(II)] were different in the waters used in the plant- and laboratory-scale studies. Table 3 shows that the lake DOC concentration was much greater (5.5 to 7.0 mg/L while not stratified) than that of the mixture of surface and bottom waters used in the jar-test (4.1 mg/L), and the lake manganese concentration was much lower (0.2 to 0.3 mg/L while mixing) than that of the waters used in the jar-test (0.41 mg/L). Chlorine dioxide may have reacted with the organic materials in the plant-scale experiments (and thus hindered their removal) and reacted with the manganese(II) in the laboratory-scale experiments. Because chlorine dioxide did not react with the organic materials in the jar-tests, DOC removal was not affected. This hypothesis was tested and is discussed later in this chapter in the section entitled "Effect of DOC on Manganese Oxidation by Chlorine Dioxide and Permanganate".

THM-Precursor Removals

During coagulation and settling in water treatment, THM-precursors can be removed either by chemical oxidation or by sorption to the coagulant which is subsequently precipitated from suspension. To determine the dominant mechanism, (oxidation versus sorption) the THM-precursor reduction when water was treated both with a coagulant and with an oxidant was compared to that which occurred by coagulation alone. Such a comparison revealed that the oxidants provided only limited increases in THM-precursor reduction and thus, sorption was believed to be the dominant mechanism of THM-precursor removal in both the water treatment plant and in the jar-tests.

During the period of lake stratification, lower percent removals were observed in the jar tests (21 to 55 percent) than were observed in the plant-scale experiments (60 to 65 percent). As with DOC removal, it is suggested that further research be performed to determine why the water treatment plant removed more THM-precursors than did the jar test.

A comparison of THM-precursor removal to DOC removal revealed that the THM-precursors were more readily removed than were the bulk dissolved organic materials. Sinsabaugh *et al.* (45) determined that the size, charge and solubility of the organic molecules affected their ability to be removed. Of these three factors, size was determined to be the most important factor. It is hypothesized that if the THM-precursors were considered as a separate class of DOC, they would be significantly larger than the majority of the DOC. This hypothesis was confirmed and is discussed later in this chapter in the section entitled "Molecular-Size Determination by Ultrafiltration".

The THM-precursor removal during the plant-scale study was greater while the lake was not stratified (75 to 90 percent) than it was while the lake was stratified (55 to 65 percent) (Table 4). Correspondingly, the THM-precursor removal during the laboratory-scale study was greater from the mixture of surface and bottom waters (typically 70 percent) than it was from the surface water (typically 50 percent). Initially, it was hypothesized that the size of precursors near the bottom of the lake were larger and, thus, more easily removed by flocculation and settling. That is, during

periods while the lake was not stratified, the bottom waters were able to mix with those waters from the surface and thus contributed larger organic molecules to the water being treated at the water treatment plant. The larger molecules would be more efficiently removed than would the smaller ones, resulting in greater reduction in THM-precursor concentrations. This hypothesis was explored and discounted later in the section entitled "Molecular-Size Determinations by Ultrafiltration" because the precursors in the bottom waters were no larger than those in the surface waters.

An alternate hypothesis, that considers the increased concentrations of THM-precursors and alum floc follows. When the lake mixed, the THM-precursors increased in concentration from about 270 ug/L to over 400 ug/L. Also, the plant operator increased the alum dose from about 40 mg/L to about 60 mg/L during this period to control the increased turbidity that occurs when the lake is not stratified. It was hypothesized that increased concentrations of both precursor and floc particles promoted more frequent contact between them and thus increased the amount of THM-precursors sorbed to the floc and removed from solution. In addition, the lower water temperatures during the winter months helped to slow the rate of floc agglomeration, (113) and may have helped increase the surface area available for sorption by the mechanism previously described in this chapter in the section entitled "Optimum Alum Dose".

Because oxidants can deactivate the chlorine substitution sites (48, 53, 55), the effect of the oxidant conditions on the removal of THM-precursors was investigated. The results of both the laboratory- and the plant-study indicated that the THM-precursors in the surface water were deactivated best by chlorine dioxide and those in the mixture of top and bottom waters (as present during periods when the lake was not stratified and as manufactured for the laboratory study) were best deactivated by permanganate.

Yield

The mass of THMs (ug) formed upon chlorination of a mass of DOC (mg) is termed yield and, in this study, is expressed as ug THM/mg DOC. The yield reductions observed in the laboratory-scale study performed with chlorine dioxide applications to the mixture of surface and bottom waters are contrasted with those observed for permanganate applications to the mixture of surface and bottom waters (Figure 29B). When chlorine dioxide was present, the yield did not decrease substantially until the dose of about 2×10^{-2} meq/L (1.3 mg/L) of chlorine dioxide was exceeded. It is hypothesized that the chlorine dioxide did not oxidize the THM-precursors until this demand (2×10^{-2} meq/L) was met. The chlorine dioxide demand was caused, at least in part, by manganese(II), 0.32 mg/L (1×10^{-2}) of which was oxidized by 2×10^{-2} meq/L chlorine dioxide (Figure 30). In contrast, when permanganate was used as the preoxidant, the yield was reduced with the initial dose of 2×10^{-2} meq/L, even though Figure 30 shows that manganese(II) was oxidized. Thus, even though an oxidant demand was placed on the permanganate, it reduced the yield of the precursors. The difference in the pattern of yield reduction was believed to reflect the differences in the mechanisms of yield reductions discussed next.

Chlorine dioxide's role in minimizing THM's in chlorinated water could be either one of *oxidizing* functional groups involved in chlorine substitution (*e.g.* carboxyl groups) or one of modifying the molecules so as to improve their sorbability to alum floc. The author believes that the former is more likely for the following reason. A comparison of the data in Tables 23 and 24 show that chlorine dioxide decreased the yield more when a coagulant was not present than when one was.

As was chlorine dioxide's role in minimizing THM's in chlorinated water, that of permanganate could also be one of oxidation or adsorption. Adsorption is believed to be the dominant mechanism because the studies on molecular-size distribution shown in Tables 23 and 24, and discussed later, show that when no coagulant is present permanganate has little affect on yield, and when a coagulant is present permanganate decreases the yield about 10 to 15 percent more than coagulation alone. These data suggest that permanganate aids in the sorption of THM-precursors more than

it oxidizes them. In summary, chlorine dioxide probably reduced the yield of surface waters by oxidating functional groups involved in chlorine substitution reaction. Permanganate reduced the yield of waters probably by increasing their ability to sorb to alum floc. The proposed mechanism for this is evaluated further in the section entitled "Molecular-Size Determinations by Ultrafiltration".

Oxidation of Iron

While the lake was stratified, the concentration of iron in the raw water was never greater than the Secondary MCL of 0.3 mg/L as (Fe); and during the period while the lake was not stratified, the iron concentration was only periodically greater than 0.3 mg/L (Figure 22). During periods when the lake was stratified and when it was not, the iron concentrations were mainly reduced during the flocculation and settling step by all preoxidants. It is not known why iron was removed better while the lake was not stratified than while the lake was stratified.

The iron(II) present when the lake was not stratified can be considered as a reducing agent, competing for the available oxidant with manganese(II). A comparison of the iron and manganese removal patterns at times when chlorine dioxide was being added (Figures 17B and 18B) show that iron was preferentially oxidized even though it was present in lower concentrations. Thermodynamically, iron is more easily oxidized than is manganese(II), as can be seen in equations [3] and [4]. Also, the reaction between iron(II) and chlorine dioxide is less dependent on an elevated pH than is the reaction between manganese(II) and chlorine dioxide (equations [10] and [11]). Stoichiometrically, iron would be expected to exert a chlorine dioxide demand of only ≈ 0.2 mg/L. Iron removal did not pose a serious problem to the water treatment plant and thus was not addressed further in the laboratory-scale study.

Oxidation of Manganese(II)

Manganese oxidation was evaluated in the plant-scale study and twice in the laboratory-scale study. This section discusses the results of the plant-scale study and those of the laboratory-scale study performed concurrent to the plant-scale study (shown in Figure 30). Manganese(II) oxidation by permanganate and chlorine dioxide will be discussed in the following order: permanganate alone itself, chlorine dioxide alone and finally, chlorine dioxide and permanganate together.

When permanganate was added as a preoxidant during the period of lake stratification, the manganese concentration *increased* after flocculation and settling (Figure 17A). While the lake was stratified and the water was being treated with permanganate, the manganese remaining in the water after flocculation and settling likely was permanganate that remained unreacted because the oxidant demand was low. (During the period of stratification, the concentrations of iron(II) manganese(II) and DOC, which are believed to exert a majority of the oxidant demand in these waters were low.) Thus, the manganese concentrations shown in Figure 17A were primarily permanganate (except for those of the raw water). The permanganate concentrations (0.6 to 0.8 mg/L as Mn) were not great enough to cause problems in the finished water as the manganese concentration decreased to below the Secondary MCL of 0.05 mg/L after the water had been filtered.

The permanganate demand on the filters may have been from manganese(II) and iron(II) that was sorbed to an oxidized, particulate form of manganese that was coating the sand grains. Knocke *et al.* (111) have reported that the filter media of water treatment plants treating manganese(II) laden waters often develop a coating of oxidized manganese to which manganese(II) and iron(II) sorbs. The reduced forms of these two metals on the filter often present an oxidant demand. A black coating, indicating the presence of MnO_x , had been observed on the media from the filters of the Abel Lake Water Treatment Plant.

In contrast to the pattern of manganese(II) removal observed during the period of lake stratification, the soluble manganese concentrations in the plant *decreased* during the flocculation and settling

step while the lake was not stratified (Figure 17B). The soluble manganese present was probably in the form of manganese(II) and the permanganate dose was adequate to meet the oxidant demand yet not so great as to leave a significant residual.

While the lake was not stratified, the pattern of manganese removal observed when chlorine dioxide was used alone was the same as that observed when no preoxidant was used. In both cases, little manganese removal occurred during flocculation and settling, and most of the manganese was removed on the filters. It is believed that two conditions likely caused the manganese(II) to remain unoxidized. First, the oxidant demand was too great for the dose of chlorine dioxide being applied and, second, DOC, not manganese(II), was the primary reducing agent. The hypothesis that DOC was preferentially oxidized is explored later in this chapter. The role of the filter in decreasing the concentration of soluble manganese(II) has previously been discussed, and this mechanism was believed to be responsible for the reductions in manganese concentrations observed both when chlorine dioxide was used and when no preoxidant was used.

Chlorine dioxide appeared to remove manganese(II) much better in the laboratory-scale study (Figure 30) than it did in the plant-scale study (Figure 17B). The improved performance possibly can be accounted for by the fact that the DOC concentrations were lower in the waters used during the laboratory-scale study.

The total oxidant dose when permanganate and chlorine dioxide were used in combination was greater than that when the oxidants were dosed separately. Thus, the increased manganese removal efficiency observed in the water treatment plant during preoxidation with this combination of oxidants was probably a dose relationship. That is, the greater oxidant doses were more successful in oxidizing manganese(II). The benefit of increased oxidant concentrations for removing manganese(II) in the water treatment plant can also be observed in Table 9, which shows that the soluble manganese concentrations in the waters dosed with the combination of oxidants was lower than those in the waters dosed with chlorine dioxide alone or with permanganate alone. The effect of the dose relationship can be better observed in the results of the laboratory-scale study (Figure 30). In this experiment, manganese(II) removal increased to close to 100 percent removal as the

oxidant concentration was increased to concentrations of from 4×10^{-10} to 5×10^{-10} . The combination of chlorine dioxide and permanganate did not remove soluble manganese better but, as was proposed previously in the Results chapter, the soluble manganese remaining in waters dosed with both oxidants was probably in the form of permanganate.

Effect of DOC on Manganese(II) Oxidation by Chlorine Dioxide and Permanganate

This section focuses on the ability of KMnO_4 and ClO_2 to oxidize manganese(II). First, the effect of increasing concentrations of DOC on the oxidation of manganese(II) will be presented. The experiments were designed to test the hypothesis that at high DOC concentrations the oxidants reacted with the organic materials instead of the manganese(II). Second, the interaction between the oxidants when they are used in combination will be discussed. Finally, kinetic coefficients, describing the rates of manganese(I) oxidation and oxidant reduction, will be used to reinforce the previous points and to define reaction rates of importance to manganese removal by water treatment plants.

Figures 35, 36, and 38, presented earlier, showed that adding fulvic acid caused the oxidation rate of manganese(II) to decrease for all three oxidant conditions (ClO_2 alone, KMnO_4 alone and ClO_2 and KMnO_4 in combination). Chlorine dioxide oxidation of manganese(II) was particularly sensitive to increases in fulvic acid concentration. When the solution containing 5.2 mg/L DOC was dosed with chlorine dioxide, the manganese(II) never decreased to concentrations below 0.16 mg/L during the entire two-hour reaction period.

Instead of viewing these chemical systems from the standpoint of the oxidants, the reaction can be viewed from the standpoint of the reducing agents. It was assumed that DOC and manganese(II) were the dominant reducing agents. At low concentrations of DOC (2.1 mg/L), the initial

manganese(II) concentration was great enough so that it was a dominant reducing agent. Increasing the concentration of the DOC increased the chances of chlorine dioxide (or any chemical species for that matter) encountering this reducing agent (DOC) in solution. For a reaction to occur, however, the contact of these two reactants must result in a successful joining of the species to form a transition species which, in turn, must spontaneously separate into the products (as opposed to returning back to the original species). Thus, when one reducing agent predominates, it does so because its concentration is great enough to allow numerous contacts with the oxidant (kinetics) and because the reaction is thermodynamically favored. Because the reduction of both chlorine dioxide and permanganate by either manganese(II) or DOC is thermodynamically favored, the kinetics of the associated reactions are believed to dictate which reactions occur. The kinetic coefficients will be discussed later.

A comparison of the permanganate data in Figure 35 to those in Figure 38 indicates that the presence of chlorine dioxide allowed permanganate to persist in solution longer than if chlorine dioxide was not present. The mechanism is not clear, but either the reducing agents reacted with chlorine dioxide before they could react with the permanganate, or the chlorine dioxide oxidized MnO_x back to permanganate. The interaction between the oxidants will be explored further when the kinetic analysis is discussed later in the text. The kinetic coefficients and half-lives were used to verify and quantify the change in manganese(II) oxidation rates, which occurred when the DOC concentrations were increased. The kinetic data verified that the addition of fulvic acid had a greater effect on manganese(II) oxidation than did the use of Abel Lake water ($\text{DOC} \approx 3.5$) instead of New River water ($\text{DOC} = 2.1 \text{ mg/L}$). For every oxidant condition, the introduction of the Suwannee River fulvic acid resulted in slower manganese(II) oxidation and faster oxidant consumption.

The following hypothesis is presented to explain the decreased rate of manganese oxidation and increased rate of oxidant consumption observed in solutions dosed with fulvic acid. (See the Methods and Materials chapter for more information on this organic material.) It is hypothesized that of the different classes of organic materials (Figure 3), fulvic acids were especially reactive towards the oxidants. The water from Abel Lake and the New River also contained fulvic acids, but this class of organic compounds typically comprises about 40 percent of the DOC present (Figure

3). Thus, if this percentage is applicable, by increasing the DOC from 3.6 to 5.2 mg/L, for example, the fulvic acid content of the water was increased from 1.4 mg/L (0.4 x 3.6 mg/L) to 3.0 mg/L (1.4 mg/L fulvic acid originally in solution + 1.6 mg/L fulvic acid added).

Kinetic Coefficients

The kinetic coefficients developed from the study of manganese(II) oxidation were used to determine the time required to oxidize manganese(II) at concentrations typical of raw water to below the 0.05 mg/L MCL. Manganese oxidation by permanganate, which was a first-order reaction, was considered first. Equation [49] was solved for time and listed below.

$$t = \frac{\ln[A_0] - \ln[A]}{k} \quad [57]$$

where:

t = time in minutes,

[A₀] is the initial manganese(II) concentration (0.2 mg/L),

[A] is the manganese(II) concentration at time = t (0.05 mg/L), and

k is the rate coefficient in minutes⁻¹.

Thus:

$$t = \frac{1.39}{k} \quad [58]$$

Under the reaction conditions given in the Methods and Materials section, manganese(II) oxidation would take 20 minutes, 13 minutes and 70 minutes at DOC concentrations of 2.1, 3.7 and 4.6 mg/L DOC, respectively. The reaction rates for chlorine dioxide were second order, so equation [51] was solved for time and the same manganese(II) concentration were used to derive equation [59]:

$$t = \frac{15}{k} \quad [59]$$

When chlorine dioxide was the oxidant, manganese(II) oxidation to 0.05 mg/l would require 2 minutes, 12 minutes and 500 minutes (8.5 hours) at DOC concentrations of 2.1, 3.6 and 5.2 mg/L, respectively. A comparison of these rates shows that chlorine dioxide oxidation of manganese(II) was faster at low DOC concentrations and slower at high DOC concentrations. Thus, chlorine dioxide was much more sensitive to increases in the DOC concentrations, and it was hypothesized that for given concentrations of DOC and manganese(II), chlorine dioxide would be more likely to react with DOC (especially fulvic acids) than would permanganate. This comparison is made on a *relative* basis, not an absolute one. As mentioned previously, the kinetic coefficients and rates of reactions are determined, in a large part, on the frequency at which the two substances [e.g. chlorine dioxide and manganese(II)] interact. The frequency of interaction increases as the concentrations of the reactants increase. Thus, increasing the concentration of one or the other reducing agents [manganese(II) or chlorine dioxide] will increase the rate of oxidation of that reducing agent, and at high enough DOC concentrations manganese(II) oxidation rates will be affected regardless of the oxidant. However, a comparison of chlorine dioxide and permanganate has revealed that chlorine dioxide is more apt to oxidize DOC than is permanganate under the reaction conditions (pH, temperature and reactant concentrations) used.

Throughout this study, chlorine dioxide's affinity for organic compounds was manifested indirectly. For example, chlorine dioxide affected DOC removal, and THM-precursor removal more than did permanganate. Thus, even in the plant-scale study, chlorine dioxide seemed to favor reactions with organic substances over reaction with manganese(II) more than did permanganate.

The half-life of permanganate was shorter than that of chlorine dioxide (Table 17). Because literature sources indicate that chlorine dioxide is a rapid oxidant (49), it was expected to dissipate more quickly than permanganate. The long half-life observed for chlorine dioxide can be attributed to its being either more stable than permanganate or less reactive towards the available reducing agents, manganese(II) and DOC. The evidence presented in other sections of this dissertation

shows that chlorine dioxide is more reactive towards both manganese(II) and DOC. Thus, it is hypothesized that under the chemical conditions used, chlorine dioxide was more stable and more efficient an oxidant than was permanganate.

For water treatment purposes, the faster chlorine dioxide and its reduction products are consumed, the less likely their concentrations leaving the water treatment plant would violate the EPA recommended 1.0 mg/L concentration for the total of the ClO_2 , ClO_2^- and ClO_3^- concentrations. Typical times for the dissipation of some assumed concentrations to below the limits were calculated as follows: Chlorine dioxide was assumed to be reduced to about 75 percent chlorite, and ClO_3^- was assumed to be absent from solution. When dosed alone, chlorine dioxide was reduced by second-order reaction rates (Table 16), so equation [51] was solved for time and used to predict the times required for the reduction of chlorine dioxide to acceptable concentrations. If concentrations of 1.3 mg/L and 0.1 mg/L for the initial and final concentrations of chlorine dioxide are assumed, one can calculate that the times required would be 90, 190 and 45 minutes if the DOC concentrations were 2.1, 3.6 and 5.2 mg/L, respectively. Permanganate residuals can be analyzed in a similar fashion. Second-order kinetics, and an initial permanganate concentration of 0.9 mg/L were assumed. The times required were 260, 115 and 35 minutes for DOC concentrations of 2.1, 3.7 and 9.6 mg/L, respectively. Two facts are obvious from a comparison of these time requirements. First, given a typical hydraulic retention time of four hours (240 minutes), and the concentrations previously listed, the EPA recommended limit for chlorine dioxide and chlorite would not be violated and the SMCL for manganese would be violated only when this oxidant was dosed in the water with a low (2.1 mg/L) DOC concentration. Second, with the exception of the solution with 2.1 mg/L DOC, the times required for the dissipation of these two oxidants were similar. It is not known why permanganate remains in solution so much longer than does chlorine dioxide. The experiments were only performed once and the results could be in error.

The interaction between the oxidants can be further explored. A comparison of the half-lives (Table 17) shows that chlorine dioxide dissipated more quickly when it was added with permanganate than when it was dosed by itself. Conversely, permanganate's half-life increased when it was added with chlorine dioxide. To help determine whether the reducing agents were re-

acting with chlorine dioxide before they had a chance to react with permanganate, or if the chlorine dioxide was oxidizing permanganate's reduction product (MnO_x), the half-life of manganese(II) (one of the reducing agents) was examined. When both of the oxidants were dosed, the half-lives of manganese(II) were most similar to the solutions in which permanganate alone was dosed. In addition, manganese(II) oxidation rates followed first-order kinetics both when permanganate was the only oxidant and when chlorine dioxide and permanganate were dosed together. One can infer from these observations that permanganate oxidized manganese(II) and that chlorine dioxide oxidized both the permanganate reduction product and the DOC. However, in a thorough study of the oxidation of permanganate reduction products, Hair (112) found that the oxidation of MnO_x particles by chlorine dioxide was not likely to occur. Thus, the mechanism by which chlorine dioxide prevents the oxidation of permanganate is not clear. It is suspected that the MnO_x particles formed in Hair's study (112) were too stable to be oxidized to permanganate. When the two oxidants were in solution simultaneously, the chlorine dioxide may have been able to oxidize the soluble MnO_x before it reached saturation concentrations.

The chemistry of chlorine dioxide is complicated, especially that of its reduction products. The main reduction product formed upon the reaction with manganese(II) has been proposed to be chloride (Cl^-) (48). The formation of chloride from chlorine dioxide is difficult to measure directly in natural waters because the methods available for chloride determinations are not sensitive enough to distinguish between the background chloride, and chloride formed from the reduction of chlorine dioxide. Thus, the reduction products from chlorine reductions are largely based on the measurements of chlorine dioxide and chlorite concentrations. The data in Figure 37 show that only about 0.5 mg/L out of the original 3.0 mg/L (about 17 percent) is reduced to a species other than chlorite. Theoretically, the demand posed by the 0.2 mg/L manganese(II) would be 0.4 to 0.5 mg/L as ClO_2 . Although this concentration matches well with the concentration of the "missing" reduction product, there is an inconsistency in the data. Not all of the manganese(II) in the solution containing 5.2 mg/L DOC was oxidized, and the amount of reduction product formed (other than chlorite) did not decrease. Thus, the data in this study do not support the contention that Cl^- is the major reduction product of ClO_2 when manganese(II) is oxidized.

Werdehoff and Singer (51) have reported that when ClO_2 reacts with organic materials, about 70 percent of it is reduced to ClO_2^- and the remaining 30 percent is reduced to chlorine. In turn, the chlorine undergoes substitution reactions with the organic carbon to form chlorinated hydrocarbons. This reaction was proposed to occur so quickly that the chlorine would not typically be detected. The results of this study were similar to those of Werdehoff and Singer (51). About 83 percent of the reduction product was chlorite and during the course of the reactions studied, the chlorine concentration (not shown) never increased appreciably. Thus, it was concluded that ClO_2^- is the primary reduction product of chlorine dioxide and any further reduction to Cl_2 or Cl^- can be considered as a secondary reaction of less consequence.

Molecular-Size Determinations by Ultrafiltration

As an introduction, the problems and benefits of using ultrafilters to obtain molecular-size determinations is discussed. The two major problems associated with this technique are first that ultrafilters do not measure molecular size, but measure the permeability of organic materials through an ultrafilter membrane. Permeability is affected by ionic strength, sorption to the membrane, molecular size, and molecular shape. Second, permeability is not a particularly revealing parameter; very little is known about the nature of the materials after their permeability is measured. However, correlations exist between the permeability of organic materials and their ability to be removed by coagulation and settling (45). So, whatever is being measured, ultrafiltration does yield a measure of how easy or difficult it is to remove the organic materials.

Before the molecular sizes of the naturally occurring organic materials were determined by ultrafiltration, the filters were tested for the reproducibility of flow rate and filtrate DOC concentration. For a specific pore size, flow rates were not consistent, but the effluent DOC remained fairly consistent (Table 18). Little evidence of sorption of DOC to filters existed. There was, however a positive relationship between the retentate DOC concentration (DOC concentration of

solution in the ultracell) and the permeate DOC concentration (DOC concentration of the solution passing the membrane) (Figure 41). That is, as the filtration process progressed and the DOC in retentate became more concentrated, the effluent DOC concentration increased.

Positive relationships between retentate and permeate DOC concentrations have been observed previously (89), but no mechanism has been proposed. It is hypothesized from the results of the present study that the increases in effluent DOC concentration associated with an increase in permeate DOC concentration were a result of the non-uniform pore sizes in the membrane. Naturally occurring organic molecules vary widely in size, from those that are small enough to readily pass the smallest pores to those that are too large to pass the largest pore. It is hypothesized that most of the molecules have some difficulty passing most of the pores. The solution that first permeates the membrane probably contains many of the organic molecules that readily pass all pores, but these are thought to be relatively few in number, and the concentration of organic molecules in the retentate increases. After the smallest organic molecules pass, most of the remaining molecules have some difficulty passing the membrane and their successful passage is more dependent on their encountering a pore large enough to allow passage at the correct orientation. As the concentration of the retentate increases, the frequency with which the molecules impacted the membrane surface, and the frequency of molecular passages, increases.

Because the permeate DOC concentration will be a function of the retentate concentration, the same volume fraction should be collected from every filtration event so that the data are as consistent as possible. That is, the permeate collected later in the filtration process, after the retentate had become concentrated, had a greater DOC concentration than had the permeate collected previously in the filtration process. This phenomenon was most readily seen in Figures 40 and 41. The volume fractions between 0.3 and 0.5 was the least variable and showed the least dependence on the permeate DOC concentration.

A solution of lake water was filtered repeatedly through many filters, and the resulting permeate DOC concentrations were analyzed by the Rosin-Rammler method (Table 20). This method of linearizing the molecular-size data resulted in coefficients of determination between 0.84 and 1.00,

and was considered a good model of the molecular-size distributions. In addition, the characteristic molecular size had a coefficient of variation (COV) of about 0.10 which was considered acceptable precision. The measure of the width of distribution of molecular sizes, n , had a slightly greater COV of 0.12. These numbers indicate that the data from ultrafiltration were precise enough to be meaningful. However, it is suggested that when comparing data from the ultrafiltration, the analyst should process and analyze at least two samples and then the linear relationships derived from the Rosin Rammler analysis by ANCOVA techniques. One precaution should be noted: The Rosin Rammler transform of the permeate DOC concentration [$\log \ln (1/1-Y)$] is extremely sensitive to the value used for the DOC concentration of the bulk solution. This relationship is based on the value of Y , which is the DOC concentration of the permeate divided by the bulk DOC concentration. In this study, the bulk DOC concentration in the analysis was that which remained after filtration of the water through a 0.45 μm pore size membrane filter to remove particles. The concentration prior to filtration could also have been used, but its use would have resulted in drastically different values for n and X_0 . Thus, the values for X_0 and n obtained in one study may not be directly comparable to those from another study.

When the sizes of the naturally occurring organic materials found at the various locations in the lake while it was stratified were examined, no size differences were found (Table 21). These results were surprising because the molecules nearer the sediment were expected to be larger than those at the surface because humification and decay occurs in the sediments. Organic materials near the sediment have been reported to be in the earlier stages of degradation (17) and thus are larger than those further from the sediment. These data show that the molecular-sizes were uniform from top to bottom and the distance from the lake sediment had little to do with molecular size. Also, the organic molecules in running water have been reported to be larger than those in stagnant water (17), but in this study, the precursors were the same size in the inlet as in the lake. It should be noted that a long period of drought preceded the collection of these samples and that a large portion of the water in the inlet may have been back-water from the lake. had backed-up into the stream.

The sizes of THM-precursors taken from the various locations and depth in the lake did not vary while the lake was stratified (Table 21). This class of organic compounds was larger than the bulk

DOC. The removal efficiencies of the DOC and THM-precursor in the plant-and laboratory-scale study can be viewed in light of the relative sizes of these two classes of organic materials. THM-precursors were routinely removed more easily by alum coagulation than were the bulk DOC because, as a subclass of the DOC, the precursors were larger.

While the lake was not stratified, the organic materials comprising the bulk DOC did not vary in size (Table 22). on the other hand, the size of the THM-precursors did vary with location and those in the stream were significantly smaller (on a statistical basis) than those in the lake. The inlet water contained precursors that mainly originated from the decay of allochthonous sources (*e.g.* leaf litter) as opposed to the precursors in the lake which can originate from a variety of sources inside and outside the lake basin (*e.g.* runoff, sediment, and algae). The range of the molecular-size distribution for the precursors in the surface of the lake was significantly larger than those of the precursors both in the bottom of the lake and in the inlet. The wide range in molecular sizes of the precursors was probably a reflection of the number of different sources contributing THM-precursors to these waters.

The effect of chlorine dioxide and permanganate on the sizes and yields of the DOC was examined to determine how DOC and THM-precursor removals might have been affected by these oxidants (Table 23). Chlorine dioxide, and to a limited extent permanganate, decreased the yield of THM's from the DOC. Coagulant addition changed the magnitude of the yield reductions to some extent (Table 24). Chlorine dioxide was still more effective than was permanganate at decreasing the yield, but the addition of coagulant decreased the effectiveness of chlorine dioxide while increasing the effectiveness of permanganate. In addition, the yield reductions observed when a coagulant was present (*e.g.* ≈ 10 percent in the plant-scale study, and ≈ 30 percent in the previous laboratory-scale studies) were greater than those observed when the oxidant was added without a coagulant. It is hypothesized that the organic materials adsorb to the coagulant before chlorine dioxide can oxidize the chlorine substitution sites on the organic materials. It is noteworthy that the effects of a combination of permanganate and chlorine dioxide on the yield reduction were not additive, but instead were intermediate between that achieved by chlorine dioxide and permanganate applied separately. Chlorine dioxide was probably responsible for most of the yield reductions in the solution dosed

with both oxidants, and the yield reduction was intermediate because the chlorine dioxide dose was lower when dosed in combination with permanganate than it was when it was dosed alone, but still high enough to effect a greater yield reduction than was possible with permanganate alone.

When the oxidants were dosed without a coagulant they both decreased the molecular-size of the DOC (Table 25). Chlorine dioxide effected a greater decrease in size than did permanganate and again seemed more reactive towards the organic material than did permanganate. The large reduction in size observed with chlorine dioxide may explain why the DOC removal in the water treatment plant suffered when chlorine dioxide was used as a preoxidant. It is hypothesized that chlorine dioxide fragmented many of the organic molecules making them more difficult to remove by coagulation.

The molecular-size distribution of the THM-precursors was shifted when oxidized by chlorine dioxide and permanganate. The application of chlorine dioxide altered the DOC so that the size fraction containing most of the THM-precursors was smaller, and the application of permanganate altered the DOC so that the size fraction containing most of the THM-precursors was larger. Conceivably, the oxidants could have affected potential THM-precursors in two ways: First, they could fragment large organic molecules and, second, they could deactivate them so that they would no longer form THMs upon chlorination. Chlorine dioxide deactivated the smaller organic compounds more than it did the larger ones (Table 24), but this oxidant decreased molecular-size so much that the net result was a decrease in the molecular-size of the precursors. Permanganate deactivated the smaller organic compounds more than it did the larger ones and the smaller THM-precursor no longer formed THMs upon chlorination and thus they did not contribute to the molecular-size distribution of the THM-precursor pool. Permanganate did not fragment the organic molecules to the extent that chlorine dioxide did and the net result was an increase in the molecular-size distribution of THM-precursors.

It is hypothesized that permanganate decreases the yield of THMs per DOC by deactivating the smaller organic units that are too small to remove easily by coagulation. Table 25 shows that when no coagulant was present, permanganate increased the size of the THM-precursors and the larger

precursors are more readily removed by coagulation than are the small ones. Thus, permanganate is thought to help remove precursors by making them more amenable to removal by coagulation.

When a coagulant was added with the oxidants, their effect on the size distributions was the same as when the oxidants were added alone, though diminished somewhat. It was suspected that the organic materials adsorbed to the aluminum hydroxide floc at a rate similar to that required for the preoxidants to oxidize them. Chlorine dioxide decreased the size of the organic materials more than did permanganate. Permanganate did not even decrease the size of the organic compound as much as did coagulation.

SUMMARY AND CONCLUSIONS

This study evaluated two oxidants, chlorine dioxide and permanganate, as replacements for chlorine as preoxidants in water treatment. Prechlorination was terminated because of the formation of prohibitive concentrations of trihalomethanes.

The first objective of this study was to evaluate permanganate and chlorine dioxide on a plant-scale basis for their abilities to remove DOC, THM-precursors, iron, and manganese. In addition, the ability of these two oxidants to help or hinder other aspects of water treatment plant operation (*e.g.* coagulant requirements and filter operation) was investigated. Second, a laboratory study was performed to determine the proficiency of both of these oxidants to remove organic carbon, THM-precursors, and manganese. Third, the oxidation/reduction relationship between a) the oxidants themselves and b) the oxidants and two reducing agents (manganese(II) and organic carbon) was explored. Finally, the interference of manganese in chlorine dioxide, chlorine and chlorine determinations and the use of ultrafilters for sizing naturally occurring organic molecules was investigated.

During the summer months, when the water treatment plant had difficulties with trihalomethanes, chlorine dioxide performed better than did permanganate. While the lake was not stratified and manganese(II) caused the major treatment concerns, permanganate performed better than did chlorine dioxide. Chlorine dioxide had a greater affinity for organic materials than did

permanganate which caused this oxidant (chlorine dioxide) to be more effective for removing the organic precursors to trihalomethanes and be less effective in oxidizing manganese(II). Permanganate dosed simultaneously with chlorine dioxide, remained in solution longer than did permanganate dosed by itself. If in solution long enough, permanganate could enter the distribution system and deposit in the pipes or cause aesthetic problems upon reduction.

After careful analysis of the results, the following conclusions can be made.

- Chlorine dioxide has a greater tendency to react with organic materials than has permanganate. Consequently, chlorine dioxide is more effective than is permanganate for reducing the potential of organic materials to form THMs. However, chlorine dioxide does not oxidize manganese(II) as well as does permanganate when elevated DOC concentrations (greater than ≈ 5 mg/L) are present. Chlorine dioxide fragments naturally occurring organic-molecules, making them more difficult to remove by coagulation.
- Dosing permanganate and chlorine dioxide simultaneously retarded the rate of permanganate reduction and raises concern over permanganate entering the distribution system. However, this dosing scheme did allow the total oxidation potential to be greater than if the oxidants were dosed individually and this in turn helped meet the oxidant demand in waters containing higher concentrations of reduced matter (as are present when Abel Lake is not stratified).
- As was suspected by Aieta *et al.* (50) Manganese oxides ($\text{MnO}_x(\text{s})$ and MnO_4^-) interfere in ClO_2^- and Cl_2 determinations. Permanganate interferes in titration of ClO_2^- and Cl_2 by about 0.5 mg ClO_2^- per mg Mn(VII) and 2.3 mg Cl_2 per mg Mn(VII). The ability of amperometric titration to detect Mn(VII) can be used to measure the permanganate concentration in the presence of other species.
- Preoxidation was observed to assist in both decreasing the alum dose required for turbidity removal and increasing the filter operation times. The mechanism by which preoxidation aids these processes is not known.

RECOMMENDATIONS FOR WATER TREATMENT PLANT OPERATION

The interference of oxidized forms of manganese in chlorite and chlorine determinations may cause problems to some water treatment plants. The following guidelines are presented to help the operator of a water treatment plant decide when when the manganese concentrations are great enough that they will cause greater than ten percent error in the determination of chlorine or chlorine. Particulate manganese concentration greater than 0.1 mg/L (as Mn) will cause significant error in the determination of chlorine and chlorine concentrations. Water treatment plants that suspect the presence of particulate manganese should perform a manganese determination on both a filtered and unfiltered sample to determine if particulate manganese is indeed present. The difference between the two values represents the concentration of particulate manganese present. If particulate manganese is present in concentrations greater than 0.1 mg/L, then the particulate manganese concentrations should be reported along with the chlorite and chlorine data. This would allow subsequent investigators to estimate the error caused by the presence of manganese.

In those cases where particulate manganese represents an unacceptable source of error (≈ 0.5 mg/L as Mn), it is possible to exclude colloidal manganese by filtration. Normally a filter with a pore size of 0.2 μm would be recommended, but if a coagulant is present (as is the case in most water treat-

ment plants), it may be possible to use a larger filter (eg. glass fiber filter or a 0.45 um membrane filter).

Many operators and some researchers use an abbreviated method termed "short method" for chlorine dioxide and chlorite determinations that does not include titration on the purged sample (steps C and D). This method is only valid when no chlorine or chlorate are present. The formulae used to calculate ClO_2 and ClO_2^- are as follows:

$$\text{ClO}_2 = \frac{(67,450\text{mg/equivalent})AN}{V} \quad [60]$$

$$\text{ClO}_2^- = \frac{16,863\text{mg/equivalent}(B - 4A)N}{V} \quad [61]$$

where:

- N = Normality of titrant (eq/L),
- V = Volume of sample titrated (mL),
- A = Volume of titrant used in pH-7 step, and
- B = Volume of titrant used in pH-2 step.

In this study, permanganate caused chlorine dioxide to be overestimated by 4.3P and chlorite determinations to be underestimated by 3.8P, where P is the permanganate concentration in mg/L as Mn. The interference due to $\text{MnO}_x(\text{s})$ in the short procedure would be the same as it is in the standard titration procedure (0.46 mg ClO_2^- /mg $\text{MnO}_x(\text{s})$ as Mn, where $x = 1.75$). The interference of manganese in the two procedures (standard and shortened) can be compared by assuming the same concentrations as used in the last example (0.2 mg/L Mn(VII), 0.4 mg/L $\text{MnO}_x(\text{s})$). In the shortened procedure, permanganate would cause the chlorine dioxide concentrations to be overestimated by 0.86 mg/L and the chlorite concentrations to be underestimated by 0.76 mg/L. $\text{MnO}_x(\text{s})$ would cause the chlorite concentration to be overestimated by 0.18 mg/L. In total, the chlorite concentration would be underestimated by 0.58 mg/L and the combined concentration of ClO_2 , ClO_2^- and ClO_3^- would be overestimated by 0.28 mg/L. If the standard titration procedure

is followed, the oxidized manganese would not effect the chorine dioxide concentration and would cause the chlorite concentration to be overestimated by only 0.1 mg/L. For this reason, the standard procedure is suggested when permanganate is present.

Permanganate was found to be effective in the oxidation of manganese but its dose was kinetically limited by the low pH used in coagulation (6.3) and the hydraulic retention time of the plant. This may be overcome by installing a feed system for both lime and permanganate adjacent to the raw water intake. This would solve the problem in two ways. First, the permanganate would have more time to dissipate and second, the increased pH in the raw water line would increase the reaction rate. Thus, permanganate is recommended as a preoxidant for the removal of Mn^{+2} but not for reductions in THMFP or for disinfection.

To best dose both permanganate and chlorine dioxide, the following strategy is suggested. To avoid kinetic limitations, permanganate should be dosed as early as possible (preferably at the raw water intake) at as high a pH as feasible. The dose should be adjusted so that the most of the permanganate is reduced to a particule form in the flash mix where the chlorine dioxide is dosed. The dose of the chlorine dioxide should be adjusted to yield the benefits of preoxidation (disinfection, decreased optimum alum doses longer filter operation times, decreased THM formation and the oxidation of any reduced species not oxidized by the permanganate. It is hoped that these goals would not be mutually exclusive.

RECOMMENDATIONS FOR FUTURE RESEARCH

This chapter is divided into three main sections. Suggestions for research into 1) manganese oxidation, 2) the oxidation of organic materials by chlorine dioxide, and 3) potpourri. First, the nature of the manganese particle formed upon oxidation should be investigated. The surface charge, the sizes, and, the oxidation states of the particles formed should be identified. Also, the effects of the oxidant used, its concentration, the pH, the temperature, and the presence of alum floc should be included in such a study. The kinetics of manganese oxidation should also be investigated. The effects of the oxidant used, its dose, the temperature, and the pH should be studied. Finally, the mechanism of manganese oxidation should be determined, and compared to the mechanism of manganese oxygenation proposed by Kessick and Morgan (13).

The reactions between chlorine dioxide and organic materials, especially THM-precursors, should be investigated. In particular, the reaction that occurs when chlorine dioxide deactivates a precursor should be studied. It is suggested that the reaction between chlorine dioxide and model compounds be studied initially. The mechanism, the rate, and the effect of a coagulant on the reaction should be determined. The taste-and-odor problems associated with chlorine dioxide should also be addressed. As was mentioned in the text, the reason for the formation of taste-and-odor compounds when chlorine dioxide was dosed was not known, but suggestions were made. Finally, a unifying

theory for the reactivity of chlorine dioxide should be examined. It is suggested that chlorine dioxide is more apt to react with organic materials because it is smaller than is permanganate and has no charge. Permanganate is a larger molecule with a charge. This poses no problem when permanganate oxidizes a small molecule such as manganese(II) because the different charges attract and orientation is less of a factor. However, when a large organic molecule is considered, size and steric factors become more important. A successful reaction between chlorine dioxide and an organic compound is less dependant on the orientation of the two molecules upon collision than is that between permanganate and an organic compound because chlorine is smaller than is permanganate and has no charge.

The effect of oxidation on both the optimum alum dose and the filtration process needs to be further investigated. In this report, a cause and effect relationship is proposed, but the mechanism remains unknown. The last recommendation concerns ultrafiltration. The true molecular size of organic molecules should be related to the values of X_0 and n . Several solutions, each containing a known organic materials of a different size, could be passed through the ultrafilters and the resulting data analyzed by the Rosin-Rammler method. The resulting values for X_0 and n could then be compared to the known molecular sizes.

**Appendix A. Thermodynamic constants for
calculations used to generate Figure 8.**

Appendix A

Thermodynamic constants for calculations used to generate Figure 8.

Gibbs Free Energies of Formation from various sources (kJ/mole)					
Compound	Latimer (109)	CRC (2)	Stumm & Morgan (12)	Calculated	Used
MnO ₂	-464.92	-465.25	-465.1	-	-465.25
MnO(OH)	-	-	-557.70	-	-557.70
MnO ₄ ⁻	-449.43	-	-	-451.23	-449.43
ClO ₂	-	120.1	117.6	-	118.9
ClO ₂ ⁻	11.47	17.16	17.1	-	118.9
HClO ₂	0.29	5.86	-	-	5.86
H ₂ O	-237.23	-237.23	-237.18	-	-237.23
OH ⁻	-157.32	-157.32	-157.30	-	-157.32

**Appendix B. Raw data for the removal of raw water
constituents by the Abel Lake Water Treatment
Plant.**

Appendix B1

Raw data for the removal of soluble manganese while the lake was stratified.

Pre-oxidant	Lake Condition	Date	Concentration of soluble manganese			
			Raw Water (mg/L)	Settled Water (mg/L)	Filtered Water (mg/L)	Clearwell Water (mg/L)
ClO ₂	Stratified	06/19/85	<0.01	<0.01	<0.01	ND
ClO ₂	Stratified	07/02/85	0.01	0.01	<0.01	ND
ClO ₂	Stratified	09/04/85	<0.01	<0.01	<0.01	<0.01
ClO ₂	Stratified	09/05/85	<0.01	0.01	0.01	0.02
KMnO ₄	Stratified	07/09/85	<0.01	0.07	0.05	ND
KMnO ₄	Stratified	07/11/85	0.02	0.07	0.01	ND
KMnO ₄	Stratified	09/20/85	<0.01	0.10	0.06	0.01
KMnO ₄	Stratified	09/22/85	0.02	0.06	<0.01	<0.01
ClO ₂ & KMnO ₄	Stratified	06/20/85	<0.01	0.05	<0.01	ND
ClO ₂ & KMnO ₄	Stratified	06/28/85	0.01	0.02	ND	ND
ClO ₂ & KMnO ₄	Stratified	07/19/85	0.01	0.06	0.04	ND
ClO ₂ & KMnO ₄	Stratified	07/30/85	0.02	0.07	0.01	ND
ClO ₂ & KMnO ₄	Stratified	10/01/85	0.01	0.04	0.03	0.04
ClO ₂ & KMnO ₄	Stratified	10/03/85	<0.015	0.05	0.02	0.03
None	Stratified	08/09/85	0.01	0.01	0.01	ND
None	Stratified	08/10/85	0.01	0.01	0.01	0.01

ND = No Data

Appendix B2

Raw data for the removal of soluble manganese while the lake was mixing.

Pre-oxidant	Lake Condition	Date	Concentration of soluble manganese			
			Raw Water (mg/L)	Settled Water (mg/L)	Filtered Water (mg/L)	Clearwell Water (mg/L)
ClO ₂	Mixing	01/17/86	0.37	0.28	0.11	0.10
ClO ₂	Mixing	02/26/86	0.24	0.22	0.07	0.04
ClO ₂	Mixing	03/07/86	0.22	0.20	0.06	0.04
KMnO ₄	Mixing	11/17/85	0.13	0.06	0.04	0.04
KMnO ₄	Mixing	01/27/86	0.26	0.10	0.05	0.05
KMnO ₄	Mixing	02/12/86	0.18	0.05	0.03	0.02
ClO ₂ & KMnO ₄	Mixing	11/07/85	0.22	0.01	0.01	0.01
ClO ₂ & KMnO ₄	Mixing	11/08/85	0.21	0.01	0.01	0.01
None	Mixing	11/30/85	0.30	0.20	0.10	0.10
None	Mixing	12/18/85	0.30	0.30	0.10	0.10
ND = No Data						

Appendix B3

Raw data for the removal of soluble iron while the lake was stratified.

Pre-oxidant	Lake Condition	Date	Concentration of soluble iron			
			Raw Water (mg/L)	Settled Water (mg/L)	Filtered Water (mg/L)	Clearwell Water (mg/L)
ClO ₂	Stratified	06/19/85	0.09	0.03	0.02	ND
ClO ₂	Stratified	07/02/85	0.11	0.03	0.02	ND
ClO ₂	Stratified	09/04/85	0.06	0.02	<0.02	0.03
ClO ₂	Stratified	09/05/85	0.08	0.03	<0.02	0.03
KMnO ₄	Stratified	07/09/85	0.11	0.03	0.03	0.04
KMnO ₄	Stratified	07/11/85	0.28	0.14	0.13	ND
KMnO ₄	Stratified	09/20/85	0.04	0.06	0.05	0.04
KMnO ₄	Stratified	09/22/85	0.03	0.02	0.02	0.03
ClO ₂ & KMnO ₄	Stratified	06/20/85	0.12	0.06	0.04	<0.02
ClO ₂ & KMnO ₄	Stratified	06/28/85	0.18	0.03	ND	<0.02
ClO ₂ & KMnO ₄	Stratified	07/30/85	0.31	0.18	0.13	0.06
ClO ₂ & KMnO ₄	Stratified	10/01/85	0.04	0.05	0.03	0.03
None	Stratified	08/09/85	0.28	0.20	0.19	ND
None	Stratified	08/10/85	0.17	0.07	0.05	0.05

ND = No Data

Appendix B4

Raw data for the removal of soluble iron while the lake was mixing.

Pre-oxidant	Lake Condition	Date	Concentration of soluble iron			
			Raw Water (mg/L)	Settled Water (mg/L)	Filtered Water (mg/L)	Clearwell Water (mg/L)
ClO ₂	Mixing	01/17/86	0.14	0.01	0.03	0.04
ClO ₂	Mixing	02/26/86	0.20	0.02	0.03	0.04
ClO ₂	Mixing	03/07/86	0.26	0.04	0.03	0.02
KMnO ₄	Mixing	11/17/85	0.52	0.04	0.05	0.06
ClO ₂ & KMnO ₄	Mixing	10/29/85	0.16	<0.02	<0.02	<0.02
ND = No Data						

Appendix B5

Raw data for the removal of dissolved organic carbon while the lake was stratified.

Pre-oxidant	Lake Condition	Date	Concentration of dissolved organic carbon			
			Raw Water (mg/L)	Settled Water (mg/L)	Filtered Water (mg/L)	Clearwell Water (mg/L)
ClO ₂	Stratified	06/19/85	3.8	2.7	2.7	ND
ClO ₂	Stratified	07/02/85	5.1	2.6	3.2	2.6
ClO ₂	Stratified	09/04/85	2.5	1.3	1.3	1.3
ClO ₂	Stratified	09/05/85	4.2	2.1	3.0	2.1
KMnO ₄	Stratified	07/09/85	5.3	2.3	2.2	2.2
KMnO ₄	Stratified	07/11/85	4.1	1.8	1.7	1.8
KMnO ₄	Stratified	09/20/85	3.8	1.9	1.8	1.7
KMnO ₄	Stratified	09/22/85	3.9	2.0	1.8	1.9
ClO ₂ & KMnO ₄	Stratified	06/20/85	3.6	1.9	1.7	1.6
ClO ₂ & KMnO ₄	Stratified	06/28/85	4.0	2.1	1.8	1.8
ClO ₂ & KMnO ₄	Stratified	07/19/85	3.6	1.8	1.5	1.6
ClO ₂ & KMnO ₄	Stratified	10/01/85	3.6	1.9	1.8	1.7
ClO ₂ & KMnO ₄	Stratified	10/03/85	3.6	1.9	1.5	1.8
None	Stratified	08/09/85	2.6	1.9	1.5	1.4
None	Stratified	08/10/85	2.5	1.3	1.1	1.1

ND = No Data

Appendix B6

Raw data for the removal of dissolved organic carbon while the lake was mixing.

Pre-oxidant	Lake Condition	Date	Concentration of dissolved organic carbon			
			Raw Water (mg/L)	Settled Water (mg/L)	Filtered Water (mg/L)	Clearwell Water (mg/L)
ClO ₂	Mixing	01/17/86	8.1	7.2	6.9	7.0
ClO ₂	Mixing	02/26/86	4.6	2.6	2.5	2.4
ClO ₂	Mixing	03/07/86	4.0	2.4	2.8	2.3
KMnO ₄	Mixing	11/17/85	7.1	3.4	3.3	3.2
ClO ₂ & KMnO ₄	Mixing	10/29/85	5.5	2.6	2.7	2.6
ND = No Data						

Appendix B7

Raw data for the removal of trihalomethane precursors while the lake was stratified.

Pre-oxidant	Lake Condition	Date	Concentration of trihalomethane-precursors			
			Raw Water (mg/L)	Settled Water (mg/L)	Filtered Water (mg/L)	Clearwell Water (mg/L)
ClO ₂	Stratified	06/19/85	265	100	85	45
ClO ₂	Stratified	07/02/85	330	120	140	140
ClO ₂	Stratified	07/05/85	310	135	100	130
ClO ₂	Stratified	09/04/85	210	85	85	90
ClO ₂	Stratified	09/05/85	225	85	95	95
KMnO ₄	Stratified	07/11/85	265	135	150	90
KMnO ₄	Stratified	09/20/85	205	100	120	115
KMnO ₄	Stratified	09/22/85	235	95	95	95
ClO ₂ & KMnO ₄	Stratified	06/20/85	250	120	120	105
ClO ₂ & KMnO ₄	Stratified	06/28/85	350	125	130	120
ClO ₂ & KMnO ₄	Stratified	07/19/85	340	150	140	130
ClO ₂ & KMnO ₄	Stratified	07/30/85	280	115	110	110
ClO ₂ & KMnO ₄	Stratified	10/01/85	220	105	110	90
ClO ₂ & KMnO ₄	Stratified	10/03/85	155	70	75	90
None	Stratified	08/09/85	250	150	115	120
None	Stratified	08/10/85	335	120	120	110
ND = No Data						

Appendix B8

Raw data for the removal of trihalomethane precursors while the lake was mixing.

Pre-oxidant	Lake Condition	Date	Trihalomethane formation potential			
			Raw Water (ug/L)	Settled Water (ug/L)	Filtered Water (ug/L)	Clearwell Water (ug/L)
ClO ₂	Mixing	01/17/86	580	135	130	135
KMnO ₄	Mixing	11/17/85	600	40	50	40
ClO ₂ & KMnO ₄	Mixing	10/29/85	400	65	65	64
ND = No Data						

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