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INVESTIGATION OF MANGANESE SEQUESTRATION BY SILICATES AND POLYPHOSPHATES WITH OXIDANTS

A Dissertation

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ABSTRACT

Manganese is usually present in groundwaters at a concentration of 0.05 to 1.0 mg/L, and groundwaters are seldom found which have manganese levels greater than 7 mg/L. Common aesthetic problems associated with high manganese concentrations include colored water ("red water"), stains, turbidity and taste. To eliminate these problems, EPA recommends that the manganese concentration in drinking water not exceed 0.05 mg/L.

Most manganese removal methods involve manganese oxidation to an insoluble higher oxidation state and the separation of the solid phase from the liquid phase by sedimentation and filtration. Although manganese removal eliminates color and turbidity problems, manganese removal is relatively expensive for small communities. An economical alternative would be to control manganese problems by chemical addition without removing it from the groundwater, as manganese is not toxic but is merely an aesthetic problem. The fact that sludge generation could be eliminated and substantial savings in the capital, operation and maintenance costs could be obtained by sequestering the manganese without removing it from the groundwater makes sequestration a viable alternative to other manganese removal techniques. However, several attempts to sequester manganese without removing it from groundwater have not yielded acceptable results. There is no effective technique for sequestering manganese. The

physical/chemical principles of this method are not well understood, and the mechanism of manganese sequestration has not been previously investigated.

This experimental investigation was aimed at identifying an effective technique to sequester manganese. Sequestration is the addition of chemicals to groundwater to maintain low color and turbidity without removing manganese and iron. The application of this technique to different groundwaters which vary in water quality (pH, presence/absence of calcium, etc.) was tested in this research using model groundwater prepared in the laboratory. Various sequestrant/oxidant combinations were tested: silicate/chlorine dioxide; polyphosphate/chlorine dioxide; polyphosphates and silicates in conjunction with chlorine dioxide; and polyphosphate/hypochlorite. Specific objectives of this experimental investigation are:

1. to determine the best sequestrant/oxidant combination for effective manganese control;
2. to determine the mechanism of sequestration, i.e. how is manganese sequestered? For example, is a manganese colloid formed and dispersed by sequestrants in successful studies as in iron sequestration or is manganese sequestration different? What is the mechanism by which success is achieved by this technique?

3. to determine the effects of several variables including water quality (pH, presence and absence of hardness) on manganese treatability. Variables tested in this research are explained in Section 1.5.

Turbidity, color, and percentage filterable iron were the criteria used to analyze treatment effectiveness. Streaming current detectors were used to determine whether streaming current can predict good treatment. X-ray diffraction and equilibrium modeling studies were done to evaluate the manganese and calcium species formed in sequestration.

Results from laboratory experiments indicate that manganese colloids formed in manganese treatment by silicate or polyphosphates with chlorine dioxide were stabilized, and high filterabilities (using 0.1 micron filters) could be obtained. High filterability indicates that the manganese particles did not grow to sizes larger than 0.1 micron, the membrane filter nominal pore size. This indicates that in actual practice, manganese will not precipitate in pipelines or fixtures when treated by this method, as the coalescence, growth, and subsequent settlement of manganese precipitates were limited by the addition of polyphosphates. However, these methods are not recommended for manganese sequestration because high discoloration was produced due to manganese oxidation by chlorine dioxide.

Effective manganese stabilization was achieved with polyphosphate and sodium hypochlorite. Polyphosphates inhibited manganese oxidation by hypochlorite, and no noticeable color was

produced. This inhibition of manganese oxidation was determined to be an important mechanism in the success of this technique. Manganese retention on 1000 molecular weight (MW) cut-off ultrafiltration membranes indicates that manganese may have complexed with polyphosphate (sequestrant) which had a molecular weight higher than the ultrafilter cut-off level. It is hypothesized that complexation with polyphosphates made the manganese-polyphosphate complex more resistant to oxidation than free Mn^{2+}. In the presence of polyphosphates, manganese was not oxidized by hypochlorite and produced no discoloration for a period of 10 days, whereas in the absence of polyphosphates manganese was slowly oxidized and produced discoloration. Also, in the absence of polyphosphates, manganese was retained on 0.1 micron and 200,000 MW ultrafilters filters. These results imply that polyphosphates would inhibit manganese oxidation and subsequent precipitation in pipelines and fixtures when used with hypochlorite in actual facilities. Thus, the dual purposes of disinfection and manganese stabilization can be achieved with this technique.

The effects of two important water quality parameters (pH and calcium) on manganese treatment were studied to determine the applicability of the polyphosphate/hypochlorite technique to natural ground waters. Higher turbidities (proportional to the polyphosphate dosage) were noted in the presence of calcium than in its absence, due to the formation of a calcium-phosphate precipitate. The precipitate could not be identified by x-ray diffraction studies, as it was x-ray amorphous. Equilibrium

modeling studies were done using MINTEQ (a geochemical equilibrium model). MINTEQ predicted that hydroxyapatite, $Ca_5(PO_4)_3OH$ precipitation is thermodynamically favored. Even though hydroxyapatite is thermodynamically the most stable precipitate that would form under the experimental conditions, other calcium-phosphate precipitates could initially form and slowly transform to hydroxyapatite. This phenomenon is discussed further in Section 2.2.1 of the literature review. In the presence of calcium, the best treatment was obtained at a dosage of 5 mg/L as total phosphate. The turbidity was below permissible limits (1.0 NTU) at this dosage, and high filterability and low discoloration was obtained.

Manganese treatability by the polyphosphate/hypochlorite technique was also tested at various pH levels (6, 7, and 8). The best treatment was obtained at pH 6, due to the absence of calcium-phosphate precipitation.

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1.0 INTRODUCTION

1.1 PROBLEMS CAUSED BY MANGANESE IN WATER SUPPLIES

Manganese is widely distributed in nature and frequently associated with shale, sandstone and alluvial deposits. Hence, the manganese concentration is likely to exceed the maximum recommended levels for potable water (0.05 mg/L) when wells are developed in such deposits (49). Though manganese concentrations as high as 7 mg/L have been encountered in some groundwaters (74), manganese concentrations in groundwaters usually range from 0.05-1.0 mg/L. For example, some groundwaters in Ontario have manganese concentrations varying from 0.03 to 0.05 mg/L, and the manganese concentration of some groundwaters at Oneida, Tennessee has been found to be about 0.50 mg/L. Even though these concentrations appear to be low, manganese concentrations higher than 0.05 mg/l may cause aesthetic problems in water supplies (47, 48). The magnitude of this problem becomes even more significant when communities have to rely mostly on groundwaters in the absence of surface sources. Although manganese does not have any related toxicity at the levels normally encountered in water supplies (8), manganese concentrations above 0.05 mg/L may result in colored water, stains, turbidity and taste (47, 48). Therefore, manganese standards were recommended to prevent the occurrence of such aesthetic problems. These aesthetic

problems commonly occur when manganese is oxidized by chemical oxidants added for disinfection purposes. Economic feasibility is the principal reason that chemical disinfectants are employed almost exclusively for water supplies, in preference to the other non-chemical methods (102) which may not cause these manganese problems to occur. Additionally, strong bleach is often used for laundry. In these situations, manganese may be oxidized and cause discoloration. Other problems include acceleration of biological growths in the distribution system due to deposition of manganese oxides which further increases the taste, odor, and color problems.

1.2 TREATMENT TECHNIQUES FOR MANGANESE CONTROL

About 40% of the public water supplies in the United States have manganese concentrations which exceed the recommended standards of 0.05 mg/L. Even though several reliable techniques are available for iron treatment, in the case of manganese removal no single process is uniformly effective (49). Iron in ground water can easily be removed by aeration (oxidation by oxygen), sedimentation or detention and filtration whereas manganese is more resistant to oxidation by oxygen alone (11) and may require chemical addition to oxidize the manganese. In this process, Mn^{2+} is oxidized to the insoluble valences Mn^{3+} or Mn^{4+} prior to sedimentation and filtration. Chlorine, potassium permanganate (50, 51), ozone (102), and chlorine dioxide (99) have been used as oxidants in manganese removal processes. Successful manganese removal depends on several factors: pH (38), manganese

concentration (64), presence of other ions (39), and the method used in the manganese removal processes (49). Hence, in many cases, it may be necessary to try several of the available methods to obtain acceptable results. Various methods that are used in manganese removal processes are reported elsewhere (5, 11, 12, 26, 50, 51, 53, 69, 88, 102). However, manganese removal is relatively expensive for small utilities and has practical problems. As manganese is not toxic but is only an aesthetic problem, an alternative process known as "sequestration" which has been found to be successful in treating iron can also be applied to manganese. Substantial savings in cost has been obtained with this technique (13, 14) in iron treatment. The method has been found to be simple and reliable. By successfully applying this technique to sequester manganese, conventional manganese removal methods can be eliminated resulting in substantial savings in cost.

1.3 PRINCIPLES OF THE SEQUESTRATION PROCESS

"Sequestration" is a process in which mettallic ions interact with a suitable reagent added to water to stabilize these ions through the formation of a soluble compound or a stable colloidal phase. The chemicals most commonly used in sequestration are sodium silicates and polyphosphates. The silicate/chlorine and polyphosphate/chlorine methods are frequently used to sequester manganese. Of these two methods, manganese treatment by sodium silicate and chlorine has been researched more extensively than

treatment by polyphosphates (86). The common practice is to add sodium silicate and chlorine simultaneously. However, while this technique is reliable in the case of iron treatment, it has not been found to be effective in manganese control, and there is generally no accepted reliable technique for sequestering manganese. Polyphosphates have been tested for some time in attempts to sequester manganese. However, some water suppliers are satisfied with polyphosphates while others have discontinued their use (86). Polyphosphates may or may not be used with chlorine already in use in existing facilities. Chlorine may be added before or after the addition of polyphosphates for disinfection purposes. However, very little information is available on the physical/chemical principles of the polyphosphate method in manganese treatment. The water quality for which polyphosphates will be successful is also not known. Hence, further research is required in this area to better understand the mechanism of treatment, determine the best sequestrant or oxidant combination for effective manganese stabilization, study the effects of several variables on manganese treatability and provide a basic understanding of how manganese is sequestered or why it fails to be sequestered by various techniques.

Manganese oxidation (due to the addition of oxidants which are added with the sequestrants), precipitation, colloidal dispersion, and stabilization (prevention of coalescence, growth and subsequent settlement of particles formed during treatment) are generally believed to be an important part of the sequestration process.

Although very little information is available on these processes in manganese sequestration, these processes have been studied in iron sequestration. Several researchers (6, 43, 58, 74, 79) who investigated iron sequestration by the phosphate/chlorine and silicate/chlorine methods found that an iron precipitate was formed during treatment. Precipitation refers to the formation of a solid phase from a supersaturated solution (crystallization) and its presence in the suspended form (as particulates) after the formation of this phase. In sequestration, phosphates and silicates disperse the precipitated iron oxides in the colloidal form causing a decrease in their particle size and an overall increase in their surface area. Phosphates are subsequently adsorbed onto these iron oxide surfaces, converting them into stable negative colloids. This obviously increases the repulsive forces between these colloids and limits their coalescence, agglomeration and settlement. This is similar to the observed effects of phosphates on clay suspensions (98). Phosphates are known to adsorb onto the surfaces of clay particles present as colloidal dispersions and prevent their agglomeration and subsequent settlement. The stabilizing action of phosphates and silicates on preformed iron oxide sols have been verified by Hazel (27, 28)

Although precipitation from solution and subsequent dispersion in the colloidal form is important for successful treatment in iron sequestration and is determined to be an important aspect of the sequestration process, the importance of these processes for

successful manganese treatment has not been studied. The present study therefore investigates the mechanism(s) of manganese sequestration and the effectiveness of several techniques (to identify an effective technique to treat manganese) by testing the effects of several variables.

Manganese is more resistant to oxidation than iron. Hence, it may not precipitate from solution, and therefore, a colloidal dispersion may not be present. Also, manganese could be present in the colloidal form or as a complex with polyphosphates in manganese sequestration. However, Robinson and Ronk (78) hypothesized that manganese should be oxidized and be dispersed in the colloidal form for treatment to be effective. Hence, this hypothesis was tested in the present research. Particularly, this research investigated the importance of these processes (oxidation, precipitation from solution and colloidal dispersion) in manganese sequestration. An analytical technique (described in Section 3.0) was used to determine the degree of manganese oxidation. X-ray diffraction and equilibrium models were used to evaluate the precipitates formed during treatment. Filtration studies were performed to verify the dispersion of these precipitates in the colloidal form by silicates and polyphosphates. Streaming current studies were done to determine if streaming current can predict good treatment. Other studies are outlined in Section 1.5 (research objectives), and the results of this investigation are discussed in

Section 4.0 along with the other significant findings of this experimental investigation.

1.4 ECONOMICS OF THE SEQUESTRATION PROCESS AND NEED FOR FURTHER RESEARCH

Sequestration has several economic and practical advantages over conventional processes. A small water supply system which depends mainly on ground waters containing manganese is less likely to build and operate a conventional manganese removal plant or soften the water by lime-soda ash treatment to remove manganese. Many small communities feel they cannot afford the capital, operation, and maintenance costs. Other disadvantages of conventional treatment include the need for experienced operators and the generation of a sludge during treatment. Even for a very small town of 200 people, the cost of building a manganese removal plant would be about $100,000, which would be about $500 per person (51). The cost of constructing a 50 gpm filtration plant is about $140,000. In contrast, sequestration would cost only about $14,000 (the well pump facility) for a sequestration plant and about $5 per person per year for sequestering chemicals (79). The cost of the sequestrant chemicals averages from $6.50 to $7.50 for each mg/L of sequestrant per million gallons treated (58). Chemical costs would run about $1,000 per year for a polyphosphate feed rate of 5 mg/L and a cost of $2.00 per kg of polyphosphate. No sludge is generated

in this method. It has the advantage of being simple to apply and requires very little supervision (58).

As sequestration is more economical compared to conventional removal processes, the Trace Inorganics Substance Committee (TISC) recommended further studies on the manganese sequestration process to control manganese problems by this technique. TISC (86) recommended further research:

1. to identify a method for effective manganese treatment;
2. to determine the effects of water quality on the treatment process;
3. to understand the chemistry of manganese treatment; and
4. to define the mechanism of sequestration.

1.5 RESEARCH OBJECTIVES

The objective of this research is to demonstrate a viable technique for manganese control, determine its applicability to different ground waters which vary in chemical composition, determine the mechanism by which manganese is sequestered and identify variables which affect manganese treatability. Several techniques are investigated in this research to identify techniques by which manganese oxidation and the discoloration it causes could be reduced or prevented. These techniques involve addition of sequestrants and oxidants to model ground water prepared in the

laboratory. The effectiveness of these techniques is assessed by determining the effects of several variables on the treatment parameters color, turbidity and filterability. Filterability studies are intended to quantify the effectiveness of these techniques for limiting precipitation in the distribution system when implemented by facilities. Manganese treatability with different sequestrant/ oxidant combinations (polyphosphate/hypochlorite, polyphosphate/ chlorine dioxide and silicate/chlorine dioxide) and the effects of several variables such as degree of manganese oxidation, pH, presence/absence of calcium, size and charge of manganese particulates, identity of manganese precipitates, and the correlation between characteristics of different polyphosphates and treatment success are studied in this research. Variables studied in this research and the criteria for selecting these variables for this experimental investigation are discussed in the following paragraphs.

1.5.1 Degree of Manganese Oxidation in polyphosphate/ hypochlorite and polyphosphate/chlorine dioxide methods

In iron sequestration by polyphosphates and hypochlorite, it has been found that iron was oxidized and formed dispersed colloids or high molecular weight polymers (79). Polymeric phosphates have been found to be more effective than orthophosphates (2). Even though plausible mechanisms by which polyphosphates sequestered iron were given, the mechanism by

which polyphosphates sequester manganese is unclear as no method has been identified to produce effective manganese treatment. Since researchers (14, 78) have stated that the effectiveness of the manganese sequestration process would be highly dependant on manganese oxidation, the degree of manganese oxidation is studied in this research to determine to what extent the manganese is oxidized; for example, is the manganese oxidized or unoxidized when it is sequestered or fails to be sequestered by polyphosphates? In particular, the degree of manganese oxidation is studied as a function of pH, type of oxidant and in the presence or absence of polyphosphates or polyphosphates and silicates in conjunction. A further discussion of each of these aspects follows.

1.5.1.1 Effect of pH on Manganese Oxidation

Dart and Foley (14) stated that manganese treatability by silicate and hypochlorite could be improved by raising the pH, which accelerates manganese oxidation. However, Robinson and Ronk (78) observed the reverse effect, suggesting that higher pH is not favorable to manganese treatment. Manganese treatment in the presence of iron, which is believed to catalyze manganese oxidation, also gave poor results. In this research, manganese treatment is studied at pH 6, 7 and 8 to determine pH effects on the degree of manganese oxidation and determine its relationship to manganese treatability in the presence of polyphosphates and hypochlorite.

1.5.1.2 Effect of Different Oxidants on Manganese Oxidation

The failure of the silicate/hypochlorite method in Robinson and Ronk's studies on manganese sequestration was attributed to poor manganese oxidation by hypochlorite. It was stated that for silicates to disperse manganese in the colloidal form, manganese should be oxidized before silicate depolymerizes. In order to determine if manganese treatability can be improved by using stronger oxidants, chlorine dioxide is used in addition to hypochlorite in this research. Treatment effectiveness is determined by filterability analysis and measurement of turbidity and color, and the effects of chlorine and chlorine dioxide on the degree of manganese oxidation are compared.

1.5.1.3 Effects of Polyphosphates on Manganese Oxidation

Stumm and Morgan (63) cite work by Blinski and Morgan who found that traces of pyrophosphate retarded manganese oxidation to higher valence states. It was hypothesized that manganese oxidation was retarded due to the formation a manganese-phosphate complex which was more resistant to oxidation than Mn^{2+}. Whereas manganese oxidation by oxygen was observed in their investigations, in this research, hypochlorite and chlorine dioxide are used. Hence, it is desired to know if manganese is oxidized by these oxidants in the presence or absence of polyphosphates. This study would promote a better understanding of the sequestration process and the mechanism(s) by which

polyphosphates sequester manganese. Additionally, polyphosphates and silicates in conjunction are tested in this research to determine if manganese treatability can be improved by this method.

1.5.1.4 Analytical Method to Measure the Degree of Manganese Oxidation

The analytical technique used in this research to determine the degree of manganese oxidation is semi-quantitative. It is a colorimetric method in which the extent of color formation is proportional to the quantity of Mn^{2+} oxidized by hypochlorite or chlorine dioxide. When manganese is present as Mn^{2+}, no color develops.

1.5.2 Water Quality

Ground waters vary widely in water quality. Two important water quality parameters are pH and hardness. In practice, these parameters may have a significant effect on manganese treatability and hence their importance needs to be assessed. Previous studies by this researcher on iron sequestration by polyphosphate and hypochlorite indicate that calcium adversely affects treatment, and that lower pH is favorable to iron treatment when calcium is present. Hence, these effects are studied in this research on manganese sequestration.

1.5.3 Size of Manganese Particulates

Robinson and Klueh (79) found that in iron treatment by sodium silicate and chlorine, an iron colloid is formed which flocculates very slowly unless multivalent ions such as calcium are present. A similar colloid may be formed in manganese sequestration also, but has not been investigated. The ratio of manganese present in the colloidal form to manganese present as Mn^{2+} will depend on the degree of manganese oxidation and several other factors. Since colloids are charged particles which vary in size (approximately 0.001 micron to 1 micron), this research investigates the size of these colloids to determine the effects of polyphosphates on the particle size and investigate the mechanism of treatment. Treated samples are filtered through ultrafilters (1000 MW cut-off and 200,000 MW cut-off with pore sizes of 0.0013 microns and 0.0073 microns respectively) and 0.1 micron filters to determine the particle size ranges of these colloids. Streaming current detectors are used to determine whether streaming current can predict good treatment.

1.5.4 Identity of Manganese and Calcium Precipitates

The identification of precipitates formed in manganese sequestration and factors which influence their formation will promote a better understanding of the sequestration process. Since different precipitates have different characteristics, these characteristics may have a direct bearing on treatment effectiveness. If the type of precipitates formed and factors

favoring their formation are known, process variables such as pH and type of oxidant can be changed to prevent the formation of precipitates detrimental to manganese treatment. For example, the formation of a calcium-phosphate precipitate causes high turbidities in the treated water. If the type of calcium-phosphate precipitate formed in manganese sequestration is known, pH could be changed so that this precipitate formation could be reduced or prevented. In this research, x-ray diffraction studies are done to determine if a mineral can be identified for the manganese and calcium precipitates. Equilibrium modeling is done using MINTEQ (a geochemical equilibrium model) to predict the calcium and phosphate levels at which a calcium-phosphate precipitate would form at pH 6, 7, and 8 which is the normal pH range of most natural waters.

1.5.5 Correlation Between Polyphosphate Characteristics and Treatment Success

Various commercially available polyphosphates have different ratios of total phosphate to orthophosphate. This ratio is a measure of the phosphate which is present in the polymeric form. The rate of reversion to orthophosphate, molecular weight and the phosphate percentage is also different for each type of polyphosphate. Since these variables could affect the success of treatment by polyphosphates, the effects of these variables are studied in this research to provide a basis for the selection of a particular type of polyphosphate from a wide range of commercially

available phosphates. Four commercially available polyphosphates are used in this research to determine the effects of these variables on treatment effectiveness.

2.0 LITERATURE REVIEW

2.1 OBJECTIVE

The objectives of this chapter are:

1) to present the factors which affect oxidation, precipitation, dissolution and colloidal dispersion of manganese in aqueous systems; and
2) to discuss previous research on iron and manganese sequestration and explain difficulties encountered in the past in treating manganese.

In the present study, the effectiveness of various manganese sequestration techniques has been tested in the presence of significant variables discussed in the following review of literature available on sequestration. The objective in presenting discussions on oxidation, precipitation, and colloidal dispersions of iron and manganese in aqueous systems in this literature review is to illustrate how several variables which affect these chemical processes can have a significant influence on manganese treatability. This section also discusses the different techniques used in sequestration to point out the advantages and disadvantages of each technique and highlight those techniques which have the most promise for manganese sequestration.

This literature review primarily focuses on previous studies of manganese sequestration, but because many factors which affect iron sequestration have been found to have similar effects on manganese sequestration, certain aspects of iron sequestration are also discussed in some detail. However, one major difference exists in the treatment mechanisms by which phosphates and hypochlorite sequester iron and manganese: In successful attempts to sequester manganese (by the polyphosphate/hypochlorite method) in the present studies, most of the manganese was present as Mn^{2+}, whereas in previous investigations on iron sequestration, Fe^{2+} was completely oxidized to Fe^{3+} (79). Polyphosphates inhibited manganese oxidation by hypochlorite leading to the conclusion that this inhibition of manganese oxidation is an important mechanism for the success of this technique. This is also consistent with Stumm and Morgan's findings that phosphates accelerate iron oxygenation (oxidation by oxygen) and retard manganese oxygenation (63). This difference is critical because manganese oxidation should be retarded for successful treatment, whereas iron oxidation has to be accelerated. Oxidation of manganese causes high discoloration (discussed Section 4.0) in the treated water.

2.2 AN OVERVIEW OF THE PHYSICAL/CHEMICAL PROCESSES IN SEQUESTRATION

In this section, the chemistry of oxidants added for disinfection purposes, their effects on the sequestration process and the physical/chemical processes are discussed in some detail.

Physical/chemical processes highlighted in this section include chemical oxidation, precipitation, colloidal dispersion, adsorption, agglomeration and settlement of particulates. Later sections (2.4-2.7) contain a more comprehensive review of these processes. Since very little information is available on the principles of manganese sequestration, a broad understanding of the sequestration process is obtained only from past work on iron sequestration. Hence, important aspects of iron sequestration are discussed initially in this section, and possible mechanisms for manganese treatment are also presented.

The first step in the sequestration process is the oxidation of iron by chlorine. Although iron oxidation is important for successful treatment in iron sequestration, findings of the present study (discussed Section 4.0) indicate that oxidation should be reduced or prevented for successful manganese treatment. In this study, polyphosphates were used to retard manganese oxidation by hypochlorite. The chemistry of chlorine and chlorine dioxide and their reactions with iron and manganese are discussed below.

When chlorine is added to water, it disproportionates to form hydrochloric and hypochloric acids, as illustrated by the equation:

$$Cl_2(gas) + H_2O \quad <\!\!\longrightarrow \quad HCl + HOCl$$

Hypochlorous acid dissociates into a proton and the hypochlorite ion:

$$HOCl \longleftrightarrow H^+ + OCl^- ; \quad pK_a = 7.5$$

At pH 7.5, the activities of HOCl and OCl^- or their concentration are equal (as activity = activity coefficient x concentration, and the coefficient tends to unity for dilute solutions). At pH values below 7.5, HOCl predominates while at higher pH levels OCl^- is the predominant species.

If chlorine is added as a salt of hypochlorous acid (NaOCl), dissociation to sodium ion and the hypochlorite ion will take place:

$$NaOCl \longrightarrow Na^+ + OCl^-$$

If calcium hypochlorite is used, dissociation to the calcium ion and hypochlorite will occur:

$$Ca(OCl)_2 \longrightarrow Ca^{2+} + 2OCl^-$$

From an operational point of view both hypochlorous acid and the hypochlorite ion constitute "free available chlorine" and oxidize iron and manganese. The use of calcium hypochlorite is not recommended for sequestration, as calcium ions have an adverse effect on the sequestration process. Sodium ions have comparatively little effect on the sequestration process. Therefore, in this research on manganese sequestration, sodium hypochlorite has been used. Another oxidant used in this research is chlorine dioxide (ClO_2). For chlorine dioxide, at pH 6-8 (the pH levels studied in this research), the equilibrium

$$2ClO_2 + H_2O \longleftrightarrow \underset{\text{(chlorous acid)}}{HClO_2} + \underset{\text{(chloric acid)}}{HClO_3}$$

is shifted far to the left indicating that chlorine dioxide is stable at the pH levels studied in this research. HOCl, OCl^- and ClO_2 react with iron and manganese as follows:

$$OCl^- + 2Fe^{2+} + 2H^+ \longleftrightarrow 2Fe^{3+} + Cl^- + H_2O$$

$$HOCl + 2Fe^{2+} + H^+ \longleftrightarrow 2Fe^{3+} + Cl^- + H_2O$$

$$OCl^- + Mn^{2+} + H_2O \longleftrightarrow MnO_{2(s)} + Cl^- + 2H^+$$

$$HOCl + Mn^{2+} + H_2O \longleftrightarrow MnO_{2(s)} + Cl^- + 3H^+$$

$$ClO_2 + 5Fe^{2+} + 4H^+ \longleftrightarrow 5Fe^{3+} + Cl^- + 2H_2O$$

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

Factors which affect oxidation of iron and manganese in aqueous solutions and the usual steps which lead to the precipitation of a solid phase are discussed in Sections 2.4 (crystallization) and 2.6 (iron and manganese oxidation). It is believed that the iron precipitate formed in sequestration may be subsequently dispersed in the colloidal form by polyphosphates or silicates. Due to the high surface area of these colloids, phosphates may be adsorbed onto these surfaces to produce a relatively stable colloidal system as illustrated by the reaction:

$$FeOOH(s) + HPO_4^{2-} \longrightarrow FeOHPO_4^-(\text{surface}) + OH^-$$

FeOOH is one of the several Fe^{3+} forms that may result from oxidation. Formation of different iron and manganese precipitates and factors favoring their formation are discussed in Section 2.4. Phosphate and silicate effects on iron colloids and silicate stabilization of manganese colloids are explained in Section 2.7.

Rice (74) also found manganese to be sequestrable by the phosphate/chlorine method. Rice studied several treatment plants that used phosphates to control manganese problems. Some groundwaters with manganese concentrations as high as 7.2 mg/L were successfully treated by phosphates, eliminating almost all complaints received prior to the phosphate treatment. Consistent with results obtained by Henry (41), Mayhan (58) and Robinson and Klueh (79), Rice found both iron and manganese treatment to be effective when phosphate was added prior to chlorine. Mayhan stated that the treatment will fail if iron is allowed to be oxidized by chlorine and precipitate before the phosphate is added. To be successful, the phosphate must be applied while the iron is still in solution and in the ferrous (Fe^{2+}) state. Similar results were obtained by Browman (6) while studying the silicate/chlorine method of iron treatment. However, although a plausible mechanism was given for the success of this technique in iron treatment, the mechanism by which manganese is sequestered was unclear. It is not known if manganese was present in the colloidal form as the very insoluble valences Mn^{3+} and Mn^{4+} or as Mn^{2+} in Rice's studies. Equations presented earlier illustrate that manganese

present as Mn^{2+} may be oxidized to manganese dioxide, $MnO_{2(s)}$. However, other conditions may influence the oxidation process. Since polyphosphates were added with chlorine in Rice's studies, a polyphosphate-manganese complex which is resistant to manganese oxidation may have formed. Polyphosphates form strong complexes with manganese, as discussed in Section 2.8. In Blinski and Morgan's studies on manganese oxidation by oxygen (cited by Stumm and Morgan), polyphosphates retarded manganese oxidation by oxygen. These studies were done at a pH of 9.65, manganese concentration of 11 mg/L, and total carbonic species concentration of $1x10^{-2}$ moles/L. Therefore, in Rice's studies, manganese may have been present as Mn^{2+} in solution rather than the insoluble valences Mn^{3+} or Mn^{4+}. In addition to the effects of polyphosphates on manganese oxidation, other factors such as the pH of the solution and the presence of other ions may also have a significant effect. These factors are investigated in this present research and presented in Section 4.0.

2.3 PREVIOUS INVESTIGATIONS ON SEQUESTRATION

In this section, results of several investigations on iron and manganese sequestration are presented, to highlight practical considerations which are necessary for the application of this technique to control iron and manganese problems in groundwater. The limitations of this technique and further recommendations to improve this technique are discussed. The following subjects are dealt with extensively:

1) application of the phosphate and silicate technique to ground waters;

2) effect of water quality (presence/absence of calcium and other ions and pH) on treatment;

3) effect of other variables (type of phosphate, aging of phosphates and silicates, silicate ratios, and silicate dilutions and lag time between silicate and hypochlorite addition);

4) mechanism of treatment; and

5) methods used to quantify and compare the effectiveness of different techniques.

2.3.1 Sequestration by Polyphosphates

Sequestration of iron and manganese by polyphosphates has been studied since as early as the 1940's. In October 1946, Rice (74) showed that Calgon, a sodium-based phosphate, could be used to prevent the precipitation of dissolved iron from well water when added before chlorination. This application of phosphates in iron treatment was found to be very useful at a time when water works superintendents were receiving many complaints about "red water" and were unable to correct the situation. It was speculated that adsorption of phosphate onto iron oxide particulates formed during chlorination limited coalescence and particle growth to such a size as to cause a noticeable discoloration of the water. The polyphosphate

dosage required for effective iron stabilization was found to be twice that of the iron concentration. Manganese was also found to be treatable by this method. Further studies on the polyphosphate/chlorine technique in sequestration were performed by Henry (41). The water supply studied had a hardness of 240 mg/L as calcium carbonate. Henry studied iron treatability with different polyphosphates and orthophosphates to identify the most suitable phosphate for iron treatment. Two different polyphosphates, mono-, di-, and trisodium phosphates and sodium silicates were used in his studies. Initial studies with polyphosphates indicated that more than 90% of the iron could be kept in suspension for a period of 2 days without causing any red water problems. In the absence of polyphosphates only 60% of the iron could be kept in suspension. The rate of iron settlement was measured as quiescent settling in glass stoppered bottles. It was found that older polyphosphates which had been exposed to moist air for over a year and had reverted to simpler forms such as orthophosphate gave better treatment than fresh polyphosphates.

Consistent with Robinson's and Klueh's results (79), Henry found that high turbidity was produced when groundwaters containing calcium were treated with polyphosphate and chlorine. While testing silicates under similar conditions, dosages of 5 mg/L as silica (SiO_2) did nearly as well as 5 mg/L of polyphosphate in delaying iron settlement and produced very little turbidity. Based on these observations, Henry concluded that on a straight weight-

for-weight basis, sodium silicate is more effective than polyphosphates in iron sequestration. However, in later investigations, Illig (45, 46) used polyphosphates to successfully treat iron and manganese. In Illig's studies, proper stabilization of iron and manganese by sodium hexametaphosphate prevented color from developing in the treated water. It was stated that in order for iron and manganese stabilization to be effective, polyphosphates must be added and mixed thoroughly, prior to oxidation of iron and manganese by chlorination. Illig (46) stated that the phosphate should be fed directly to the well at the pump intake when dissolved iron or manganese concentration is greater than 0.3 mg/L. Illig speculated that polyphosphates formed a colorless complex with iron and manganese, limiting particle growth and subsequent sedimentation. Differences noticed in iron treatability in separate investigations discussed so far (41, 45, 46, 74) indicate that the water quality for these investigations as well as the type of polyphosphate used were different. For example, calcium hardness could have been absent or minimal in Illig's (45, 46) and Rice's (74) studies since successful application of polyphosphates were reported by them. Also, Rice used Calgon (pyrophosphate) and Illig used sodium hexametaphosphate, whereas Henry (41) used orthophosphates and two other polyphosphates (designated as type "A" and "B"). Consistent with Henry's results, Robinson and Klueh (79) found that treatment by polyphosphate and hypochlorite produced high turbidity when calcium was present. In the absence of calcium very little turbidity was noticed. From these results it

can be concluded that the polyphosphate/chlorine treatment will be successful in producing the desired iron stabilization in the absence of calcium, but calcium adversely affects treatment. As the effects of calcium on manganese treatability have not been investigated, this lack of information is addressed in the present study, and the results are discussed in Section 4.0.

In the next section, the success and limitations of the silicate technique in iron and manganese sequestration are discussed.

2.3.2 Sequestration by Silicates

2.3.2.1 Iron Sequestration

Dart and Foley (13, 14) demonstrated the use of sodium silicates in sequestration of iron by performing a simple filtration test. Iron retention on the filter decreased with silicate addition to the ground water. At a sodium silicate dosage of 5 mg/L, iron retention on the filters approached a minimum value. Dart and Foley speculated that the reaction of the silicate ion with ferric iron produced a complex which impeded floc formation and subsequent settlement of iron particulates. Very few reports were received from consumers after application of the silicate technique. Results of their studies are outlined below.

1) The presence of hardness in groundwater increased the silicate requirement for iron treatment. An

increase in hardness from 0 to 100 mg/L was accompanied by a five-fold increase in the minimum silicate requirements to stabilize the iron.

2) Lesser silicate dosages were required at higher pH levels to treat ground waters having low hardness and high background silica.

3) Activated, partially neutralized, or excessively prediluted and aged silicates were not as effective as fresh concentrated silicates.

In Browman's studies (6), a dosage of 13.9 mg SiO_2/L stabilized 2 mg/L of iron for a period of 7 days in the absence of calcium. Browman used 0.1 micron filters in his studies to observe significant differences in filterability between the various lag times, compared to the asbestos fibre filters of a much larger pore size, used by Dart and Foley (13,14). Most of the iron particulates were present at a size less than 0.1 micron (the membrane filter pore size), when treated by silicates, whereas in the absence of silicates, the particle size was well over 0.1 micron, as indicated by almost 100% retention of iron on the filters. Silicate limited the coalescence, growth and agglomeration of iron particulates. Among undiluted sodium silicate ($Na_2O.nSiO_2$) solutions of different SiO_2/Na_2O molar ratios (n=1.80-3.75), at a constant silica dose, the level of observed iron stabilization improved with increasing silicate ratios, and concentrated solutions were found to be more effective

than dilute solutions at a given silicate ratio. The progressive improvement in iron stabilization with increasing silicate ratios was also noticed by Hazel (27), while studying the effects of silica sols on preformed iron oxide colloids. Other variables studied by Browman include the effect of pH and lag time between silicate and hypochlorite addition on iron treatability. Browman found that allowing the pH to drift to higher pH levels (8 to 8.5) would be more favorable to iron treatment than where the pH was controlled at ~ 7. These studies were done in the absence of calcium, using undiluted silicate solutions which were diluted by a factor of 10, 50 and 500. The optimum lag time for sodium silicate application was 15 to 150 seconds prior to the addition of sodium hypochlorite. Hypochlorite addition prior to silicate decreased filterability.

Since Browman's studies were done in the absence of calcium, results of these studies can be applied extensively only to ground waters in which calcium is absent. Robinson et al. (43) studied the effects of several cations and anions including calcium (as well as sodium, sulfate, chloride, and bicarbonate) on iron treatment by sodium silicate and hypochlorite. These studies confirmed and quantified Dart and Foley's conclusions (13, 14) about the effects of calcium on iron treatability. The effects of other ions were compared with calcium. Consistent with Dart and Foley's findings, Robinson et al. found that calcium adversely affected treatment even at low concentrations and increased the silicate dosage required to produce the desired iron stabilization. At a

silicate dosage of 16 mg/L as SiO_2, iron was stabilized for a period of 10 days in the absence of calcium while the same dosage stabilized iron for a period of only 5 days in the presence of 25 mg/L calcium as calcium carbonate. But in these experiments the adverse effects of calcium on iron treatment by sodium silicate and chlorine were more pronounced than was suggested by Dart and Foley's findings. Whereas Dart and Foley found that an increase in calcium concentration from 0 to 100 mg/L as calcium carbonate would increase the required silicate dosage by a factor of 5, Robinson et al found that such an increase in calcium carbonate concentration would require that the silicate dosage be increased by a factor of 64. Other ions were found to have only minor effects compared to calcium. Even though sodium ions were present at concentrations much higher than calcium, they did not affect treatment significantly.

In order to account for the increase in silicate requirements when calcium was present, Robinson et al. studied the possibility of calcium-silica precipitate formation. Equilibrium modeling studies revealed that this would not be thermodynamically possible. Hence, the increase in silica requirements could not be explained by hypothesizing calcium-silica precipitate formation. Robinson et al. postulated that the iron precipitates were negatively charged in these experiments, and were therefore destabilized to a significant extent by divalent cations such as calcium. The effects of calcium ions on colloidal iron is explained by the Schulze-Hardy rule

according to which divalent cations such as calcium should destabilize negatively charged colloids to a greater extent than monovalent cations and divalent or monovalent anions.

Results obtained by various researchers in iron treatment by silicate can be summarized as follows:

1) Iron treatment by silicate was widely successful.

2) Calcium affected treatment, requiring higher silicate dosages for iron stabilization. Other ions had only minor effects.

3) Increase in silica requirements in the presence of calcium could not be explained by calcium-silica precipitate formation.

4) Iron was present as colloidal particulates when treated by silicates. It is possible that silicates adsorbed onto iron particles enhanced the surface charge and limited flocculation, consistent with results obtained by Hazel (27) while studying silicate effects on preformed iron oxide colloids.

5) Iron stabilization improved with increasing silica ratios consistent with Hazel's results, and concentrated silicate solutions were more effective than dilute solutions in producing the desired iron stabilization.

6) Higher pH (> 7.5) was favorable to iron treatment when low hardness waters were treated by silicates.

2.3.2.2 Manganese Sequestration

Dart and Foley (14) studied manganese sequestration by the silicate and chlorine method to control manganese problems in water supplies at Ontario. However, poor manganese treatability was obtained with this technique. Best results were obtained in the case of null treatment (absence of silicate and chlorine addition), though as noted previously, null treatment is not a realistic alternative, due to the necessity of chlorine as a disinfectant. Their studies indicate that almost 100% filterability is possible in the case of no silicate and chlorine addition, whereas only 30% filterability can be achieved even after a silicate-manganese reaction period of about 3 hours. Similar results were obtained by Robinson and Ronk (78) who studied the silicate/chlorine method to control manganese problems in ground waters. Their studies indicate that manganese was not as effectively treatable as iron by the same method. Comparing these results with similar experiments on iron sequestration (6), Robinson and Ronk found that iron could be completely stabilized. Again, the best manganese treatment was observed in the case of null treatment. It was hypothesized that poor manganese oxidation by oxygen alone was the reason for the observed good treatment in the absence of silicate and chlorine addition. Robinson and Ronk hypothesized that for manganese colloids to be effectively dispersed and stabilized by silicate

treatment, manganese should be rapidly oxidized before silicate depolymerization takes place. Alternative oxidants, polyphosphates, or polyphosphates and silicates in conjunction were recommended for future studies.

Robinson and Ronk cite O' Connor (68), who reported that chlorine is not an effective oxidant for manganese at lower pH levels. Since manganese oxidation is much faster at higher pH levels, treatment should have been better at a higher pH according to Robinson and Ronk's hypothesis, as most of the manganese may have been oxidized before the silicate depolymerizes. However, Robinson and Ronk's results show that worse treatment was obtained at higher pH levels. Subsequent studies carried out by Robinson and Ronk in the presence of iron, which is believed to catalyze manganese oxidation, also yielded poor results.

Though results obtained by Robinson and Ronk as well as Dart and Foley (14) indicate that treatment by silicates and chlorine provided less manganese stabilization than null treatment, Mirando and Marini (59) found that in actual field practice, silicate/chlorine treatment provided much better stabilization than null treatment. In the absence of silicate treatment, iron and manganese present in the treated ground water was oxidized and deposited in transmission mains due to catalysis whereas silicate/chlorine treatment prevented this from taking place even though iron and manganese may have been oxidized. The catalysis was speculated to be due to the action of iron and manganese oxides previously

deposited in transmission mains. Mirando and Marini also found that silicates performed better than polyphosphates at elevated temperatures (about 140°F).

Heaney and Hyslop (37) cite Jim Dart (no reference given), who studied the effectiveness of the silicate/chlorine technique for controlling iron and manganese problems in water supplies for the city of Prince George. Though earlier studies by Dart and Foley indicated that silicates were not effective in controlling manganese problems in ground water supplies at Ontario (14), sequestration tests at the city of Prince George indicated that manganese could be effectively sequestered by this technique. Review of the water quality indicated that any potential problems such as manganese staining of laundry or fixtures could be prevented by this technique, as manganese was effectively stabilized following silicate/chlorine addition. Based on these positive results, the silicate/chlorine technique was adopted, and the new treatment plant was commissioned shortly thereafter. However, water treated by the new plant did not live up to the positive expectations of the initial testing and predictions. Excessive complaints were received from consumers after commissioning of the treatment plant, so further studies were carried out by Heaney and Hyslop (37) to test the effectiveness of the silicate technique. These studies showed that complete manganese sequestering could be achieved at a chlorine dose of about 3 mg/L, and silicate dosages greater than 7 mg/L. Further tests were performed to study the performance of the

treated water at higher chlorine dosages commonly encountered in laundry-type situations. In these studies, hydrogen peroxide was added with chlorine and silicate, as recommended by Dart and Foley. These studies showed that at chlorine dosages as high as 100 mg/L, manganese and iron filterability exceeded 90% when the reaction time between the silicate and chlorine addition and filtration was 10 minutes or less. When the reaction time was greater than 30 minutes, significant iron and manganese retention was observed. However, Heaney and Hyslop concluded that staining problems would not be encountered as long as the wash cycle during which the laundry was in contact with bleach was 10 minutes or less. Based on their test results they concluded that addition of silicate with chlorine and hydrogen peroxide would be more effective than silicate and chlorine alone.

It is not clear whether hydrogen peroxide functioned as a reducing agent or as an oxidizing agent in Heaney and Hyslop's studies. Barnett and Wilson (3) stated that hydrogen peroxide could function as an oxidizing agent or a reducing agent depending upon the pH of the solution. In an acid solution, hydrogen peroxide oxidizes iron and reduces manganese, whereas the reverse takes place in alkaline solutions. Barnett and Wilson give the following reactions to illustrate these effects:

Acid solutions:

$$2Fe^{2+} + H_2O_2 + 2H^+ \quad \longleftrightarrow \quad 2Fe^{3+} + 2H_2O$$

$$MnO_2 + H_2SO_4 + H_2O_2 \longleftrightarrow MnSO_4 + 2H_2O + O_2$$

Alkaline solutions:

$$2Fe^{3+} + H_2O_2 + 2OH^- \longleftrightarrow 2Fe^{2+} + 2H_2O + O_2$$

$$Mn^{2+} + H_2O_2 + 2OH^- \longleftrightarrow MnO_2 + 2H_2O$$

Since the raw water pH at the city of Prince George (37) was about 8, it is possible that manganese was oxidized and iron was reduced when hydrogen peroxide was added with silicate and chlorine.

The following findings summarize the results of studies on manganese sequestration by silicate and chlorine:

1) Manganese sequestration by silicate and chlorine was generally successful when hydrogen peroxide was added with silicate and chlorine.

2) Some researchers reported that better results were observed with null treatment than with silicate and chlorine. In actual field studies, better treatment was obtained in the presence of silicate and chlorine than in its absence. Iron and manganese were oxidized and precipitated in pipelines when silicates were not added.

3) Further studies using stronger oxidants were recommended.

This concludes the historical survey of iron and manganese sequestration. In the following sections, the physical/chemical processes that play an important role in the sequestration process will be discussed. These processes are outlined below.

1) Crystallization;

2) Dissolution, precipitation, and identity of iron and manganese, and calcium-phosphate precipitates;

3) Manganese and iron oxidation;

4) Surface charge;

5) Hydrolysis of polyphosphates;

6) Polyphosphate complexes; and

7) Depolymerization of silicates.

2.4 CRYSTALLIZATION

In Section 2.3.1 it was pointed out that high turbidity was produced in the polyphosphate/hypochlorite technique of iron sequestration. The present study tests the hypothesis that this turbidity is due to the formation of a calcium-phosphate precipitate (discussed in Section 4.0). This section (2.4) provides more insight into the steps of the crystallization process which lead to calcium-phosphate precipitation by reviewing previous studies of this aspect of the sequestration process. Snoeyink and Jenkins (83) stated that

the precipitation of calcium-phosphates from supersaturated solutions proceeds through a number of steps: induction, nucleation, precipitation of an amorphous phase, phase transformation and crystal growth.

In supersaturated solutions, there is initially an induction period during which nuclei are formed. Nuclei are fine particles on which precipitation of solid phases takes place. A nucleus is formed in a supersaturated solution from ions or foreign particles unrelated to the precipitate. Homogeneous nucleation takes place when nuclei are formed from component ions of the precipitate. When foreign particles serve as the nuclei, it is referred to as heterogeneous nucleation. Since aqueous solutions normally contain foreign particles, most nucleation is heterogeneous. Following nucleation the precipitation of an amorphous phase (solid that does not have a well-organized crystal structure) occurs. The solid that is initially formed during precipitation may not be stable, but over a period of time the solid phase will transform slowly to the thermodynamically stable phase. Stabilization may take anywhere from a few months to several years to occur. Because the thermodynamically stable phase is often less soluble than the initially formed amorphous solid, transformation to the stable phase may be accompanied by additional precipitation and a reduced solution concentration. The thermodynamically stable phase can be identified by equilibrium calculations.

Reactions which take place in sequestration processes may not reach equilibrium within the time period of observation in this research; thus the solid that is initially present may be different from the stable solid. Since the solubility of the initially formed solid phase would be much greater than the solubility of the stable solid present at equilibrium, actual dissolved calcium-phosphate levels can far exceed calculated values for the thermodynamically stable solid. For example, hydroxyapatite is predicted to be the thermodynamically most stable solid (83) under typical natural water conditions. If phosphate concentrations of natural waters were controlled by hydroxyapatite, only 3.7×10^{-12} M phosphate could be present in solution at equilibrium when the calcium concentration is equal to 150 mg/L as $CaCO_3$ (83). However, phosphate concentrations in natural waters far exceed concentrations predicted by the hydroxyapatite equilibrium. In the present study (discussed Section 4.0), x-ray diffraction techniques and MINTEQ (a geochemical model based on the principles of thermodynamics) are used to evaluate the precipitates formed during treatment and predict the calcium phosphate levels at which precipitation may occur. The results of these studies are used to identify the calcium and phosphate levels at which calcium-phosphate precipitation would take place in sequestration.

2.5 DISSOLUTION, PRECIPITATION AND IDENTITY OF PRECIPITATES

2.5.1 Manganese Dissolution and Precipitation

In this section, factors which affect solubility of manganese in ground water are discussed in detail to show the normal manganese concentrations that would be prevalent in many ground waters and determine if precipitation of manganese compounds from solution is a major concern in sequestration. The manganese precipitation discussed in this section (2.5.1) refers to the formation of a solid manganese phase from solution which may cause high turbidity in the sequestration process. This is different from the precipitation of insoluble manganese oxides which adversely affects the sequestration process by causing high discoloration in the treated water.

Solubility of manganese in ground water depends on several factors, including pH, temperature, presence of common ions, and formation of surface complexes (83). Weand et al. (99) have stated that in the absence of other anions, the solubility of Mn^{2+} in groundwaters is determined by the manganese hydroxide solid phase, as illustrated by the equation:

$$Mn(OH)_2(s) \quad <\!\!\longrightarrow\!\!> \quad Mn^{2+}_{(aq)} + 2OH^-_{(aq)} \qquad (1a)$$

The saturated equilibrium relationship (solubility product) for the above reaction would be:

$$K_{s\,Mn} = [Mn^{2+}]\,[OH^-]^2 = 10^{-12.9} \qquad (1b)$$

However, since the solubility of divalent ions are affected to a significant extent by the formation of hydrolysis products (83), these equations alone would not suffice to describe the solubility of manganese in ground waters. Hence, the effects of complex ion formation should also be accounted for in solubility calculations. The following equilibria relate to the complex ion formation or hydrolysis reactions which affect the solubility of manganese hydroxide in water:

$$Mn^{2+}_{(aq)} + OH^-_{(aq)} \longleftrightarrow MnOH^+_{(aq)} \; ; K_3 = 10^{3.9} \qquad (2)$$

$$Mn^{2+}_{(aq)} + 3OH^-_{(aq)} \longleftrightarrow Mn(OH)_3^-{}_{(aq)} \; ; K_4 = 10^{8.3} \qquad (3)$$

The mass balance for total soluble manganese would then be,

$$[Mn]_T = [Mn^{2+}] + [MnOH^+] + [Mn(OH)_3^-] \qquad (4)$$

Substituting $MnOH^+$ and $Mn(OH)_3^-$ from (2) and (3) for $MnOH^+$ and $Mn(OH)_3^-$ in (4) we obtain the following equation:

$$[Mn]_T = [Mn^{2+}] + K_3[Mn^{2+}][OH^-] + K_4[Mn^{2+}][OH^-]^3 \qquad (5)$$

Since $[OH^-] = K_w / [H^+]$, the above equation may be written as,

$$[Mn]_T = [Mn^{2+}] \{1 + K_3K_w/[H^+] + K_4(K_w)^3/[H^+]^3 \} \qquad (6)$$

Substituting Mn^{2+} from (1a) for Mn^{2+} in (6) and replacing OH^- by K_w/H^+,

$$[Mn]_T = \{K_{s\,Mn}/[(K_w/H^+)]^2\}\{1+K_3K_w/[H^+]+K_4(K_w)^3/[H^+]^3\} \quad (7)$$

The equilibrium iron and manganese concentrations at any pH may be obtained directly from the above equation or from log [species] vs. pH diagrams (Figure 1). The following equations derived from (1), (2), and (3) were used in plotting these diagrams:

$$\log[Mn^{2+}] = 15.1 - 2pH$$

$$\log[MnOH^+] = 5.0 - pH$$

$$\log[Mn(OH)_3^-] = pH - 18.6$$

As this figure illustrates, the minimum solubility of $Mn(OH)_2$ occurs at pH 14. However, the pH of groundwaters is generally within 1 to 2 pH units either side of neutral pH. Hence, it is possible to have fairly high manganese concentrations in ground waters when solubility is controlled by the $Mn(OH)_2$ solid phase, i.e. in reducing conditions where the manganese exists as Mn^{2+} rather than the very insoluble valences Mn^{3+} or Mn^{4+}.

Since a significant amount of alkalinity is present in most groundwaters, the equilibrium concentration of aqueous Mn^{2+} is controlled by the solubility of $MnCO_3$. The following equilibrium relationships can be used in obtaining the Mn^{2+} solubility at any pH:

$$MnCO_{3(s)} \longleftrightarrow Mn^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \quad (8)$$

$$K_{sc\,Mn} = [Mn^{2+}]\,[CO_3^{2-}] = 10^{-10.4} \text{ at } 25^oC \quad (9)$$

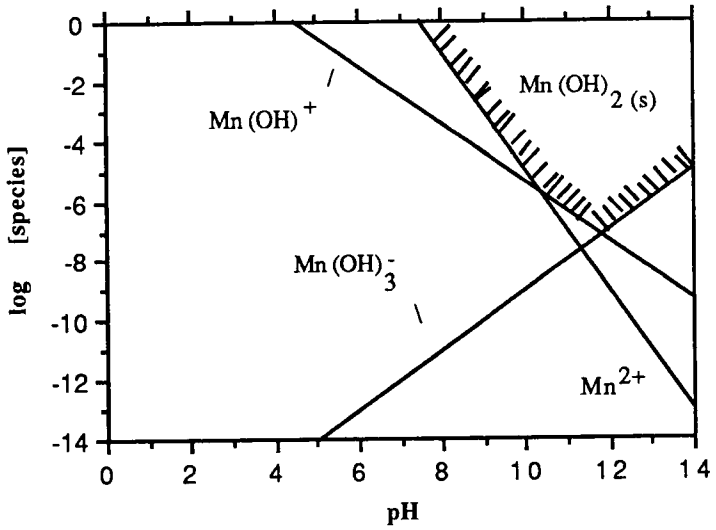

Figure 1. Solubility diagram for $Mn(OH)_2$-H_2O system

Substituting Mn^{2+} from (9) for Mn^{2+} in (6), the total manganese concentrations, when solubility is controlled by carbonate, and OH^- is the only complexing species present, may be expressed as

$$[Mn]_T = \{K_{sc\,Mn}/[CO_3^{2-}]\}\{1 + K_3K_w/[H^+] + K_4(K_w)^3/[H^+]^3\}$$

where $[CO_3^{2-}] = \mu_2 C_T$ where μ_2 = ionization fraction,

and C_T = total equilibrium carbonic species concentration.

The following equations for constructing the log [species] versus pH diagrams shown in Figure 2 are derived from (2), (3), and (9):

$$\log [Mn^{2+}] = -10.4 - \log \mu_2 - \log C_T \quad (10)$$

$$\log [MnOH+] = pH - 20.5 - \log \mu_2 - \log C_T \quad (11)$$

$$\log [Mn(OH)_3^-] = 3pH - 44.1 - \log \mu_2 - \log C_T \quad (12)$$

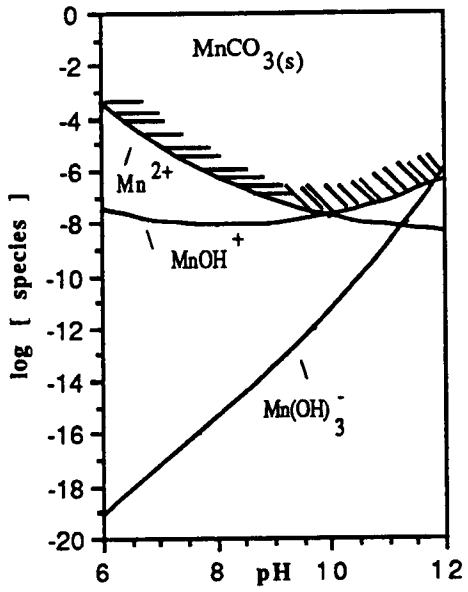

Figure 2. Solubility diagram for $MnCO_3$-H_2O system for $C=10^{-2}$ M

The equilibrium manganese concentrations at any pH can then be directly estimated from the above equations or from Figure 2.

Weand et al. (99) have stated that for a given pH, $MnCO_3$ solubility is inversely proportional to the equilibrium carbonic species concentration; i.e. the higher the carbonate species concentration is, the lower the soluble metal concentration will be. Figures 1 and 2 show that manganese solubility would be about 250 times greater in the absence of carbonate ($C_T = 10^{-2}$ M). Manganese solubility would be 2.2 mg/L when carbonate is present ($C_T = 10^{-2}$ M). At $C_T = 3 \times 10^{-3}$ M, which is the normal carbonic species concentration in this research, manganese solubility would be 6.9 mg/L. Since manganese is present at a concentration of 1 mg/L in

this experimental investigation, manganese precipitation as $MnCO_{3(s)}$ will not be a concern.

2.5.2 Identity of Manganese Precipitates

In the present research, manganese precipitates (solid phases) that form in sequestration were evaluated by x-ray diffraction techniques and equilibrium modeling (discussed in Section 4.0). Equilibrium modeling was done to predict the species concentration and pH levels at which these precipitates may form so that these variables could be changed to reduce or eliminate this precipitation. However, other conditions and mechanisms may greatly influence this precipitation. Hence, the results of several investigations to determine the identity of manganese precipitates in aqueous solutions are discussed in this section, to provide an overview of the conditions under which some precipitates are formed and also to highlight the factors which favor the formation of a particular type of precipitate.

Compared to $MnCO_3$, manganese oxides are less soluble or even insoluble. This is illustrated by their solubility products. For example, the solubility product of $MnCO_{3(s)}$ is $10^{-10.4}$ whereas the solubility product of γ-MnOOH is approximately 10^{-42}. At pH 7, the equilibrium concentration of Mn^{3+} will be about 10^{-22} M, which is several orders of magnitude lower than the Mn^{2+} concentration when solubility is controlled by carbonate. Hence, manganese oxides will always be present as precipitates in natural water

systems unless other complexing agents are present. Robinson et al. (78) cite several authors who studied the identity of manganese precipitates and the conditions under which these precipitates were formed. The findings of these studies are outlined below:

1) In ammonia-buffered solutions MnOOH was the precipitate that was initially formed during autooxidation of Mn^{2+} at pH 9.

2) In a different experiment, the precipitate β-MnOOH was identified by x-ray diffraction when millimolar levels of manganese were oxygenated. MnOOH continued to be oxidized to the more stable MnO_2. It was pointed out that at higher pH and rapid oxidizing conditions, Mn^{2+} may be directly oxidized to MnO_2.

3) Species other than oxygen and hydroxide have caused a different mineral to crystallize. Several minerals such as $MnCO_3$ (rhodocrosite), (Mn,Fe)SiO3 (pyroxmangite ferroan), and γ-MnOOH have been identified under such conditions.

4) In one treatment plant, the black manganese precipitates were identified (9) as the Mn-oxide birnessite ($Na_4Mn_{14}O_{27}.9H_2O$).

The identity of iron precipitates are discussed in the next section.

2.5.3 Iron Precipitates

Studies of the identity of iron precipitates are also relevant to an understanding of manganese sequestration, as manganese precipitates may act similarly. Robinson et al. (77) found that "lepidocrocite," (γ–FeOOH) was the precipitate at pH less than 9, when oxygen was the oxidizing agent and the silica concentration was less than 7 mg/L as SiO_2. An increase in the silica concentration caused the formation of a more amorphous precipitate, decrease in the particle size and a more negative zeta potential. Similar results were obtained by Carlson and Schwertmann (9), who found that at silica concentrations less than 4 mg/L, lepidocrocite (γ–FeOOH) was formed. Ferrihydrites ($5Fe_2O_3.9H_2O$) containing 3%-7% Si (strongly associated with the precipitate) were formed by rapid oxidation of ground waters with 1-23 mg/L Fe, 7-12 mg/L Si, and pH 6-7. These precipitates had a high surface area of about 325-433 m^2/g. Further studies by Torrent and Gusman (85) revealed that ferrihydrite transformed to crystalline iron oxides in NaCl, KCl, $CaCl_2$, $MgCl_2$, $Mg(NO_3)_2$, $MgSO_4$, Na_2SO_4, $NaNO_3$ and LiCl solutions. However, this transformation took place over several months.

It is evident from the above results that the types of precipitates formed and their characteristics depend to a significant extent on:

1. the rate of oxidation;

2. presence or absence of other ions;

3. concentration of these ions; and

4. pH.

It is important to evaluate the precipitates formed in sequestration as this would promote a better understanding of this technique. Hence, x-ray diffraction and equilibrium modeling studies are done in this research and the results of these studies are discussed in Section 4.0.

2.5.4 Calcium-Phosphate Precipitate

As documented in Section 2.3.1, high turbidity was produced when groundwaters containing calcium were treated with polyphosphates (13, 78). This could be due to several factors. For example, increase in turbidity could be due to the formation of an insoluble calcium-phosphate species such as hydroxyapatite. Stumm and Morgan (63) as well as Snoeyink and Jenkins (83) have stated that hydroxyapatite should be considered as a likely precipitate in most natural waters as it is thermodynamically more stable than other calcium-phosphate forms. The conversion of calcite to hydroxyapatite in the presence of phosphate is illustrated in the following reaction and Figure 3:

$$10\ CaCO_{3(s)} + 2H^{+} + 6HPO_4^{2-} + 2H_2O \longleftrightarrow Ca_{10}(PO_4)_6(OH)_{2(s)} + 10HCO_3^{-}$$

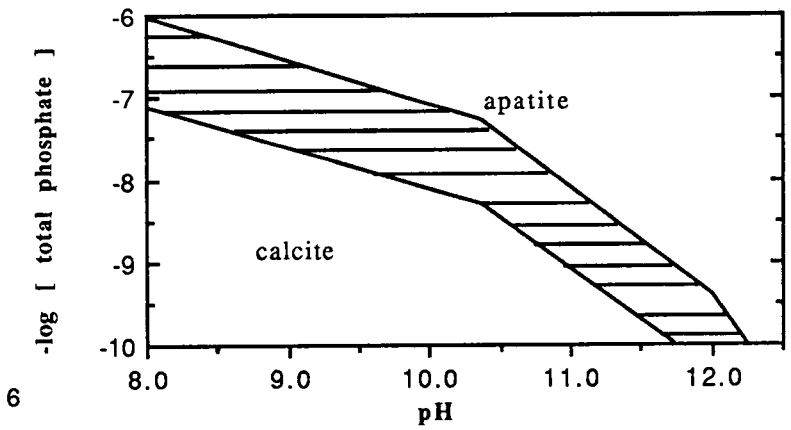

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Figure 3. Conversion of calcite to hydroxyapatite in the presence of phosphate

Wazer (97) stated that an insoluble hydroxyapatite precipitate was formed when phosphate was added to the water during calcium carbonate precipitation. Hence, even though silicate did not interact with calcium to a significant extent as noted by Robinson et al. (43), phosphate-calcium interactions could result in the formation of an insoluble hydroxyapatite precipitate, which would give rise to high turbidity in the treated water. Formation of a calcium-phosphate precipitate depends on various factors such as pH, temperature, calcium and phosphate concentrations and presence of other ions. The present study uses equilibrium modeling to determine the equilibrium concentrations of calcium and phosphate in solution at different pH levels, and the amount of calcium-phosphate precipitate that would be formed. The presence

of calcium-phosphate precipitates is verified by filtering treated samples through 0.1 micron filters.

2.6 IRON AND MANGANESE OXIDATION

Oxidation is an important chemical process by which changes in the valence of iron and manganese as well as other elements occur, causing a significant change in their physical and chemical characteristics. A review of these characteristics is especially important because changes in solubility, complexing capacity or sorptive behavior as a result of oxidation can have a significant effect on the sequestration process. Hence, iron and manganese oxidation in aqueous systems is discussed in this section to illustrate how characteristics of iron and manganese precipitates change due to oxidation and also highlight several factors which have a significant influence on iron and manganese oxidation.

In sequestration, oxidants are added to the ground water with sequestrants for disinfection purposes, and oxidation has been shown to be detrimental to the manganese sequestration process whereas it is beneficial to iron treatment. Hence, sufficient understanding of the factors which influence manganese oxidation is indispensable to any study of sequestration for practical application in actual water treatment practices.

2.6.1 Factors Affecting Iron Oxidation

As several factors which influence iron oxidation affect manganese oxidation also, factors which affect iron oxidation and their relation to manganese oxidation are discussed in this section. For example, both iron and manganese oxidation are catalyzed by increasing pH (63). At low pH levels (< 4), the oxidation rate of iron is independent of pH while in the high pH range, iron oxidation is strongly dependent on pH (oxidation of Fe^{2+} by oxygen is very slow below pH 6, and oxidation of Mn^{2+} is observed only at pH values above 8.5). Iron and manganese oxidation both follow the same rate law: $k \alpha (OH^-)^2$, where k represents the rate constant for iron oxidation and the autocatalytic rate constant in the expression for manganese oxidation by oxygen. Also, certain substances (HPO_4^-) which catalyze iron oxidation have been found to retard manganese oxidation (63), and both iron and manganese oxidation depend on p_{O2}. Schenk and Weber (81) point out that sodium silicates can accelerate ferrous iron oxidation by raising the pH as well as by acting as a catalyst. They give an empirical equation of the form shown below to describe the catalytic effects of silica on oxidation of ferrous iron by oxygen:

$$-d[Fe^{2+}]/dt = \{kp_{O2}[OH^-]^2 + k_{si}[H_4SiO_4]^n\,[OH^-]^m\}\,[Fe^{2+}],$$

where $-d[Fe^{2+}]/dt$ = 'k_o' the observed rate of oxidation,

k = Iron oxidation rate in a bicarbonate system,

k_{si} = Rate coefficient for the catalytic effect of silica on Fe^{2+} oxidation,

and p_{O2}= partial pressure of oxygen

Studies by various researchers can be summarized as follows:

1) The reaction rates for Mn^{2+} and Fe^{2+} oxidation are strongly pH dependent.

2) Catalysts such as HPO_4^{2-} accelerate iron oxidation, but retard manganese oxidation.

2.6.2 Factors Affecting Manganese Oxidation

Manganese can exist in a number of oxidation states ranging from -III to +VII (65). Of these, the II, III and IV states are of greatest importance to this research, as the other oxidation states are unstable at the pH levels found in most natural waters. In conventional water treatment practices, manganese is removed by oxidation to insoluble Mn^{3+} or Mn^{4+} and subsequently removed by filtration, whereas manganese sequestration is a process which involves the addition of sequestrants to prevent the oxidation of Mn^{2+} to higher valence states during disinfection. Manganese may be present as Mn^{4+} in some surface waters, but in most groundwaters, manganese is present as Mn^{2+} due to low pE levels (78). Morgan (65) states that Mn^{2+} is the most stable oxidation state

of the element and compares its resistance to oxidation with Cr^{2+} and Fe^{2+} by the corresponding oxidation potentials (E^o):

$$Mn^{2+} \longleftrightarrow Mn^{3+} + e^- \qquad E^o = -1.5v$$

$$Fe^{2+} \longleftrightarrow Fe^{3+} + e^- \qquad E^o = -0.77v$$

$$Cr^{2+} \longleftrightarrow Cr^{3+} + e^- \qquad E^o = +0.41v$$

Even though manganese is more resistant to oxidation than iron and chromium, in natural waters manganese oxidation may be accelerated by various factors, including pH, manganese concentration, dissolved oxygen, and availability of iron oxide surface sites for catalyzation. Morgan et al. (66) state that γ-FeOOH (a product of ferrous oxygenation) catalyzes manganese oxidation. The following empirical equation illustrates the catalytic effects of the iron oxide on manganese oxidation:

$$-d[Mn^{2+}]/dt = k[\gamma\text{-FeOOH}]_o\,[O_2]\,[H^+]^{-2}\,[Mn^{2+}]$$

Morgan et al. state that the rate of oxidative manganese removal increases greatly with increasing pH and the amount of oxide surface or surface sites. Catalyzation of manganese oxidation occurred when manganese was adsorbed onto the iron oxide surface. Oxidation of manganese due to sorption reactions of Mn^{2+} with Mn and Fe oxides has been reported by various researchers (16, 65, 63, 62, 66, 64). Oxidation of Mn^{2+} is also catalyzed by $MnO_{2(s)}$ and other oxidation products of Mn^{2+} oxidation (autocatalyzation). Hence, a rate expression for manganese oxidation should also include an

autocatalytic rate constant "k". Stumm and Morgan (63) give an integrated rate expression of the following form for the oxidative removal of manganese by oxygen in the absence of iron, where $k = k' [OH^-]^2 p_{O2}$:

$$-d[Mn^{2+}]/dt = k_o [Mn^{2+}] + k [Mn^{2+}] [MnO_X]$$

The reaction may be visualized to proceed according to the following steps:

$$Mn^{2+} + 1/2\ O_2 + H_2O \xrightarrow{\text{slow}} MnO_{2(s)} + 2H^+$$

$$Mn^{2+} + MnO_{2(s)} \xrightarrow{\text{fast}} Mn^{2+}.MnO_{2(s)}$$

$$Mn^{2+}.MnO_{2(s)} + 1/2\ O_2 + H_2O \xrightarrow{\text{slow}} 2MnO_{2(s)} + 2H^+$$

Morgan and Stumm (61) stated that the products of Mn oxygenation in bicarbonate waters were finely divided colloidal dispersions of MnO_X. Due to the large surface area available for sorption of Mn^{2+} in such waters, it would appear that the degree of manganese oxygenation should be significant. However, due to the low manganese concentrations normally found in most natural waters and the strong dependence of the autocatalytic rate constant on pH, oxygenation of manganese is particularly slow in most natural waters (16, 64). Figure 4, plotting autocatalytic manganese oxygenation, shows that the rate of manganese oxygenation decreases from pH 9.5 to 9.0 (Mn^{2+} = 0.0045M).

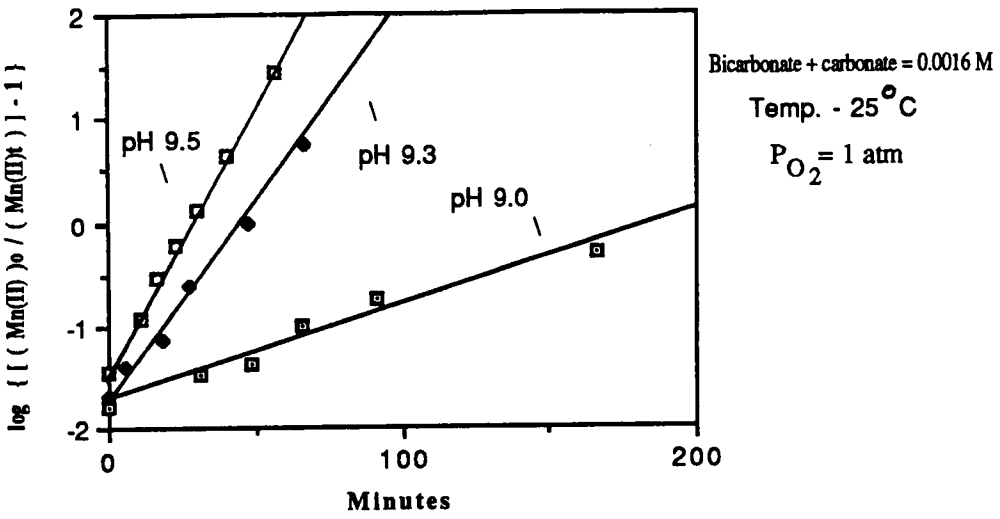


Figure 4. Manganese oxidation rate as a function of pH

Results obtained by various researchers on manganese oxidation can be summarized as follows:

1) Manganese oxygenation is particularly slow at pH levels found in most natural waters.

2) Manganese oxidation rate increases with increasing pH [$k \alpha (OH^-)^2$], manganese concentration, and available oxide surface sites.

3) Products of manganese oxygenation such as MnO_2 and certain iron oxides catalyze manganese oxygenation.

These results clearly show that pH has a significant effect on manganese oxidation. The effect of pH on manganese oxidation and its influence on manganese treatability are further studied in the present research.

2.7 SURFACE CHARGE

In previous sections, the oxidation and precipitation of iron and manganese were discussed. These precipitates will be dispersed in the colloidal form by sequestrants (polyphosphates or silicates) which may enhance the surface charge of these particulates and stabilize them, thus limiting the agglomeration and subsequent settlement of particulates. However, addition of other ions may result in charge neutralization (destabilization) of these colloids resulting in subsequent settlement in the distribution system. Therefore it is important to recognize which ions or polymers stabilize these colloids and identify those ions which destabilize them. Hence, in this section, the origination of surface charge on colloids and factors which influence this charge are discussed.

2.7.1 Origin of Surface Charge

Surface charge on colloids may arise from the ionization of functional groups on the surfaces of the solids: e.g., -OH, -COOH. The electric charge of a silica surface in water can be explained by the acid-base behavior of the silanol (-Si-OH) groups found on the surface of hydrated silica:

$$\text{-Si-OH}_2^+ \quad \overset{k_1}{<\!\!\longrightarrow\!\!>} \quad \text{-Si-OH} \quad \overset{k_2}{<\!\!\longrightarrow\!\!>} \quad \text{-Si-O}^-$$

The charge is positive at low pH values and negative at higher pH levels. Such amphoteric behavior is seen in the case of several

oxides and hydroxides; thus the charge is pH-dependant. At some intermediate pH, the surface charge will be equal to zero. This pH is defined as the pH of zero point of charge (pH_{zpc}). Charge can also originate when solutes are adsorbed onto solid surfaces. These processes are referred to in the literature as surface reactions. The following equations illustrate these effects:

$$FeOOH(s) + HPO_4^{2-} = FeOHPO_4^{-}(surface) + OH^-$$

$$MnO_2.H_2O(s) + Zn^{2+} = MnOOHOZn^{+}(surface) + H^+$$

The electric charge on the surface of the colloids and the bulk of the solution are related to each other, as chemical reactions take place between the surface of a solid and the ionic constituents in solution. These ionic constituents are called "potential determining species." Shown below are some chemical reactions between potential determining species and the colloidal surface (with potential determining species shown in italics):

$$FePO_4(s) + \mathit{H_2PO_4^-} = Fe(HPO_4)_2^{-}(surface)$$

$$FeOOH(s) + \mathit{H^+} = Fe(OH)_2^{+}(surface)$$

$$FeOOH(s) + \mathit{OH^-} + H_2O = Fe(OH)_4^{-}(surface)$$

$$SiO_{2(s)} + \mathit{OH^-} = SiO_2(OH)^{-}(surface)$$

The origin of surface charge and factors which affect the surface charge are very important in evaluating the stability of dispersions. In the present research, the surface charge is determined using

streaming current detectors to study the effect of treatment on manganese colloids formed during oxidation.

2.7.2 Principles of Stabilization and Destabilization of Colloids

Stabilization or destabilization of colloidal particulates by multivalent cations is a critical factor in sequestration, as this would decrease or increase the effectiveness of a sequestrant. Hazel (27) found that adsorption of multivalent cations such as calcium onto the surfaces of stabilized iron oxide sols decreases the negative charge on the sols, opposing the stabilizing action of silicates.

A colloidal suspension (dispersion) can be viewed as stable when it shows no tendency to aggregate. Colloids with a high surface charge are more stable, as repulsive forces between these particles disperse them and limit particle contact, growth and subsequent sedimentation. However, even particles with a high surface charge can be destabilized by counterions (ions of opposite charge to that of the colloid) present in the solution. Every charged particle has a double layer surrounding it. This double layer is comprised of a fixed layer (stationary layer) of ions attracted to the charged surface and a diffuse layer of counterions surrounding the stationary layer. Electrostatic forces attract these counterions to the charged surface. When the colloid is negatively charged, positive ions are attracted to the charged surface and there is a high concentration of positively charged ions in the neighborhood of the

charged particle. Since negatively charged ions are repelled by the charged surface, there is a deficiency of negatively charged ions in the neighborhood of the particle. At equilibrium, the average local concentration of ions (n+) at a distance "d" from the charged surface with an electric potential "ϕ_o" can be expressed as a function of the electric potential "ϕ" at that distance, the concentrations of ions "n+*" in the bulk solution, and the valence "v+" of the ions:

$$n+ = n+^* \exp(-v+c\phi/kT)$$

and where "c," "k" and "T" are the following constants.

"c" = elementary charge of the electron,

"k" = Boltzmann's constant, and

"T" = temperature in Kelvin.

The potential "ϕ" at any distance "d" from the charged surface can be found from the following equation:

$$\phi = kTy/vc$$

where $$y = 2\ln[(e^{z/2} + 1 + (e^{z/2} - 1)e^{-dx}]/[e^{z/2} + 1 + (e^{z/2} - 1)e^{-dx}]$$

and $$z = vc\phi_o/kT.$$

"y" and "z" are dimensionless quantities, and "d" is the distance from the charged surface. The inverse of the double layer thickness "x" can be found from the following equation:

$$x = (8\pi n_o c^2 v^2/EkT)^{1/2}$$

where "n_o" = number of ions/L

and "E" = dielectric constant.

According to the above equations, the decay of the potential with distance from the charged surface due to the destabilizing effects of counterions would be more pronounced for divalent electrolytes than for monovalent electrolytes. This could be further understood by considering the effects of 10mM NaCl (monovalent electrolyte) and 5mM $CaSO_4$ (divalent electrolyte) solutions on the decay in potential from a charged surface maintained at a constant potential of -35 mV. The decay in potential with distance from the charged surface is more pronounced in the presence of calcium sulfate than in the presence of sodium chloride. In the presence of calcium sulfate, at distances of 1 and 100 angstroms from the charged surface, the potential decays to -33.1 mV and -0.03 mV respectively, whereas for sodium chloride, the potential decays from a value of -33.8 mV to only about -1.52 mV for the same distance. Also, the concentration of calcium ions at a distance of 1 angstrom from the charged surface is about 1.8 times greater than the concentration of sodium ions.

Figures 5 and 6 show the potential versus distance and the ionic concentration versus distance from the charged particle maintained at a potential of -35 mV for 10 mM NaCl and 5 mM $CaSO_4$. Figure 5 illustrates that the decay in potential with distance from the charged surface is more pronounced for calcium than for sodium. Decrease in potential with distance will result in a corresponding decrease in the range of repulsive forces between similarly charged particles (destabilization), permitting particles to contact, grow in size (flocculate) and subsequently settle. Destabilization adversely affects the sequestration process as it results in particle growth (flocculation) which may cause an increase in turbidity and subsequent settlement of these flocs. Weber states that the concentration of Na^+ and Ca^{2+} required to destabilize a negatively charged colloid are observed to vary approximately in the ratio of $1:10^{-2}$. This is also consistent with the Schulze-Hardy rule which states that monovalent ions such as sodium have very little effect on the stability of negatively charged colloids even at very high concentrations. These results imply that divalent ions such as calcium should destabilize iron and manganese colloids to a significant extent in sequestration, requiring higher sequestrant dosages to offset these effects.

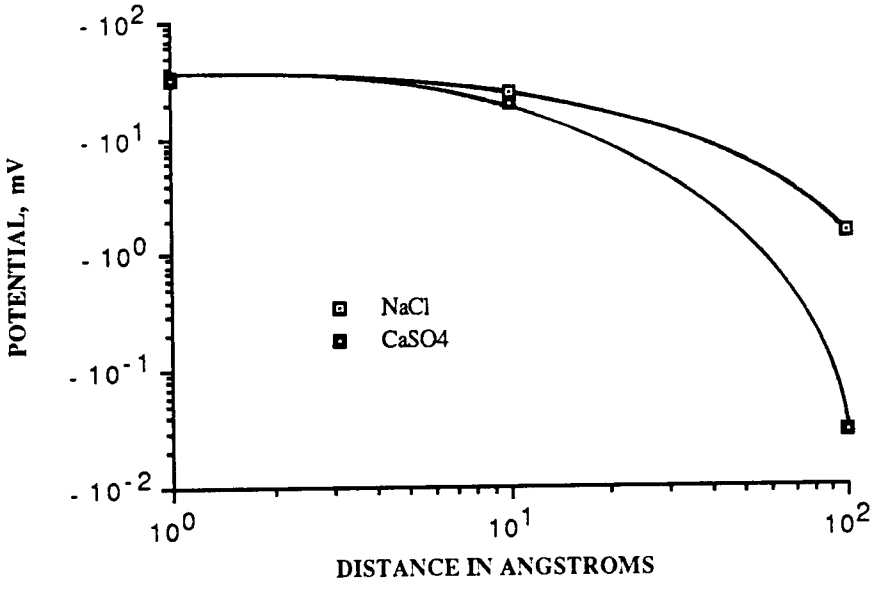


Figure 5. Potential versus distance from the charged surface

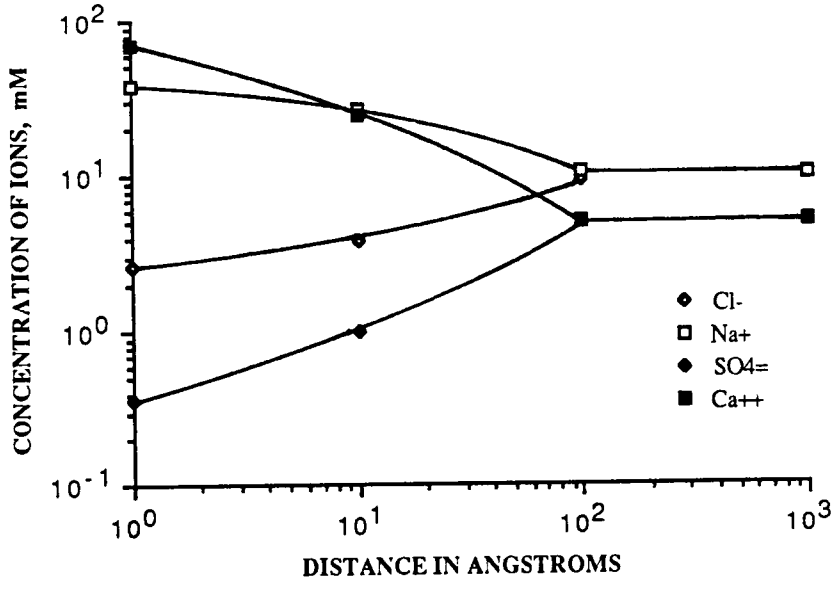


Figure 6. Ionic concentration versus distance from the charged surface

2.7.3 Effect of pH on Colloidal Charge

In addition to the presence of other ions, the pH of the groundwater can also have a significant effect on the charge of colloidal particulates formed in sequestration. The effects of pH have been studied in the present research to determine its effects on manganese treatability. The importance of this variable is explained in the following discussion.

Stern (86, 87) has given an equation of the form shown below to determine the surface potential of a colloid as a function of the concentration of the potential determining species:

$$\phi_o = [kT/ve] \ln [C]/[C_o],$$

where

"k" = Boltzmann's constant

"T" = Temperature in Kelvin

"e" = elementary charge of the electron

"v" = valence of the potential determining ion

"C" = concentration of the potential determining ion at different pH levels

"C_o" = concentration of the potential determining ion at the pH_{zpc} of the colloid (26).

As C_o varies with pH_{zpc}, pH_{zpc} must be determined to solve this equation. Various researchers (63, 71) have given a pH_{zpc} for MnO_2 varying from 2 to 4.5. Stumm and Morgan (63) have stated that the pH_{zpc} for $FePO_4$ lies between 5 and 6. Considering a value of 5 as pH_{zpc} for colloidal MnO_2 and $FePO_4$, the surface potential for these colloids at various pH levels can be calculated in a specific case, where H^+ is the potential determining ion. The results presented in Table 1 show that the charge is negative at pH levels above the pH_{zpc}, and that the strength of the negative charge increases with pH:

Table 1. Surface potential as a function of pH

pH:	2	3	4	5	6	7	8	9	10
f_omV:	+17	+12	6	0	-6	-12	-17	-23	-29

So far, theories on the origin of surface charge on colloids, the role of potential determining ions in determining this surface charge, adsorption (surface reactions), stabilization and destabilization of colloids and effects of pH on surface charge were discussed to illustrate the relationship between a colloidal surface and the bulk of the solution. In the next section, experiments performed to quantify this surface charge on iron and manganese colloids are discussed.

2.7.4 Factors which Affect Surface Charge of Iron and Manganese Colloids

In this section, the effect of phosphates and silicates on the colloidal charge of iron oxides and the effects of silicates on manganese dioxide colloids in the presence and absence of calcium are discussed. The extent to which stabilized colloids are destabilized by calcium ions have been quantified by these investigations.

2.7.4.1 Effects of Phosphates and Silicates on Iron Oxide Colloids in the Presence and Absence of Calcium

Various researchers (28, 30, 34, 33) have found that the addition of negative ions to iron oxide colloids (sols) convert them to the stable negative form. While studying the effects of phosphates and silicates on preformed iron oxide sols, Hazel (28) found that charge reversal and stabilization of the sols took place at higher ionic concentrations of the phosphate and silicate species. The iron oxide sols were present at a concentration of 80 mg/L, and the silicate dosage was 80 mg/L as SiO_2. In phosphate studies, the phosphate dosage varied from 3.1 mg/L to 44.1 mg/L, and iron oxide sols were present at concentrations of 0.2 g/L to 2.75 g/L. Among the various phosphate types used in Hazel's studies, sodium hexametaphosphate had the greatest effect in stabilizing the iron oxide sols (0.2 g/L) at pH 4.4 and 6.0 whereas orthophosphate had the least effect. The dosage of sodium hexametaphosphate required

to stabilize the system (0.2 g iron oxide sol/L) at pH 4.4 and 6.0 was only 4.3 mg/L, whereas higher dosages of pyrophosphate and orthophosphate were required to produce the same effects. The ratio of dosages of sodium hexametaphosphate ($Na_6P_6O_{18}$): pyrophosphate (NaP_2O_7): orthophosphate (Na_3PO_4) was 1 : 1.65 : 2.45. Similar results were obtained by Wazer and Besmertnuk (98) in their studies on the effects of polyphosphates on clay suspensions. It was found that the more complex polyphosphates caused a significant increase in the zeta potential of clays and stabilized them. In the absence of polyphosphates, the zeta potential of clays was observed to be -71 mV, whereas in the presence of sodium orthophosphate and sodium pyrophosphate, the zeta potential increased to -109 and -114 respectively.

In the presence of calcium, Hazel found that a greatly increased amount of the phosphate was required to impart a sufficient negative charge to the iron oxide colloids and stabilize them. The dosage of hexametaphosphate required to stabilize 0.2 g/L of the iron oxide sol varied from 15.3 mg/L to 1224 mg/L for calcium dosages of 22.2 mg/L to 222.0 mg/L. In other words, increase in calcium chloride dosage by a factor of 10 increased the phosphate requirement to stabilize the sol by a factor of 80. Similar results were obtained by Hazel (27) when calcium chloride was added to stabilized iron oxide sol/silicate solutions. This behavior was attributed to the adsorption of calcium ions which decreased

the strength of the negative charge on the iron particulates, making them less stable as a colloidal suspension.

Hazel (28) also found that the phosphate dosages required to stabilize ferric sols depended on three factors: first, the pH of the system; second, the presence of other ions, particularly multivalent ions such as calcium; and third, the concentration of iron oxide. In the absence of calcium, less phosphate dosage was required to stabilize the iron oxide sols at higher pH values; thus, while 2.7 mg/L of hexametaphosphate was required at pH 5.6, only 1.2 mg/L was required at pH 6.8. Calcium ions had the reverse effect, as less phosphate was require to stabilize the sols at lower pH levels. An explanation for this behavior can be attributed partly to the desorption of calcium ions from the iron oxide surface. Stumm and Morgan (63) stated that cations would desorb from oxide surfaces when the pH is lowered. Hence, the extent of destabilization should also be minimal at these lower pH levels. These results indicate that in sequestration by polyphosphates, lower pH levels may be more favorable to treatment in the presence of calcium. These effects are also examined in the present research.

2.7.4.2 Effects of Silicates on Manganese Dioxide Colloids in the Presence and Absence of Calcium

Similar to the observed effects of silicates on iron oxide sols, Hazel (29) found that silica stabilized manganese colloids also to a significant extent in the absence of calcium. The addition of

flocculating electrolytes such as potassium chloride, barium chloride and thorium nitrate had no significant destabilizing effects on the stabilized colloid. In these studies by Hazel, manganese dioxide concentration was maintained constant at 0.013 g/L whereas silica concentration varied from 0.066 to 0.33 g/L. Stabilization of manganese dioxide by silica was attributed to mutual adsorption.

Posselt et al. (72) tested the hypothesis that destabilization and coagulation occur as a result of direct charge reduction by sorption of multivalent cations such as calcium onto colloidal manganese dioxide. Manganese dioxide sols were present at a concentration of 2.5 mg/L in these studies. By introducing various dosages of calcium to colloidal suspensions of hydrous manganese dioxide and maintaining a constant pH of 5 by addition of dilute acids and bases, they found that the electrophoretic mobility of hydrous manganese dioxide decreased from -2.5 to -1 at a calcium dosage of about 10 mg/L and that coagulation occurred at this point. Decrease in MnO_2 surface charge was believed to be due to sorption of calcium onto the surface of colloidal MnO_2. It was stated that as a general rule, sorption of inorganic cations such as calcium by MnO_2 would lead to charge reduction and destabilization of the colloid in the presence of sufficiently high concentrations of the sorbing cation. According to at least two other studies (63, 75), MnO_2 has a high sorption capacity for calcium, magnesium, zinc, silver and other cations. Since pH_{zpc} of MnO_2 is about 4.5, MnO_2 should be negatively charged at the pH levels in most natural waters, and according to

the Shulze-Hardy rule should be destabilized to a significant extent by divalent cations such as calcium.

Results obtained by various researchers in stabilization and destabilization of colloidal iron and manganese can be summarized as follows:

1) Calcium destabilized MnO_2 suspensions.

2) Silica stabilized manganese dioxide sols to a significant extent (29). Higher concentrations of flocculating electrolytes were required to destabilize these colloids in the presence of silicates.

3) Higher ratio (multimeric) silicates and more polymeric phosphates produced better iron stabilization than monomeric silicates or orthophosphates.

4) Calcium destabilized preformed iron oxide colloids to a significant extent.

5) The level of iron stabilization was greater at lower pH levels when calcium was present.

2.8 HYDROLYSIS OF POLYPHOSPHATES

In the previous section it was stated that polyphosphates stabilized iron oxide sols to a significant extent. However, since polyphosphates will depolymerize and break down into

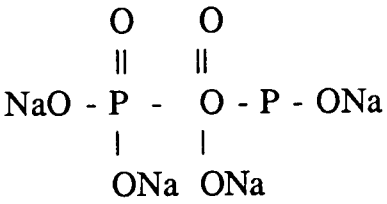
orthophosphates and monomeric silicates over time and lose their effectiveness, it is important to understand the rate at which they depolymerize and to identify factors which affect this rate. The rate of reversion of polyphosphates to orthophosphate has much significance in manganese sequestration, as researchers have observed that reversion to orthophosphates would decrease the effectiveness of polyphosphates in controlling manganese problems. Studies on reversion of polyphosphates to orthophosphates are discussed in this section.

2.8.1 Structure and Properties of Inorganic Phosphates

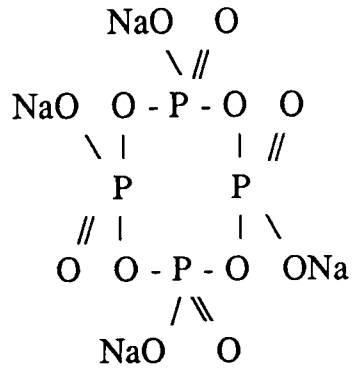
According to Weintritt (104) of Petroleum Associates, Lafayette, Inc., polyphosphates, metaphosphates and pyrophosphates are the various salts of orthophosphoric acid. The general equation for such a dehydration reaction to form the polyphosphates is:

$$(n-2)\ NaH_2PO_4 + 2Na_2HPO_4 \rightarrow Na_{n+2}P_nO_{3n+1} + (n-1)\ H_2O, \text{ for } n > 2$$

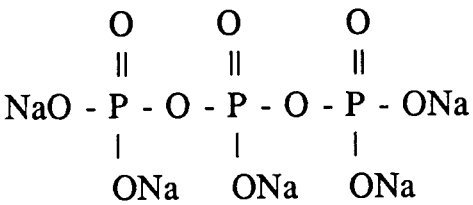
The various inorganic phosphates show variations of repeating oxygen-phosphorus (P-O-P) structures as illustrated in Figure 7. For example, it is believed that sodium hexametaphosphate has a cyclic structure with a chemical formula $Na_6(PO_3)_6$. It is highly soluble in water and is polymeric, with molecular weights as high as 13,000 according to various researchers referred to by Weintritt (104). The P-O-P bonds are highly unstable in aqueous solutions.



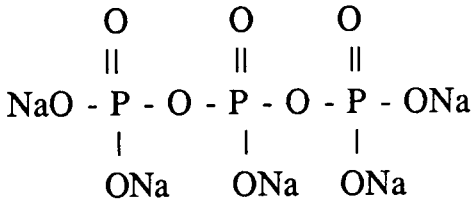
Sodium Pyrophosphate



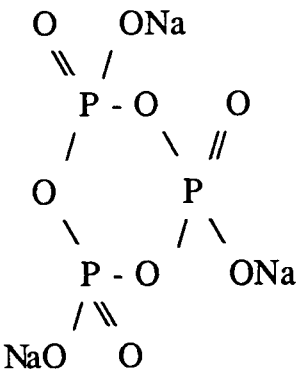
Sodium Tetrametaphosphate



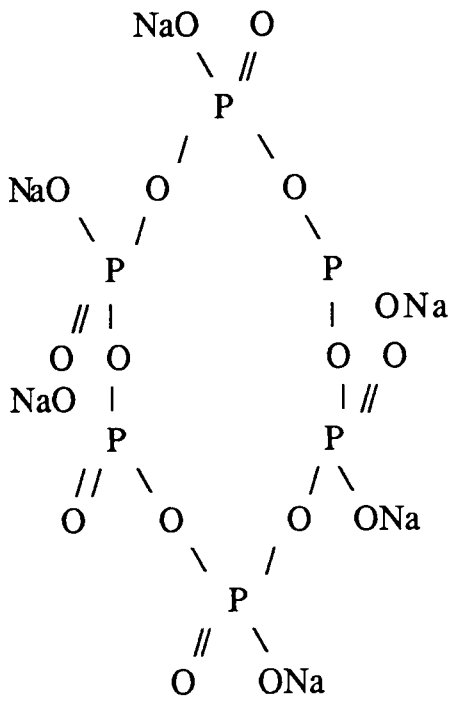
Sodium Tripolyphosphate



Sodium Polyphosphate



Sodium Trimetaphosphate



Sodium Hexametaphosphate

Figure 7. Structure of several inorganic phosphates

Polyphosphates hydrolyze (revert or depolymerize) to simpler forms such as orthophosphate when added to water. Tripolyphosphate, for example, hydrolyzes as follows:

$$HP_3O_{10}^{4-} + 2H_2O \longrightarrow 3HPO_4^{2-} + 2H^+$$

Wazer (99) stated that the activation energy for the splitting of the P-O-P linkages in phosphate chains range from 20 to 40 kcal./mole of linkages, which again depends on several variables, including temperature, pH, and phosphate concentration. Snoeyink (83) has stated that hydrolysis of polyphosphates is affected by pH, temperature and presence of calcium ions. These variables are discussed in the following sections.

2.8.2 Effect of Temperature on Polyphosphate Reversion Rate

Wazer (99) stated that the temperature is probably the best defined of all the factors affecting the reversion rate. The variation of the reversion rate constant ("k") with temperature can be denoted by the Arrhenius equation:

$$k = A\, e^{-E/RT}$$

where the term "A", is independent of the temperature and is called the "frequency factor," "E" is the activation energy required to break the P-O-P bonds and "R" and "T" are the gas constant and the absolute temperature respectively. For an average activation

energy of 25 kcal/mole and an increase in temperature of 26 ^{o}C, the rate constant increases by a factor of 9.

2.8.3 Effect of Other Ions on the Phosphate Reversion Rate

The hydrolysis to orthophosphate could further be affected by complexation of phosphates with other ions such as calcium (104). Stumm and Morgan (63) have stated that the metal-ion (Ca^{2+}, Mg^{2+}) complexing of the polyphosphates can affect the reversion rates significantly. Green (24) found that calcium accelerated the polyphosphate reversion rate. Magnesium had very little effect on the reversion rate; however, when it did have any effect, it generally tended to decelerate the rate of reversion. Weintritt also found that polyphosphate reversion rate increases significantly in the presence of bacteria, algae and enzymes. For example, the half-life of pyrophosphate and tripolyphosphate is about 4000-5000 days in distilled water whereas it is 100 to 1000 times faster in rivers and lakes, probably due to the presence of the microbial population as well as other ions.

2.8.4 Effect of pH and Phosphate Concentration on the Phosphate Reversion Rate

Snoeyink and Jenkins stated that the polyphosphate reversion rate is very sensitive to changes in pH. For example, at a temperature of 10 ^{o}C and pH 4, it would take about 1 year for 5% of a pyrophosphate solution to hydrolyze to orthophosphate whereas

at pH 10 it would take well over a century for the same amount to hydrolyze at the same temperature. The effects of pH and polyphosphate concentration on the reversion rate has been investigated by Green (24). Typical results from Green's studies are illustrated in Figure 8 and Table 2. Table 2 illustrates that there is a significant difference in the phosphate reversion rate between phosphate concentrations of 5 and 50 mg/L at the same pH. In the case of sodium tripolyphosphate, at pH 5 the reversion was 100% complete in 22.5 hours at a phosphate concentration of 50 mg/L, whereas only 87% had reverted at a concentration of 5 mg/L. At pH 9, the amount of reversion was only 19% at a phosphate concentration of 50 mg/L. At lower phosphate concentrations (5 mg/L) and pH 9, reversion increased to 25%. These results illustrate that as a general rule, the reversion rate is directly proportional to phosphate concentration at a lower pH, whereas at higher pH levels, the reversion rate is inversely proportional to the phosphate concentration. This is observed to be true for sodium tetraphosphate, sodium tripolyphosphate, Nalco no. 519 and sodium metaphosphate. Tetrasodium pyrophosphate and sodium trimetaphosphate followed a slightly different trend. However, at a fixed phosphate concentration, the reversion rate decreased with increasing pH for all phosphate types. Shen and Dyroff (80) found that the reversion rate of sodium tripolyphosphate followed first-order kinetics in concentrated solutions and increased exponentially with solids and sodium concentration.

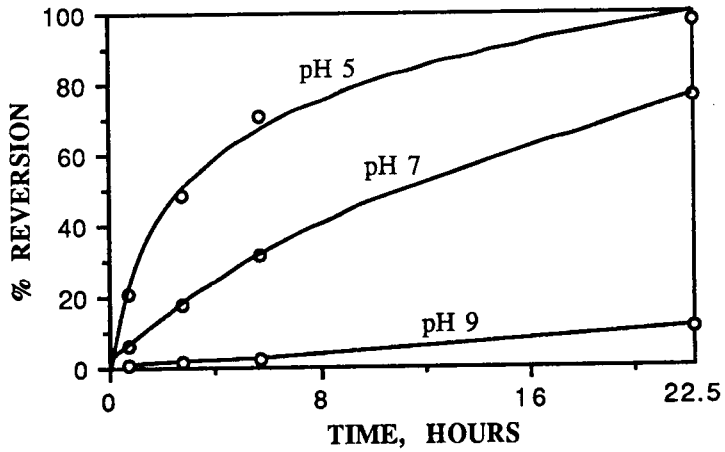


Figure 8. Reversion of tetrasodium pyrophosphate at 190°F and 50 mg/L of phosphate as PO_4

Table 2. Effect of pH and concentration on % phosphate reverted after 22.5 hrs. at 190°F

Phosphate Type	pH 5		pH 9	
	50 mg/L	5 mg/L	50 mg/L	5 mg/L
Tetrasodium pyrophosphate	98	93	10	4
Sodium tripolyphosphate	100	87	19	25
Sodium tetraphosphate	84	71	24	27
Nalco no. 519	69	56	26	33
Sodium metaphosphate	44	35	16	31
Sodium trimetaphosphate	10	13	3	11

Aulenbach (2) pointed out that there may be a particular polyphosphate that may be best suitable for ground waters with a certain chemical composition. He further stated that the suitability of a polyphosphate must be determined experimentally by testing different polyphosphates for a particular type of water and that the optimum pH and dosage must be determined experimentally. A study involving the effects of variables such as type of polyphosphate and composition of natural waters might prove to be beneficial in selecting a particular type of polyphosphate for sequestration. Aulenbach also found that polyphosphates are more effective than orthophosphates in controlling iron problems and that they cease to be effective when they break down into orthophosphates. Considering Aulenbach's findings, the present study also examines further the correlation between the polyphosphate characteristics and the success or failure of manganese sequestration treatments.

2.9 POLYPHOSPHATE COMPLEXES

The previous section explained that polyphosphates are more effective than orthophosphate in sequestration. The better performance of polyphosphates in sequestration may particularly be due to the ability of polyphosphates to be form stronger complexes with cations than orthophosphates. Polyphosphates can form complexes with a number of cations such as Ca^{2+}, Mg^{2+}, Mn^{2+} and Fe^{3+}. Wazer and Campanella (93) demonstrated that all of the chain

phosphates are strong complexing agents which tie up the cations so that precipitation and subsequent deposition will not take place. This section illustrates the potential for polyphosphates to form strong complexes with manganese in the manganese sequestration process and prevent its deposition in the distribution system. This can be understood from the equilibrium constants obtained by several researchers (39, 63, 92) for polyphosphate complexation with manganese. Hem (39) quotes Jones, Monk and Davies who give a constant of about 3.7 X 10^5 for the following equilibrium which illustrates the ability of polyphosphates to form strong complexes with manganese:

$$P_3O_9^{3-} + Mn^{2+} \longleftrightarrow MnP_3O_9^-$$

and a constant of 5.5 X 10^5 for the equilibrium

$$P_4O_{12}^{4-} + Mn^{2+} \longleftrightarrow MnP_4O_{12}^{2-}$$

It is evident from these equilibrium constants that stronger complexes are formed with the more polymeric phosphates, one exception being that a constant of 3 X 10^5 for the equilibrium

$$2P_5O_{16}^{7-} + Mn^{2+} \longleftrightarrow MnP_{10}O_{32}^{12-}$$

was reported by Wazer and Campanella (92). They report that complexing of manganese by orthophosphate and pyrophosphate was found either weak or nonexistent. However, pyrophosphates (condensed or polymeric phosphates) have been known to form strong complexes with iron and calcium in aqueous solutions.

Stumm and Morgan (63) have reported that while less than 1% of orthophosphate is complexed with iron at pH 5, more than 99% of pyrophosphate is complexed with iron at the same pH when $Fe_T=1X10^{-5}$ M and $P_T=1X10^{-5}$M. Similarly, Stumm and Morgan found that pyrophosphate forms stronger complexes with calcium than orthophosphate. According to their calculations, at pH 7, when $Ca_T=1X10^{-3}$M and $P_T=1X10^{-5}$M, only 20% of orthophosphate is complexed with calcium, whereas 60% of pyrophosphate is complexed with calcium at the same pH. When the total calcium is increased to $5X10^{-3}$M, the amount of pyrophosphate complexed with calcium increased to 90%, compared to 60% for orthophosphate. It is evident from these results that polymeric phosphates form stronger complexes than orthophosphate. Since formation of these complexes may have a significant effect on manganese treatability, in the present research, orthophosphates and four different types of polyphosphates are tested. Ultrafilters are used to verify whether these polyphosphate-manganese complexes are actually formed.

2.10 DEPOLYMERIZATION OF SODIUM SILICATES

As already documented in Section 2.8, depolymerization of polyphosphates decrease their effectiveness in sequestration. However, a review of the pertinent literature indicates that depolymerization of polymeric sodium silicates may be a more serious problem. While Robinson and Klueh (79) found that generally, the degree of depolymerization of polyphosphates was only about 35% to 50% for a 10-day time period (14,400 minutes),

Browman (6) found that 90% of silicates depolymerized within 80 minutes. These results imply that depolymerization of silicates is roughly 500 times faster than polyphosphates. The silicate depolymerization rate is influenced by several factors, including pH and silicate concentration. This tendency of silicates to depolymerize when added to water brings to light the importance of lag time between silicate and chlorine or chlorine dioxide addition. Lag time is important because the solid phase formed in sequestration during oxidation by chlorine or chlorine dioxide requires a sufficient amount of silicates in the polymeric form for its effective dispersion as a colloid. The lag time between silicate and chlorine addition has been investigated by Browman (6), but the same has not been studied for silicate and chlorine dioxide. Therefore, the aim of this section is to provide an insight into various factors which affect the silicate depolymerization rate, in order to address the importance of lag time between silicate and chlorine dioxide addition (which is also further investigated in the present study).

O' Connor (68) stated that in the silicomolybdate method of analysis, the rate-limiting step in the color development of complex silicates was the depolymerization of the silicate polymers to monomeric silicic acid. Hence, the extent of color development with time, which is proportional to the optical density, should indicate the degree of depolymerization of silicates to monomeric silicic acid. Hence, Browman (6) studied the rate of color development at 400

nm produced by the reaction of monomeric silica with molybdic acid to determine the rate at which sodium silicates of different SiO_2/Na_2O ratios and dilutions depolymerized with time. Browman found that for a 1/10 dilution of 3.22 ratio sodium silicate, more than 90% of the silicate depolymerized to monomeric silica in 80 minutes. The rate constant for the formation of b-silicomolybdate complex from depolymerization of polysilicates increased with decreasing SiO_2/Na_2O ratios, indicating that the simpler silicates depolymerized at a rate much higher than the complex silicates. Thus in the present research, a 3.22 ratio sodium silicate was used, as this was expected to have a lower depolymerization rate than the simpler silicates.

Figure 9 shows the pH versus concentration of the various silicate species (monomeric and polymeric) for informational purposes (63).

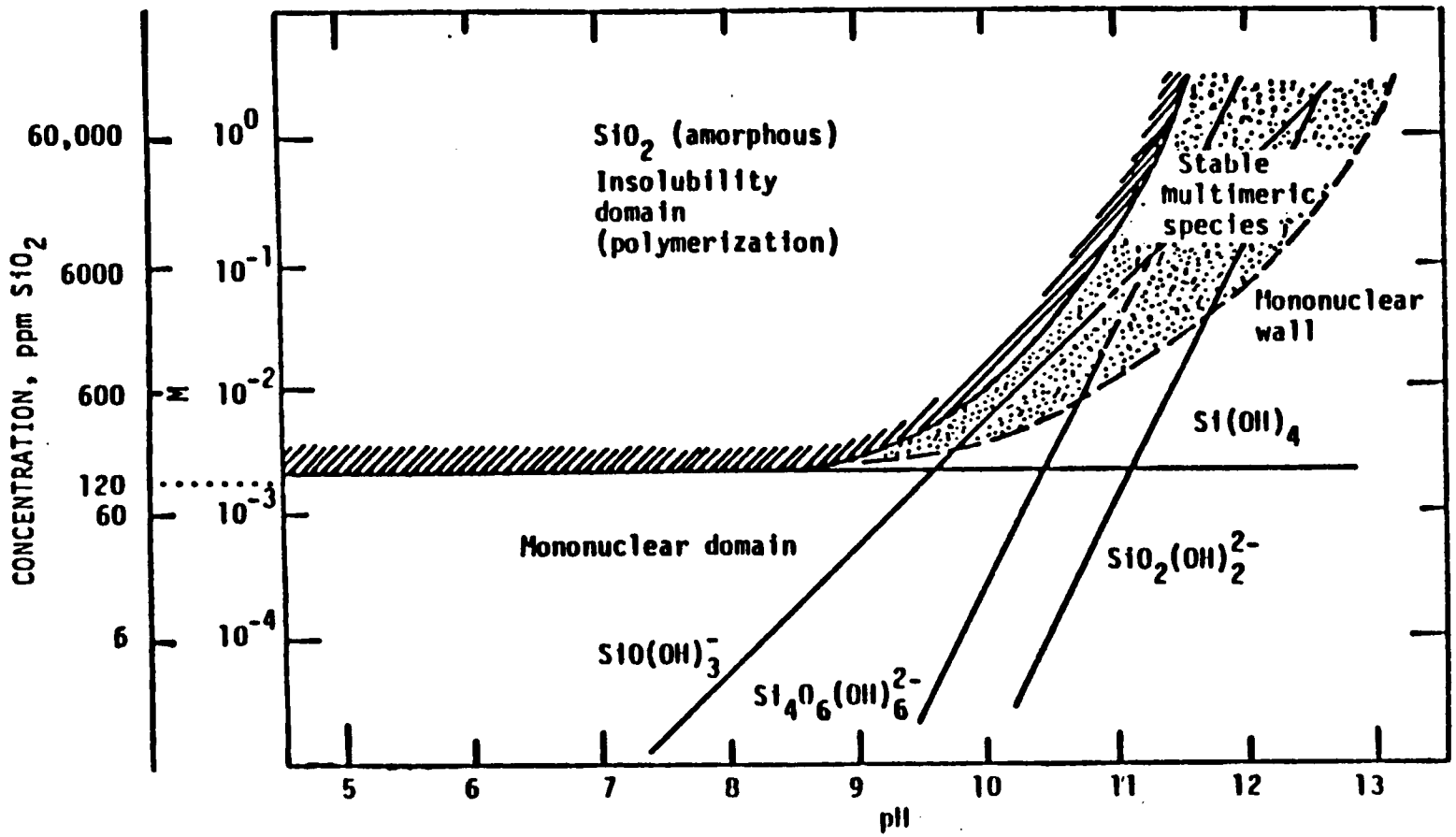


Figure 9. Solubility diagram for silica, SiO_2

3.0 METHODS AND MATERIALS

3.1 INTRODUCTION

In this chapter, the experimental procedure for preparation and treatment of a model groundwater by silicates and polyphosphates with chlorine or chlorine dioxide and analytical methods used in this research are presented. These studies were aimed at obtaining a better understanding of the sequestration process and identifying an effective technique to treat manganese.

Initially, an experiment was performed with silicate and chlorine dioxide to compare manganese and iron treatability by this method. In later experiments, the effectiveness of various techniques in manganese sequestration alone was tested. Since natural groundwaters vary in water quality, the effectiveness of various techniques were tested at different pH levels and in the presence and absence of calcium. Other variables included in this study to test the effectiveness of each technique are outlined in the next section (Section 4.0) which discusses the results of this experimental investigation. The effectiveness of any technique used in this research was determined from filterability analysis (using 0.1 micron filters) and measurement of turbidity and color. High filterability (>90%) indicates that manganese or iron is still in solution or has not deposited (for the period of study) into particles larger than 0.1 micron, which is the nominal membrane filter pore size.

Turbidity and color in treated water was compared with recommended limits (turbidity-1.0 NTU and 15 color units measured on the platinum-cobalt scale).

Samples were filtered through 200,000 MW cut-off ultrafiltration membranes to determine whether colloidal particles were formed during treatment. Also, 1000 MW cut-off ultrafilters were used to verify whether a manganese-polyphosphate complex was formed during treatment. The molecular weight of the polyphosphate used in these studies was 1785 gram/mole. The ultrafilter based molecular weight of the silicate polymers used in this research were also characterized by ultrafiltration studies.

Samples were analyzed for oxidized manganese to determine the correlation between the degree of manganese oxidation and manganese treatability. Other studies are explained in the following sections and discussions of each experiment will follow in Section 4.0. The procedure for preparation of the model groundwater which was developed by Browman (6) and slightly modified for use in this research is explained in the next section. Detailed procedures were used to ensure consistency and reproducibility of results, ensure consistency with previous research (6), and allow time to accomplish tasks. However, plots of experimental data still show large fluctuations (due to experimental error) or missing points (due to limitations of the software used for plotting, as these points were superimposed by other points which had almost similar coordinates).

3.2 MANGANESE TREATMENT OF A MODEL GROUNDWATER

A standard model groundwater was prepared having a pH of 7.0, dissolved oxygen (DO) < 0.1 mg/L. In experiment testing manganese treatability, manganese sulfate was added to provide a manganese concentration of 1 mg/L. Ferric chloride was added in experiments testing iron treatability to provide an iron concentration of about 1 mg/L. Sodium bicarbonate was added to provide an alkalinity of 150 mg/L as $CaCO_3$. Experimental variables included amounts and types of sequestrant added (polyphosphates, orthophosphate, or silicates), pH, oxidant type (sodium hypochlorite or chlorine dioxide), calcium concentration, and time lag between silicate and chlorine dioxide additions. Experiments were conducted in a constant temperature room at 20-21°C.

The standard model groundwater was prepared and treated as follows:

1. Twenty-two liters of deionized water [turbidity $\leq$ 0.08 turbidity units (NTU)] were collected in an acid-washed Nalgene carboy modified to have a spigot at the base.

2. This water was chilled to 20-21°C (68-70°F) in the constant temperature room for 18-24 hours.

3. The water was sparged with filtered (< 0.45 micron), prepurified (99.999% N_2) nitrogen gas at about 5 L/min

to reduce the DO to < 0.1 mg/L. The dissolved oxygen concentration was measured with a submersible probe.

4. Dry sodium bicarbonate was dissolved rapidly in a small volume of deionized distilled water taken from the carboy sparged with N_2 gas, and added to water in the carboy to provide an alkalinity of 150 mg/L as $CaCO_3$. After fifteen minutes (allowed for re-equilibration) pH and alkalinity were checked.

5. The pH of the water was then adjusted to pH 7.0 for manganese treatment and pH 6.5 for iron treatment by adding CO_2 to the N_2 continuously sparging the model groundwater.

6. $CaCl_2$ was then added to give a hardness of 100 mg/L as $CaCO_3$.

7. Dry ferrous chloride ($FeCl_2.xH_2O$) or manganese sulfate ($MnSO_4.H_2O$) was dissolved rapidly in about 100 mL of deionized distilled water taken from the carboy sparged with N_2 gas and then added to water in the carboy. The model groundwater was allowed to equilibrate for 15 minutes while mixing was provided by the vigorous sparging of the N_2-CO_2 mixture. During this period, pH and dissolved oxygen levels were continuosly monitored by observing the pH and DO readings.

8. Samples were taken for turbidity measurement.

9. Model groundwater was dispensed through the spigot at the base of the carboy into 2-liter LPE (linear polyethylene) bottles in a N_2-CO_2 atmosphere.

10. In iron sequestration experiments, a 30 mL sample was taken from the 2 liter bottle for Fe^{2+} analysis.

11. The solution in the 2 liter bottle was dosed with polyphosphate or silicate (sequestrant) and sodium hypochlorite or chlorine dioxide (oxidant) according to the following procedure:

    a) silicate (20 mg/L measured as SiO_2) or phosphate (10 mg/L measured as total PO_4) was added rapidly to the model groundwater. The actual phosphate dosage varied in dosage optimization experiments and is described in the discussion for each experiment in Section 4.0).

    b) at time T = 0, (immediately after addition of silicate or phosphate), the solution was mixed vigorously for 15 seconds (for iron experiments) at 1000 rpm (30 seconds in manganese experiments). The difference in mixing time for iron experiments, i.e. 15 seconds of mixing, 15 seconds quiescent time, subsequent oxidant addition and initiation of 45 seconds mixing (at

1000 rpm) at time T = 40 seconds as explained below is based on Browman's results and recommendations (6).

c) at time T = 30 seconds (60 seconds in manganese experiments) sodium hypochlorite or chlorine dioxide was added.

d) at time T = 40 seconds (70 seconds in manganese experiments), 45 seconds of vigorous mixing at a stirring rate of 1000 rpm was initiated;

12. After adjusting the pH to the desired level (pH 6.0, 7.0 and 8.0 in experiments testing pH effects, and pH 7.0 in other experiments) and mixing for 15 seconds at 1000 rpm (using the Fisher Scientific Stedi-Speed mixer), samples were withdrawn for measurement of turbidity, color, free chlorine or chlorine dioxide, and total and filterable iron or manganese, calcium and oxidized manganese analysis.

13. The pH and DO of the treated water were measured and the pH of the treated water was adjusted to the desired level. The head space of the dosed bottle was filled with N_2-CO_2 mixture, capped and placed in the shaker for continued shaking at 10 rpm to duplicate as much as possible, the turbulent conditions found in a typical distribution system.

14. Samples were filtered through a 0.1 micron membrane filter or 1000 and/or 200,000 MW ultrafiltration membranes.

15. Steps 8-14 were repeated for each treatment.

16. On days 1, 3, and 5, after the pH of the solution-suspension was measured, samples were withdrawn for measurement of turbidity, color, total iron or manganese, filterable iron or manganese and oxidized manganese.

The sampling procedure was as follows:

a) The solution-suspension was mixed at 1000 rpm for 30 seconds, and then at 250 rpm for 10 seconds.

b) Sample were withdrawn for turbidity analysis;

c) After mixing for 10 seconds at 1000 rpm, samples were withdrawn for measurement of color, free chlorine, analysis of total and filterable iron or manganese, calcium and oxidized manganese.

d) The pH was readjusted to the desired level as in (12), head space filled with N_2-CO_2 mixture, and bottles were returned to the shaker for continued shaking at 10 rpm.

3.3 ROUTINE ANALYSIS

After equilibration for at least one minute, solution pH values were measured with a combination glass electrode using an Orion Model 407-A Ionanalizer. Turbidities were measured on a Hach 2100A turbidimeter after about 1 min equilibration. Total and filterable iron, manganese, calcium or silicate were determined on acidified filtered or unfiltered samples by atomic absorption spectroscopy on an Analytical Laboratories Video 12 spectrophotometer. Samples for iron, manganese or calcium analysis by atomic absorption spectrophotometry were acidified to < pH 2 with ultrapure concentrated nitric acid. Ferrous iron was determined using the bathophenanthroline method proposed by Lee and Stumm (1960). Bathophenanthroline forms a highly-colored complex with ferrous iron but not with ferric iron. This complex was extracted using n-hexyl alcohol, and the absorption was measured at 533 nm on a Perkin-Elmer Hitachi 200 double-beam spectrophotometer. Alkalinities were determined by titration to the methyl orange end point. Free chlorine and chlorine dioxide were measured by the N, N-diethyl-p-phenylenediamine (DPD) in accordance with Standard Methods (APHA et al. 1985) as modified by Hach and using the Hitachi 200 spectrophotometer. Dissolved oxygen (DO) concentrations were monitored with a Yellow Springs Instrumental Company Model 54 meter using a submersible polarographic probe. Color was measured with a portable Hach field laboratory. Ascorbic acid method as described by the Standard Methods (APHA et al.

1985) analytical procedure was used to determine the total phosphate, except for one variation. Samples were digested in an autoclave instead of heating over a hot plate. Phosphate analytical procedure is discussed later.

3.4 CHLORINE DIOXIDE, ClO_2

Chlorine dioxide was prepared by the procedure specified in method 410a of Standard methods (APHA et al. 1985). The chlorine dioxide concentration was measured in accordance with the DPD method of Method 410c of Standard methods (APHA et al. 1985). However, some DPD reagent powder pillows were purchased from the Hach Chemical Company.

3.5 POLYPHOSPHATE MEASUREMENT

Some polyphosphate producers claim their product resists depolymerization so strongly that some phosphate tests cannot measure all the phosphate. In order to address this concern, the analytical procedure used in this research, which met a higher temperature in the autoclave than the standard methods (APHA et al. 1985) analytical procedure, had to be validated. Results of the experiment performed to validate this procedure are shown in Table 3. The polyphosphates used in these studies were designated as A, B C and D. The characteristics of these polyphosphates are listed in Section 4.0.

Table 3. Dependence of phosphate analysis on digestion time

TIME	Poly-phosphate A	duplicate of A	Poly-phosphate B	Poly-phosphate C
30 min.	8.05 mg/L	8.14 mg/L	11.0 mg/L	10.6 mg/L
2.5 hr.	8.42	8.52	11.2	10.9
5.0 hr.	8.75	8.71	11.5	10.9
7.5 hr.	9.06	9.03	11.6	11.1
10.0 hr.	9.12	9.07	11.7	11.3

The reversion of polyphosphates to orthophosphate at different time periods was studied in this experiment to determine the optimum digestion time and also make certain that the total phosphate analytical procedure used in this research, which is a slight variation of the standard methods analytical procedure, was valid. Digestion in the total phosphate analysis as described by standard methods (method 424, APHA et al. 1985) was used, with one modification. Samples of several phosphates were digested in an autoclave at 126°C and 20 psi to reduce sample loss. In order to be confident of the results, the dependancy of this analysis on time of digestion was tested. An increase of only about 10% in total phosphate was observed between a 30 minute and a 10 hour digestion. These results support the conclusion that the phosphate analytical procedure used in this research is valid, as results indicate that a 30 minute digestion time is sufficient to convert most of the polyphosphate to orthophosphate (PO_4).

3.6 ANALYSIS TO DETERMINE THE DEGREE OF MANGANESE OXIDATION

In this research, two different sequestrants, sodium silicate or polyphosphate, and two different oxidants, chlorine or chlorine dioxide, were used. Since chlorine is a slow oxidant for manganese, it is important to determine the degree of manganese oxidation with time in order to correlate this variable with treatment success. However, standard analytical methods developed to distinguish between different oxidation states of manganese could not be found. Hence, other analytical methods from which at least a semi-quantitative measure of the degree of manganese oxidation could be determined were applied to this research. Specifically, the DPD method of chlorine analysis has been used for measuring the degree of manganese oxidation.

DPD (N, N-Diethyl-p-phenylenediamine), which is a stable reagent in the powder form, rapidly forms a pink color in the presence of oxidized manganese. It offers high sensitivity, rapid color development and minimal fading. The DPD reagents used in this research contained a buffering system that ensured accurate readings in acid or alkaline samples. The intensity of the pink color formed in the DPD method is proportional to the concentration of oxidized manganese present in the water sample. When manganese is present as Mn^{2+}, no color develops. Free chlorine in the sample must be neutralized with sodium arsenite before analyzing for oxidized manganese. The following procedure was adopted:

1. Sodium arsenite was added to a 25 ml sample. An excess of the arsenite solution (1 ml) beyond the amount required to neutralize chlorine present in a control sample was added.

2. A Hach DPD powder pillow was added to the sample.

3. Absorbance of the sample was measured at 530 nm.

Concentration of oxidized manganese was expressed in terms of equivalent free chlorine. A control bottle with Mn^{2+} and no chlorine was used in the analysis as a control to verify lack of color for Mn^{2+}. A second control bottle with chlorine but no manganese was also used to check the neutralization of chlorine by sodium arsenite, as it could otherwise interfere.

It should be noted that this method will not differentiate between Mn^{3+} or Mn^{4+} since the extinction coefficient would be different for each when reacted with DPD. Therefore, this method should be regarded as semi-quantitative.

3.7 ULTRAFILTRATION

Ultrafiltration membranes were soaked for at least 25 hr in 0.01$\underline{N}$ H_2SO_4, then for 10-15 min in deionized distilled water and then flushed with deionized distilled water (about 10 mL and 90 mL for the 1000 and 200,000 MW cut-off ultrafiltration membranes respectively) prior to sample processing. Samples for ultrafiltration were prefiltered through a 0.1 micron membrane filter to prevent

clogging of the ultrafiltration membranes during ultrafiltration. Prior to ultrafiltration, the prefiltered solution was made 0.1M NaCl with dry salt, to reduce polarization effects. This solution was then passed through a 1000 or 200,000 MW cut-off ultrafiltration membrane. The volume of sample for ultrafiltration was about 60 mL for each unit. About 5 mL was used to rinse the ultrafiltration unit; the first 5 mL of ultrafiltrate was discarded, and the next 25 mL and the remaining retentate were saved for analysis. The 1000 MW cut-off membrane filtration system was run under a pressure of 55 psi, whereas for the 200,000 MW cut-off system, a pressure only slightly greater than the atmospheric pressure was necessary because of the membrane's greater permeability.

The percentage of silicate present in the polymeric form was initially tested for stock (3.22 ratio SiO_2/Na_2O solution) dilutions as other researchers (6) stated that depolymerization of silicates would make them ineffective in sequestration. This testing included filtering stock dilutions through 1000 MW and 200,000 MW cut-off ultrafiltration membranes. The percent silicate present in the polymeric form in silicate stock (undiluted) could not be tested since undiluted silicate solutions solidify on exposure to air and are also very viscous. Hence, stock dilutions of 1/10, 1/50, 1/100, and 1/500 were prepared. All solutions were aged for 24 hours before ultrafiltration was done. Results are shown in Table 4. The ultrafilter-based MW distribution for all the dilutions are calculated from Table 4 and presented in Table 5.

Since the results given in Tables 4 and 5 are based on the MW cut-off of the membrane which is derived (by the manufacturer) from experiments on organic species, these should not be regarded as precise values. Solutes having a molecular weight above the MW cut-off rating could also pass through the ultrafiltration membrane if their molecular size is smaller than the molecular size of the organic species used in obtaining these ratings. With this limitation in view, the following results are discussed:

Table 4. Ultrafiltration of diluted silicate stock solutions

Dilution	% Filterable 1000 MW	% Filterable 200,000 MW
1:10	35.14	82.80
1:50	37.60	84.98
1:100	38.42	94.22
1:500	54.76	100.00

Table 5. Ultrafilter-based MW distribution for diluted silicate stock solutions

Dilution	Below 1000	1000-200,000	Above 200,000
1:10	35.14 %	47.66 %	17.20 %
1:50	37.60 %	47.38 %	15.02 %
1:100	38.42 %	55.80 %	5.78 %
1:500	54.76 %	45.24 %	0 %

Results tabulated in Table 4 indicate that the ultrafilter-based molecular weight distribution of silicates decreased with increasing dilution. More dilute solutions had lower percentages of multimeric (polymeric) silicates. Since more concentrated silicate had a greater percentage of high molecular weight silicate polymers, model ground waters prepared in the laboratory were dosed with undiluted silicates (stock solutions).

In addition to testing the ultrafilter-based molecular weight of silicate solutions, the ultrafilters were also used to determine the size of manganese particulates formed during treatment. This size was studied for a period of five days, in order to evaluate the effectiveness of treatment and determine the extent to which particle growth took place.

3.8 MEASUREMENT OF STREAMING CURRENT

Streaming current measurements were taken on treated samples. The streaming current detector (SCD) used in laboratory and field studies was a DUS Generation I model supplied by the Milton Roy Company. The SCD is a continuous flow detector which measures the streaming current. The particles are temporarily immobilized in the annulus of the SCD, and a piston shears the counter ion layer from the particles producing streaming current. Streaming current is related to zeta potential (7) by the formula:

$$S \alpha ZD/N$$

where S = streaming current, Z = zeta potential, D = dielectric constant, and N = viscosity of the fluid. The SCD can also detect changes in the net electric charge if any occur (18, 23).

According to Pen-Kem Inc., streaming current detectors can be used to quantify the colloidal charge of particulates effectively only when their size exceeds 0.50 microns. As the manganese particles obtained in this research were well below 0.1 microns, the objective in using streaming current detectors were only to test whether streaming current can be used to predict good treatment.

As the instrument was designed for continuous flow measurements, the SCD was operated in a closed loop sample analysis pattern. Instrument operation was carried out according to manufacturer's instructions. Procedures adopted for sample analysis are as follows:

1. The pump is started and the flow adjusted to 1500 mL/min. Tap water is pumped through the instrument for stabilization and to wash out any remaining solids from previous analyses.

2. The instrument is turned on and allowed to warm up for at least 30 minutes.

3. The power switch is turned off, and water is drained from the SCD.

4. Next, the power switch is turned on, and at least 500 mL of deionized water is allowed to flow through the SCD.

5. Step 3 is repeated.

6. The sample (at least 500 mL) is pumped through the SCD with the power switch on. The initial temperature and pH of the sample are noted. The sample container is partially immersed in tap water to maintain a constant temperature 20 $\pm$ 1 ^{o} C.

7. After 2 minutes, the SCD reading is taken and the pH and temperature noted. (The pH usually increases by 0.3 units during this period.)

8. Steps 3-7 are repeated for each sample analysis.

Standard colloid solutions prepared by diluting 7 mL of standard colloid to 1000 mL with deionized water were analyzed prior to sample analysis. Streaming current of the standard colloid never varied by more than 0.25 units from average (5% of average) in any experiment. Since the average streaming current (average of streaming current readings obtained in all the experiments) was about - 5.0, this deviation should be acceptable within the limits of experimental accuracy. Streaming current units are arbitrary and correspond only to the meter reading of the streaming current detector.

4.0 RESULTS AND DISCUSSION

4.1 INTRODUCTION

Many sequestration techniques which are effective in iron sequestration do not produce the desired manganese stabilization. For example, the silicate/hypochlorite method which is found to be effective in iron sequestration (6, 43) did not produce the desired manganese stabilization in Robinson and Ronk's experiments (78). Compared to poor results obtained in manganese treatment, iron was more effectively stabilized by the silicate/hypochlorite method in similar studies, resulting in higher filterability and lower turbidity. Rapid increase in turbidity and deterioration in manganese filterability was noticed in manganese experiments. The cause for the failure of this technique in manganese sequestration is not known.

In Robinson and Ronk's studies, experiments performed at pH 8 gave worse results than at pH 7. Robinson and Ronk hypothesized that increase in the oxidation rate at pH 8 was not sufficient to improve manganese treatability. They recommended the use of stronger oxidants in sequestration. Hence, chlorine dioxide was tested in this research with silicates and polyphosphates.

In this chapter, the results of experimental investigations to identify an effective technique for manganese sequestration are presented. Among the four techniques investigated in the present study, the most effective manganese treatment was obtained with

the polyphosphate/hypochlorite method. High manganese filterability, low turbidity and low discoloration were noticed in these experiments. As polyphosphates inhibited oxidation of manganese by hypochlorite, manganese was not oxidized to higher valence states, and was found to be present as Mn^{2+}. This inhibition of manganese oxidation is determined to be an important mechanism for the success of this technique. Results also indicate that in this method, a manganese-polyphosphate complex may be formed, supporting the hypothesis that the formation of this complex inhibits manganese oxidation.

In other unsuccessful methods tested in this research, high discoloration was produced. The discoloration was verified to be due to manganese oxidation in methods which tested polyphosphates and chlorine dioxide and polyphosphates and silicates in conjunction with chlorine dioxide. Even though the oxidation state of manganese was not identified in these experiments, the degree of manganese oxidation was quantified by the analytical method described in Section 3.0. The degree of manganese oxidation was not studied in the first experiment which tested the silicate/chlorine dioxide method, as the analytical method described in Section 3.0 was not identified prior to this experiment.

The experimental results which led to the above conclusions are discussed in the following sequence:

1. Silicate/chlorine dioxide method

2. Polyphosphate/hypochlorite method

3. Polyphosphate/chlorine dioxide method

4. Polyphosphates and silicates in conjunction with chlorine dioxide

4.2 SILICATE/CHLORINE DIOXIDE METHOD

As discussed in the literature review, Robinson and Ronk (78) hypothesized that slow oxidation of manganese by hypochlorite could be regarded as one of the reasons for poor sequestration of manganese by silicate and hypochlorite. To test this hypothesis, a stronger oxidant, chlorine dioxide, was used with silicate in this research to improve manganese treatability. The silicate used in this research was undiluted 3.22 ratio SiO_2/Na_2O obtained from PQ Corporation. The results from this experiment are discussed below.

4.2.1 Effects of Sodium Silicate and Chlorine Dioxide Addition on Manganese Treatment

Several researchers (6, 43, 78) have tested the effectiveness of the silicate/hypochlorite method in both iron and manganese sequestration whereas the silicate/chlorine dioxide method has not been studied. Hence, an experiment was performed to determine the effectiveness of this technique in both iron and manganese sequestration, using model groundwater prepared in the laboratory as explained in Section 3.1. Although the objective of this research was to identify an effective technique for sequestering manganese, it

was determined that a study of both iron and manganese treatment by this silicate/chlorine dioxide technique would promote a better understanding of the treatment mechanism(s) in this technique.

At the time this experiment was run, the importance of reducing or preventing manganese oxidation to obtain effective manganese control was not known. Researchers have stated that iron should be oxidized by hypochlorite to obtain effective iron treatment (6, 58). However, in the present research, inhibition of manganese oxidation was found to be important for obtaining effective manganese treatment. High discoloration was produced when manganese was oxidized by oxidants added with sequestrants. For example, poor manganese treatability was obtained in experiments testing polyphosphates and chlorine dioxide (Sections 4.4.2 to 4.5.1), as manganese was oxidized by chlorine dioxide and caused high discoloration. In the polyphosphate/hypochlorite method, polyphosphates inhibited manganese oxidation by hypochlorite leading to the conclusion that this inhibition of manganese oxidation is an important mechanism for the success of this technique. Since manganese oxidation by oxidants was inhibited in successful studies in the present research on manganese sequestration, whereas iron was oxidized by oxidants in successful studies by other researchers on iron sequestration, this inhibition of manganese oxidation and oxidation of iron is identified to be the major difference between iron and manganese sequestration.

In this experiment, the importance of lag time between silicate and chlorine dioxide addition was tested. The importance of this variable has been highlighted in the literature review (Section 1.10). Other analytical techniques used in this experiment are explained in Section 3.0.

The objectives of this experiment were:

1) to determine manganese treatability by substituting a stronger oxidant such as chlorine dioxide for hypochlorite in silicate treatment;

2) to determine optimum lag time between silicate and chlorine dioxide; and

3) to compare results obtained in manganese treatment with a control bottle containing iron only and no manganese;

This experiment was run in the absence of calcium, and the pH was adjusted to 7 on days of sampling. Results of this experiment are shown in Figures 10 and 11. Data for this experiment are given in Table A1 in the appendix for informational purposes. A control bottle with chlorine dioxide and no silicate was tested along with the treated bottles. Another bottle containing iron and no manganese was treated with chlorine dioxide and silicate to compare the effectiveness of iron treatment by this technique with manganese

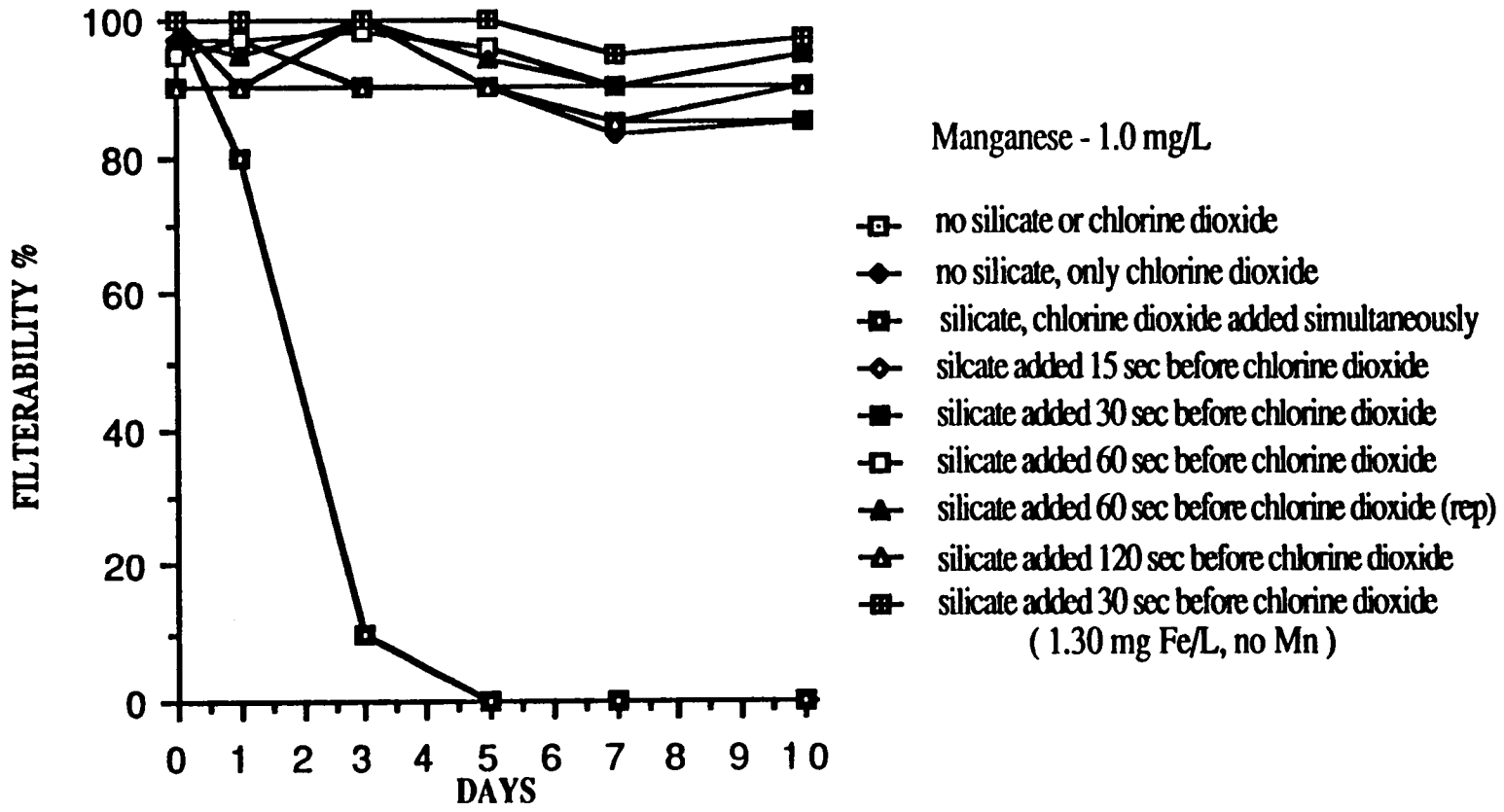


Figure 10. Lag time effects of silicate and chlorine dioxide on manganese treatment: manganese filterability

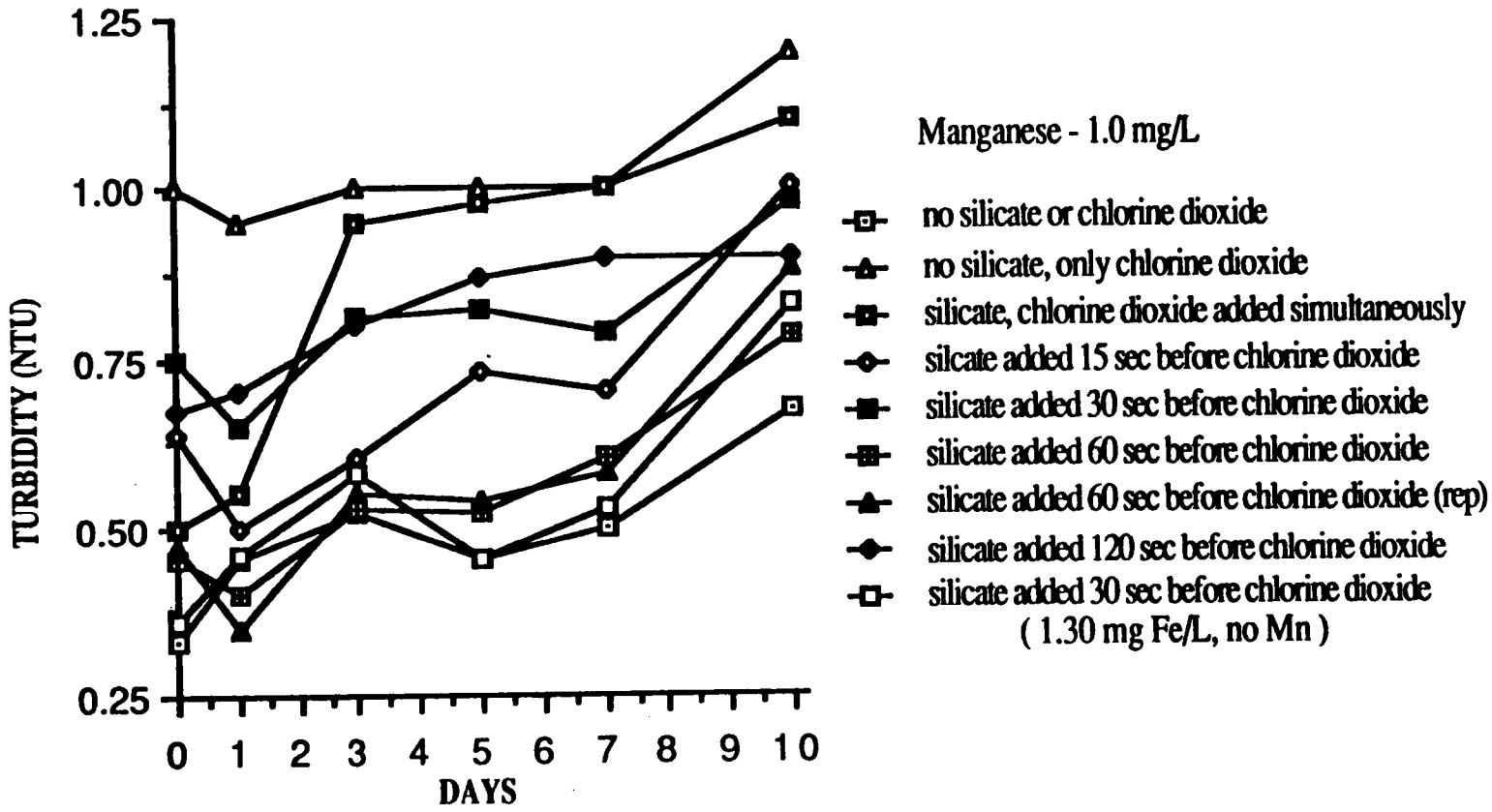


Figure 11. Lag time effects of silicate and chlorine dioxide on manganese treatment: turbidity

treatability. The dosage of chlorine dioxide in this experiment was 1.0 mg/L (twice the stoichometric dosage for oxidation of 1.0 mg/L Mn^{2+} to MnO_2). Silicate dosage was 20 mg/L as SiO_2.

Rapid decline in filterability (Figure 10) and increase in turbidity (Figure 11) was observed when silicate and chlorine dioxide were added simultaneously. No significant difference in manganese treatability was observed between other lag times (15 - 120 seconds). High filterability (> 90%) through a 0.1 micron membrane filter (i.e., $\geq$ 90% of the manganese passed through the filter) and a turbidity of less than 1.0 NTU was achieved by this method for all the lag times. Even though high manganese filterability was also obtained for the control bottle (chlorine dioxide only and no silicate), the turbidity was higher for the control bottle than for treated bottles. However, this experiment on the silicate/chlorine dioxide method was not successful in manganese sequestration, as high color (red-orange) was produced in all bottles receiving chlorine dioxide (Table 6). The color was over 240 units (based on platinum/cobalt scale and measured with a Hach DR-EL portable laboratory on day 19). Results shown in Table 6 indicate that high filterability and low turbidity did not correspond to low color in manganese sequestration. However, this method was successful in iron sequestration, as low color, low turbidity and high filterability was obtained for the bottle containing iron.

Table 6. Relationship between filterability, turbidity and color in manganese experiments

Filterability %	Turbidity NTU	Color units	Lag time seconds
100	0.64	245	15
90	0.75	270	30
95	0.45	255	60
97	0.47	285	60
90	0.67	30[1]	120

[1]Low color was observed in this bottle, as the manganese precipitate was retained on filters when samples were filtered prior to color measurements. Since the color in filtered samples were not representative of the higher color present in treated bottles, in later experiments the filtration step was eliminated.

The fact that high filterability and low turbidity did not correspond to low color for manganese treatment was unexpected because in this experiment (for the control bottle containing iron) as well as in previous studies on iron sequestration (6, 43, 79), high filterability and low turbidity always correlated with low color even though iron was oxidized. But since the color of the manganese precipitate retained on the filters on day 19 was observed to be dark brown to black in color (the characteristic color of several manganese oxides) compared to iron precipitates which had a pale yellow color, it was hypothesized that the high color and high filterability on days 1 through 10 in manganese experiments could be due to the more intensely colored manganese precipitate which was present as a colloid. Also, when samples were filtered on day 19, the filtrate was

observed to have less color than the unfiltered samples. These results indicate that the black color of the manganese precipitate may be responsible for the high discoloration obtained in manganese sequestration experiments and the pale yellow color of the iron precipitate for the low discoloration obtained in iron sequestration experiments.

Although the cause for the black color of the manganese precipitate and the pale yellow color of the iron precipitate was not determined in this experiment, results of investigations on the properties of iron precipitates bring to light several factors (color, composition of precipitates, particle size and shape) which could have caused the discoloration. Robinson et al. (77) cite several researchers who obtained iron precipitates varying in color from yellow to black. Several factors, including the type of oxidant, composition of precipitates, particle size and shape caused this discoloration. Rod shaped particles were yellow whereas large cubic particles were black in color. Smaller cubic particles had a purple color. Red-colored precipitates were also obtained. All compositions were either γ-Fe_2O_3, γ-FeOOH or β-FeOOH. Hence, several of these factors could have caused the manganese precipitate to be more intensely colored than the iron precipitate.

To determine whether oxidation of Mn^{2+} to higher valence states could be the cause for the high discoloration produced in manganese experiments, pE-pH calculations were done to determine Mn^{2+} concentration as a function of pE and pH. These calculations

(which are explained in Section 4.7) predicted that manganese would be completely oxidized by chlorine dioxide at pH 6, 7 and 8. The MINTEQ equilibrium model could not be used to predict the Mn^{2+} concentration for the conditions in this experiment (an error message was obtained), as Mn^{2+} was oxidized and its concentration approached zero during the course of the MINTEQ calculations due to the high pE levels in the presence of chlorine dioxide.

Even though the degree of manganese oxidation was not measured in this experiment, later experiments using polyphosphates with hypochlorite or chlorine dioxide (in which the degree of manganese oxidation was measured) confirmed the oxidation of manganese to be the cause for the high discoloration in manganese sequestration methods, as the degree of manganese oxidation always correlated with color in these experiments (Section 4.4.2).

Similar to the results obtained in this experiment on the silicate technique, high manganese filterability through 0.1 micron filters in later experiments (Section 4.4.2) did not correspond to low color. However, high manganese filterability through 200,000 MW cut off ultrafilters did correspond to lower color, implying that the manganese particle size was less than 0.1 microns. When high color was produced, most of the manganese which was in an oxidized form was retained on the ultrafilters. These results are discussed in Section 4.4.2 and 4.4.3.

Results of this experiment (4.2.1) on silicate/chlorine dioxide treatment indicate that this method may not be suitable for manganese treatment due to oxidation and subsequent precipitation of manganese oxides which produced high color. Compared to manganese, iron was as effectively sequestered using chlorine dioxide and sodium silicate in this experiment as when hypochlorite and sodium silicate were used in studies by other researchers (6, 43). High filterability, low turbidity and low color could be achieved in iron sequestration by both methods even though they were ineffective in manganese treatment. This implies that hypochlorite is not unique in its ability to sequester iron with silicates. Any oxidant which oxidizes iron rapidly will be effective in iron treatment when used with silicates. This study's comparison of iron and manganese treatment provides two important insights into the differences between iron sequestration and manganese sequestration:

1) Though oxidation is favorable to iron treatment, it is detrimental to manganese treatment. Manganese oxidation, as predicted by pE-pH calculations, may result in high discoloration.

2) High filterability through 0.1 micron filters and high turbidity may correlate with low discoloration for iron treatment by silicate and chlorine dioxide whereas this may not hold true for manganese treatment.

Results for total manganese, total iron and pH are given in Figures A1 and A2 in the appendix to illustrate the conditions in this experiment.

Before concluding this discussion on manganese treatability by silicate and chlorine dioxide, the effects of not adding any sequestrant or oxidant should also be discussed. In this experiment, a third control bottle containing manganese was run with no silicate or chlorine dioxide addition. Since manganese oxidation by oxygen alone is a very slow process, manganese should have been present as Mn^{2+}, and hence this bottle (the case of null treatment) correlated with best results in that no noticeable color or turbidity was produced. This is consistent with results obtained by Robinson and Ronk (78). In contrast to iron sequestration, these results indicate that for manganese sequestration to be successful, i.e. to obtain low color and turbidity and high filterability, manganese should be present as Mn^{2+} even after the addition of oxidants. However, the addition of oxidants (as disinfectants) is necessary in actual practice as almost all utilities are required to add some form of oxidant for disinfection purposes, most commonly chlorine or chlorine dioxide. Additionally, strong bleach is often used for laundry. In these situations, manganese would be oxidized and cause unacceptable color and high turbidity. Hence, a suitable sequestrant has to be identified to retard manganese oxidation. Therefore polyphosphates were subsequently tested in this research, as they are known to

accelerate iron oxidation (84) and retard manganese oxidation (63) by oxygen.

4.3 POLYPHOSPHATE/HYPOCHLORITE METHOD

Due to poor manganese treatability obtained by the silicate/chlorine dioxide method, the polyphosphate/hypochlorite method was studied to determine if better manganese treatability can be obtained with this method. Sodium hypochlorite was used in this study, as it is commonly used by utilities for disinfecting the groundwater and may affect the sequestration process by oxidizing the manganese. In this study, the effectiveness of four commercially available polyphosphates and an orthophosphate (KH_2PO_4) in retarding manganese oxidation and thus producing the desired manganese treatment was tested. The polyphosphates were designated as A, B, C, and D and contain 23%, 81%, 34% and 72% phosphate respectively, according to the manufacturer and other researchers (87, 92). The orthophosphate contained 70% phosphate. Using the method stated earlier (Section 3.0) for analyzing at least semi-quantitatively the extent of manganese oxidation, initially an experiment was performed to study the oxidation of manganese by hypochlorite in the presence and absence of polyphosphate D. The results of this experiment are discussed next.

4.3.1 Study of Manganese Oxidation by Hypochlorite in the Presence and Absence of Polyphosphates

In order to determine if manganese oxidation by hypochlorite could be inhibited by polyphosphates, the degree of manganese oxidation by hypochlorite in the presence and absence of polyphosphates was studied in this experiment. Hypochlorite was used as the oxidant, and this experiment was run in the absence of calcium and at pH 7 (Table A2). Polyphosphate D was arbitrarily chosen among the several polyphosphate types. The dosage was 10 mg/L as total phosphate. Hypochlorite dosages were measured as free chlorine. In one set of bottles, polyphosphates were absent, and free chlorine varied from 0 to 9 mg/L. In another set, polyphosphate D was added at 10 mg PO_4/L along with varying free chlorine dosages.

The pH was adjusted to 7.0 when samples were collected. The average drift in pH was observed to be 0.3 units between sampling periods. Free chlorine analysis was done periodically until the experiment was completed to verify whether a residual was present in all the bottles. In the bottle having the highest chlorine dosage, free chlorine decreased by only 3 mg/L between day 0 and day 10. Free chlorine was present in all sample bottles through the final day of sampling. Results for oxidized manganese concentration and manganese filterability are presented in Figures 12 and 13.

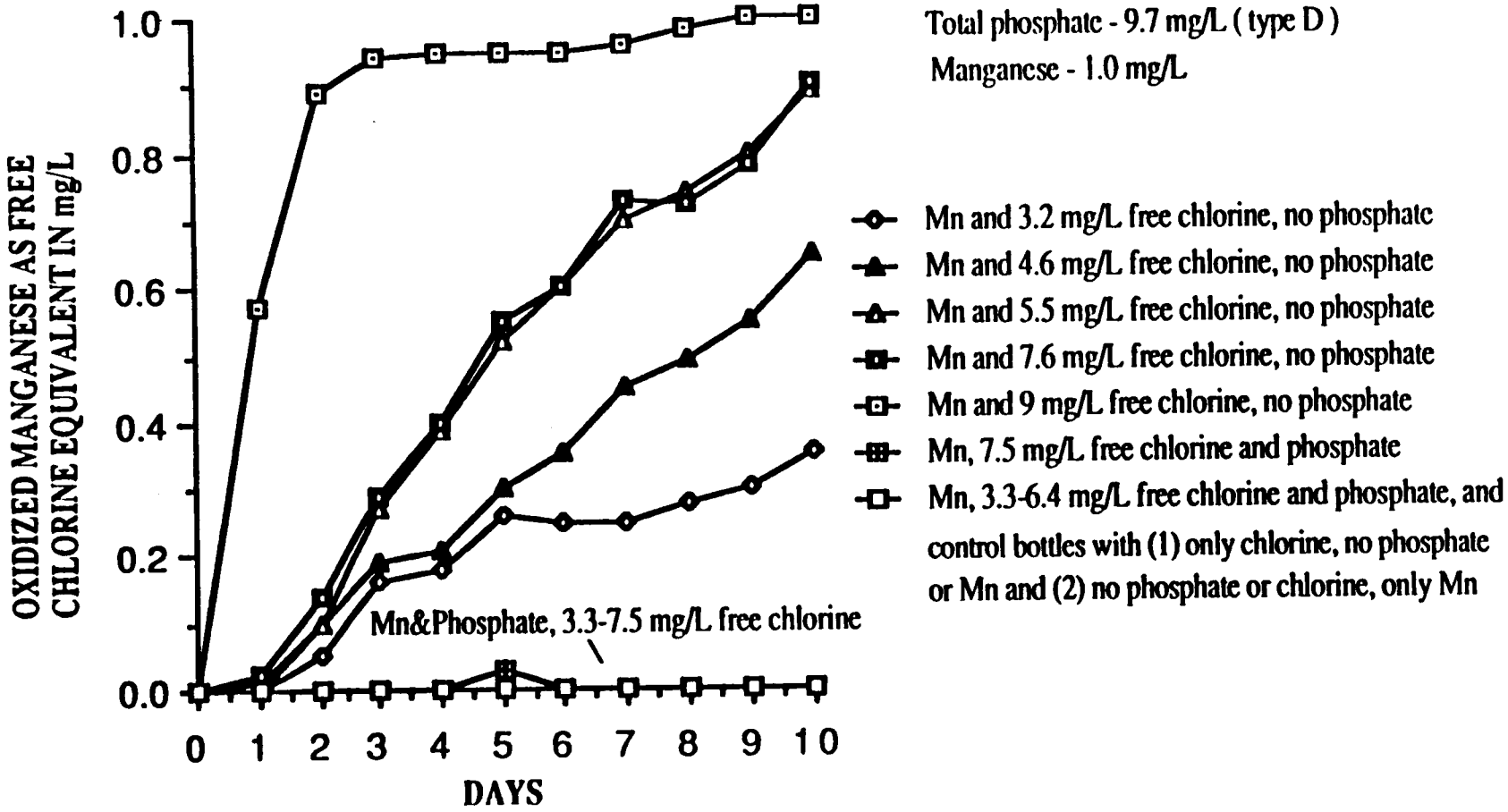


Figure 12. Study of manganese oxidation by hypochlorite in the presence and absence of polyphosphates: oxidized manganese

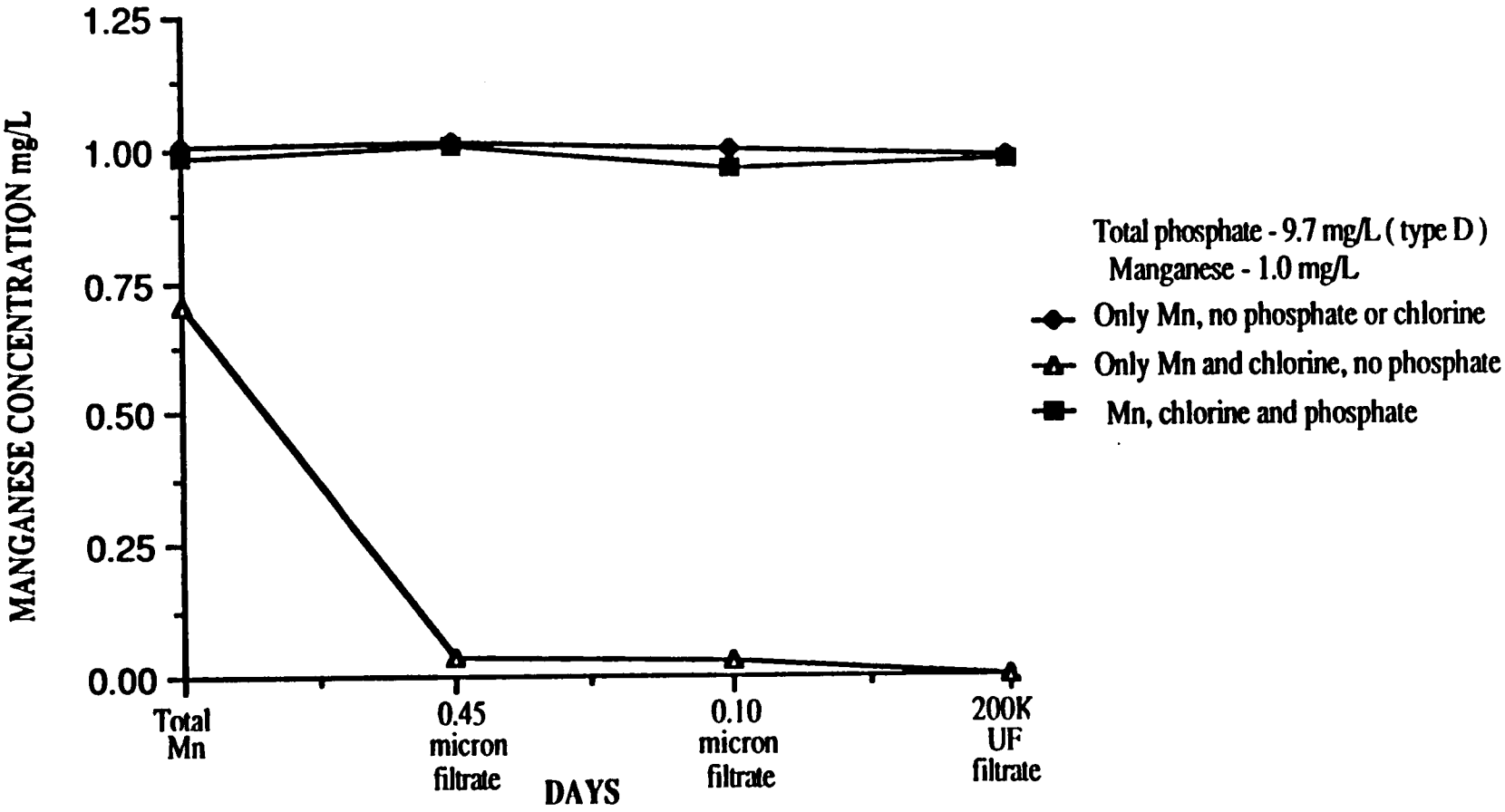


Figure 13. Study of manganese oxidation by hypochlorite in the presence and absence of polyphosphates: manganese filterability

Concentration of oxidized manganese gradually increased with time and with increasing free chlorine dosages when polyphosphates were absent (Figure 12; appendix Figures A3 and A4 show the free chlorine dosages and pH). These bottles were highly colored (red-orange color). When polyphosphate was present at 10 mg PO_4/L, the manganese was not oxidized even on day 10, and showed no visible color. Results from ultrafiltration and microfiltration on day 12 are shown in Figure 13 and support the conclusion that manganese was not oxidized by hypochlorite when polyphosphate was present, as 100 % filterability was achieved. It is evident that manganese was present as Mn^{2+} in the polyphosphate and hypochlorite containing bottles, as manganese filterability for these bottles and the control bottle (with no phosphate or hypochlorite but with manganese as Mn^{2+}) were similar. In the absence of polyphosphate, manganese filterability dropped to as low as 5% through a 0.45 micron filter, indicating that most of the particles produced due to oxidation and subsequent precipitation were present at a size above 0.45 microns and were therefore retained on the filter. This indicates that manganese would not precipitate when polyphosphates and hypochlorite are used by utilities to achieve the dual purposes of manganese sequestration and disinfection.

Decline in total manganese concentration with time was observed in bottles to which only hypochlorite was added (Figure 14)

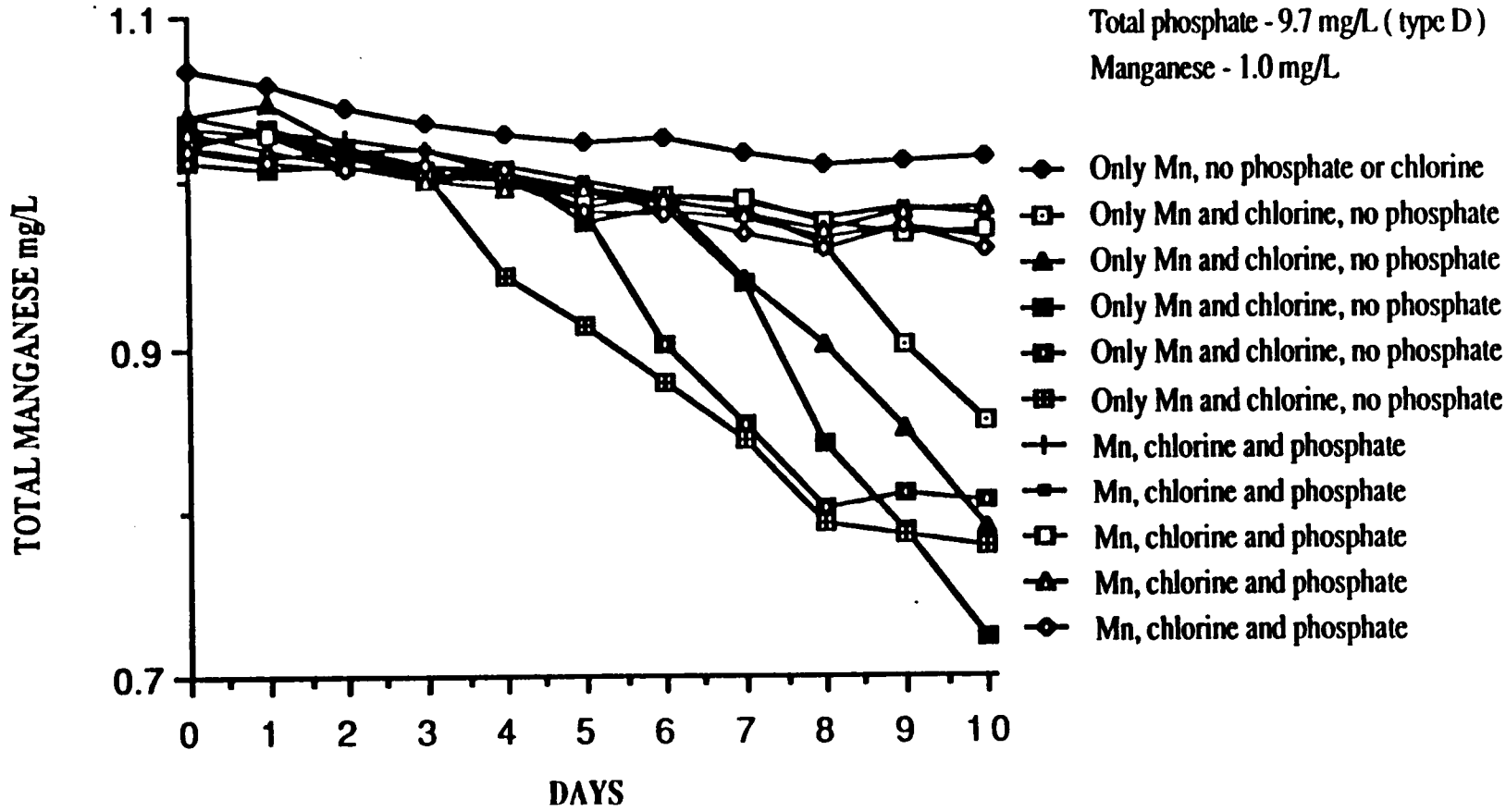


Figure 14. Study of manganese oxidation by hypochlorite in the presence and absence of polyphosphates: total manganese

indicating that oxidized manganese may have precipitated in these samples. Also, since the manganese flocs tended to stick to the bottom of the jar, they may not have been resuspended during mixing. It is also possible that the manganese flocs that were resuspended during mixing may have settled to the bottom of the sampling jar prior to sampling. This implies that in actual treatment, manganese would be oxidized by hypochlorite and settle in pipelines and fixtures when used in the absence of polyphosphates. Decline in total manganese was insignificant when polyphosphate was used, due to inhibition of manganese oxidation and subsequent precipitation of manganese oxides. This result is similar to Blinski and Morgan's findings, referred to by Stumm and Morgan (63), that traces of pyrophosphate retard oxidation of manganese by oxygen. From these results it can be concluded that the success of the polyphosphate/hypochlorite method in manganese sequestration is due to the inhibition of manganese oxidation by polyphosphates.

In this experiment, manganese treatability was studied at a constant polyphosphate dosage of 10 mg/L as total phosphate. In order to determine the optimum dosage for obtaining the desired manganese treatability, different polyphosphate dosages were tested in the next experiment.

4.3.2 Polyphosphate D Dosage Effects in the Absence of Calcium

This experiment (Figures 15-18) tested the polyphosphate D

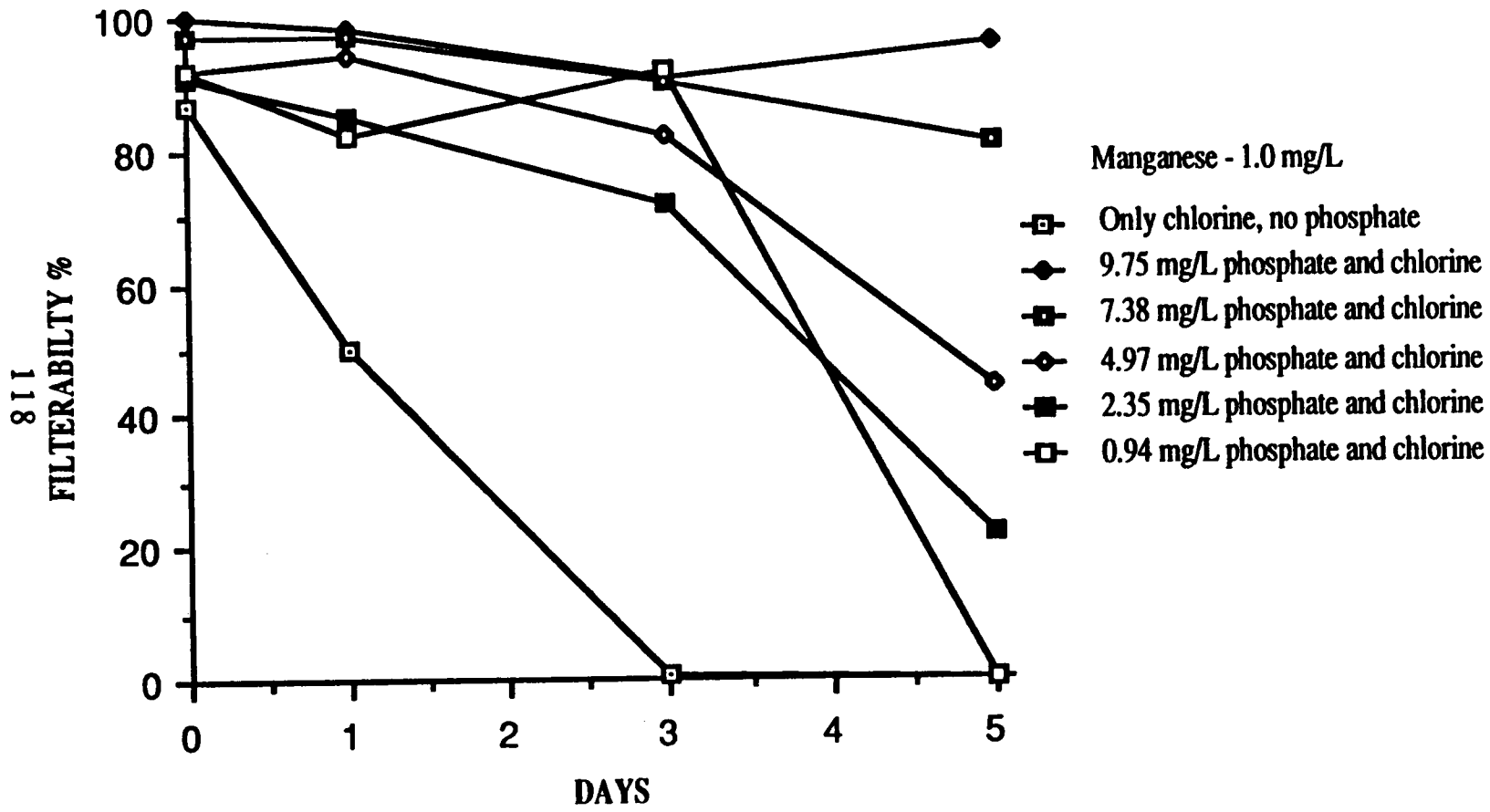


Figure 15. Polyphosphate D dosage effects in the absence of calcium: manganese filterability

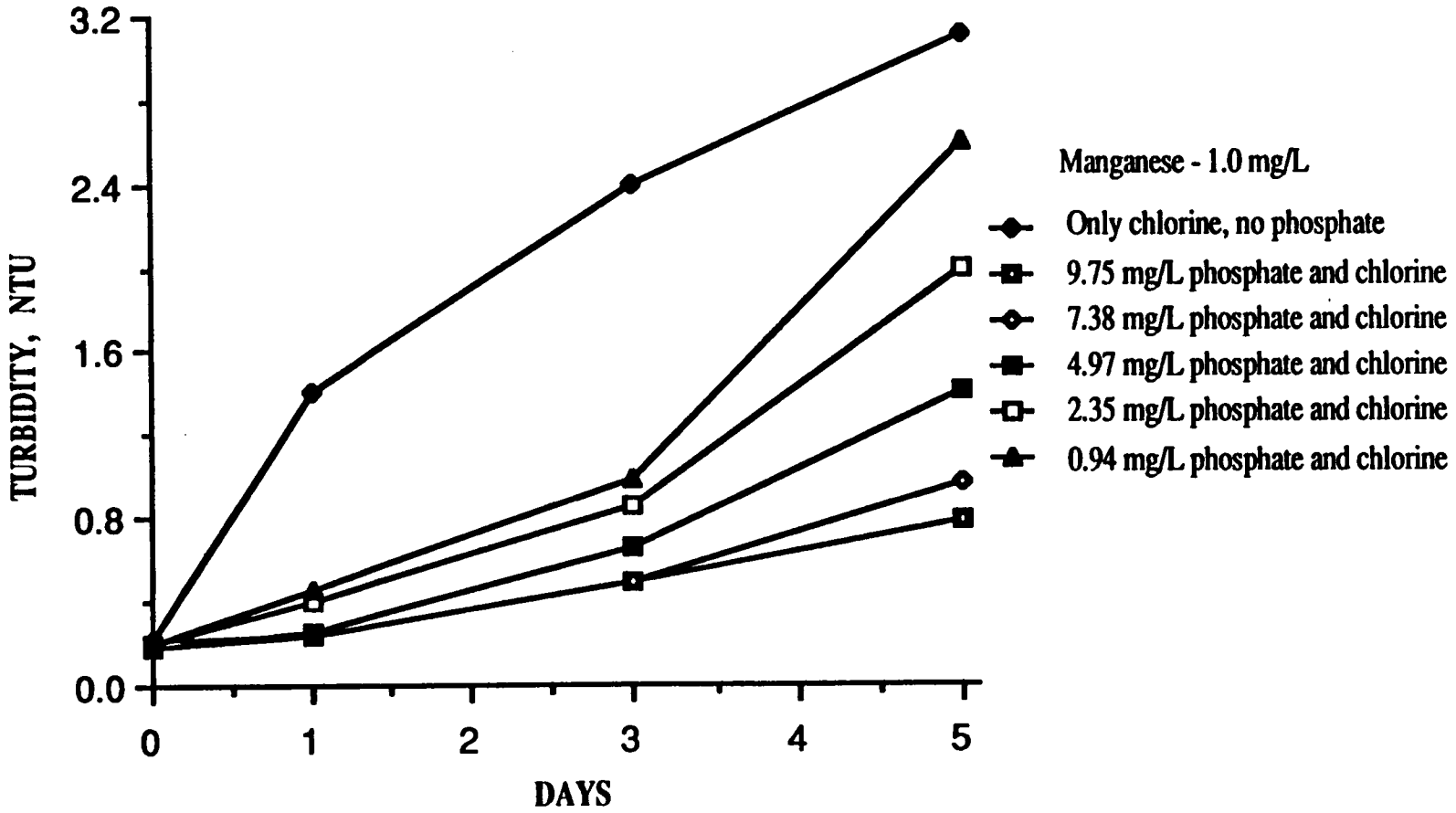


Figure 16. Polyphosphate D dosage effects in the absence of calcium: turbidity

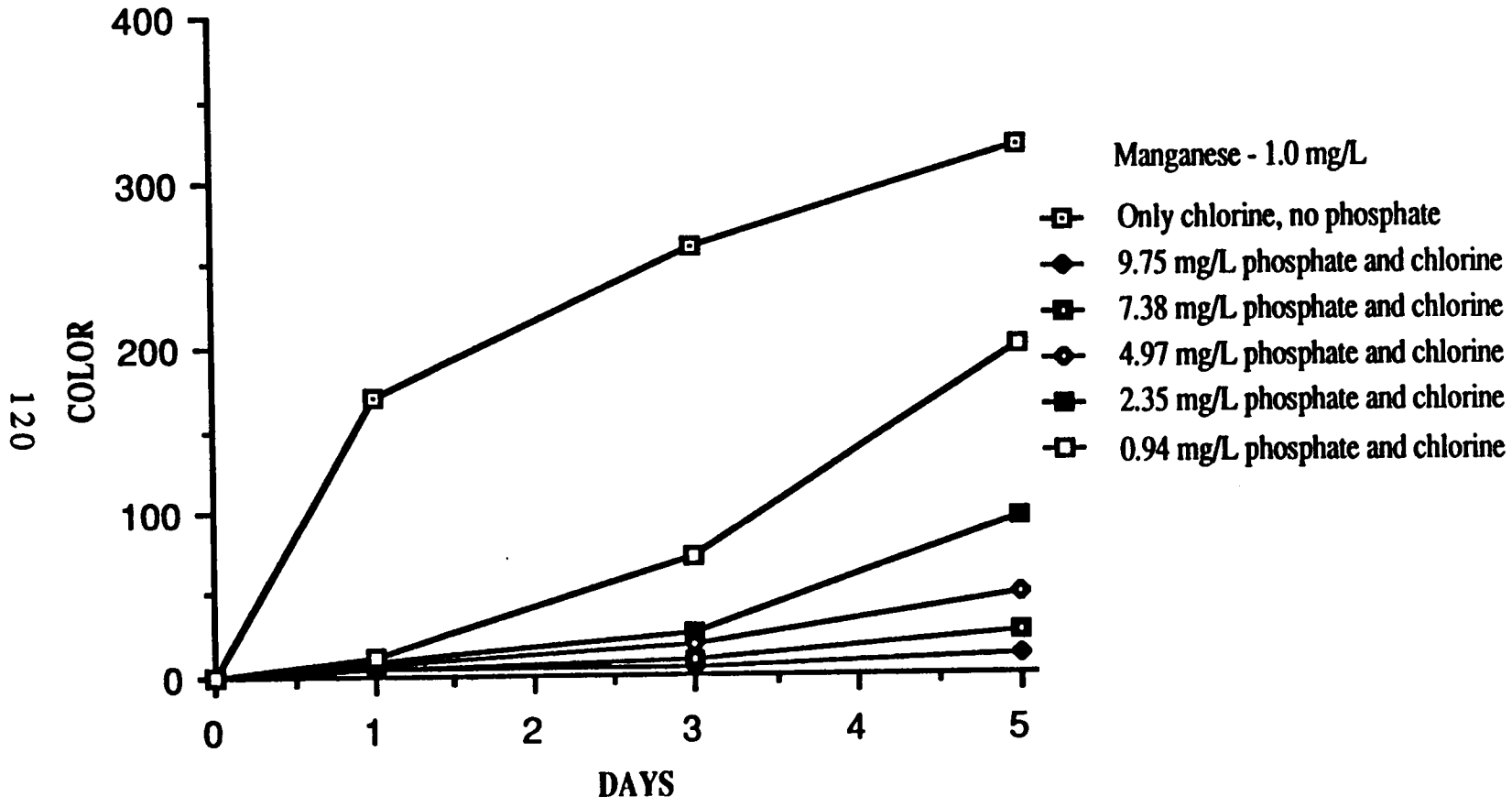


Figure 17. Polyphosphate D dosage effects in the absence of calcium: color

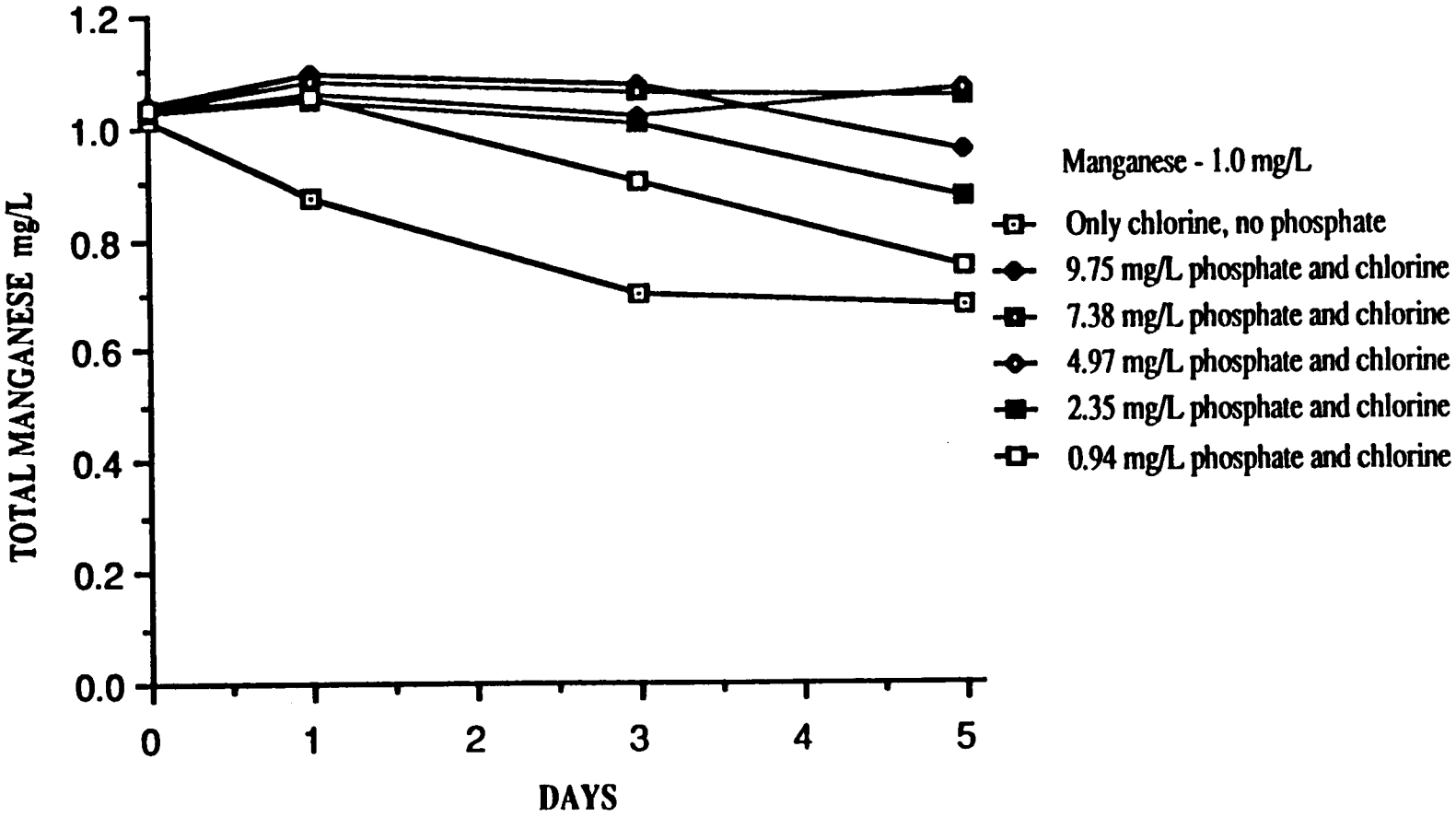


Figure 18. Polyphosphate D dosage effects in the absence of calcium: total manganese

dosage effects in the absence of calcium to determine the optimum polyphosphate dosage for sequestering manganese. Dosages of about 10.0, 7.5, 5.0, 2.5 and 1.0 mg/L were tested. Hypochlorite was added with polyphosphates as in the previous experiment. Sufficient hypochlorite (about 1.5 mg/L as free chlorine) was again added on day 3 to maintain a free chlorine residual through day 5 (the final day of sampling). Samples were collected only for a period of 5 days, as in actual water treatment practices treated water usually passes through the distribution system within this time period. Results from this experiment are reproduced in Figures 15-17 and data in Table A3. Effective manganese treatment was observed with polyphosphate. Higher dosages of polyphosphate produced higher filterability (Figure 15), lower turbidity (Figure 16) and lower color (Figure 17) and sequestered manganese for a longer period of time. However, increases in dosage above 5 mg/L as total phosphate did not significantly increase treatment effectiveness. Hypochlorite alone gave poor treatment. Filterability declined rapidly with time (from almost 50% on day 1 to 0% on day 3), turbidity was greater than 1.2 NTU on day 1 (about 2.4 on day 3), color was greater than 150 units on day 1 (about 250 units on day 3), and a significant amount of manganese precipitated (Figure 18), as evidenced by a decrease of about 30% in total manganese from an initial concentration of 1.0 mg/L. Even at a low polyphosphate dosage of about 1 mg/L as total phosphate, significant improvement in manganese treatability was noticed. Filterability was above 90% for 1 day, and turbidity was less than 1.0 NTU. However, color increased

to about 50 units on day 3, and filterability dropped to less than 90%. From these results it is evident that higher polyphosphate dosages (> 1.0 mg/L) would be required to effectively treat manganese for longer time periods. Figures A5 and A6 which illustrate the free chlorine concentration versus time and pH for this experiment are provided in the appendix.

4.3.3 Manganese Treatment by Polyphosphate D and Hypochlorite in the Presence of Calcium

In previous experiments, the effectiveness of polyphosphate D in manganese sequestration was studied in the absence of calcium. However, hardness is generally present in most natural waters. Several researchers who tested the effects of hardness on the iron sequestration process found that calcium adversely affected iron treatability to a significant extent compared to other ions (43, 79) and caused high turbidity and rapid precipitation of iron. Since similar studies have not been performed in manganese sequestration, this experiment (data given in the appendix Table A3) was run concurrently with the previous one, to study calcium effects on manganese treatability by polyphosphate D and hypochlorite. The pH was adjusted to 7.0 on sampling days as in earlier experiments, and a free chlorine residual was present in this experiment through day 5 in all the bottles.

Figures 19-22 plot the manganese filterability, color, turbidity, and total calcium for this experiment. As figures illustrate,

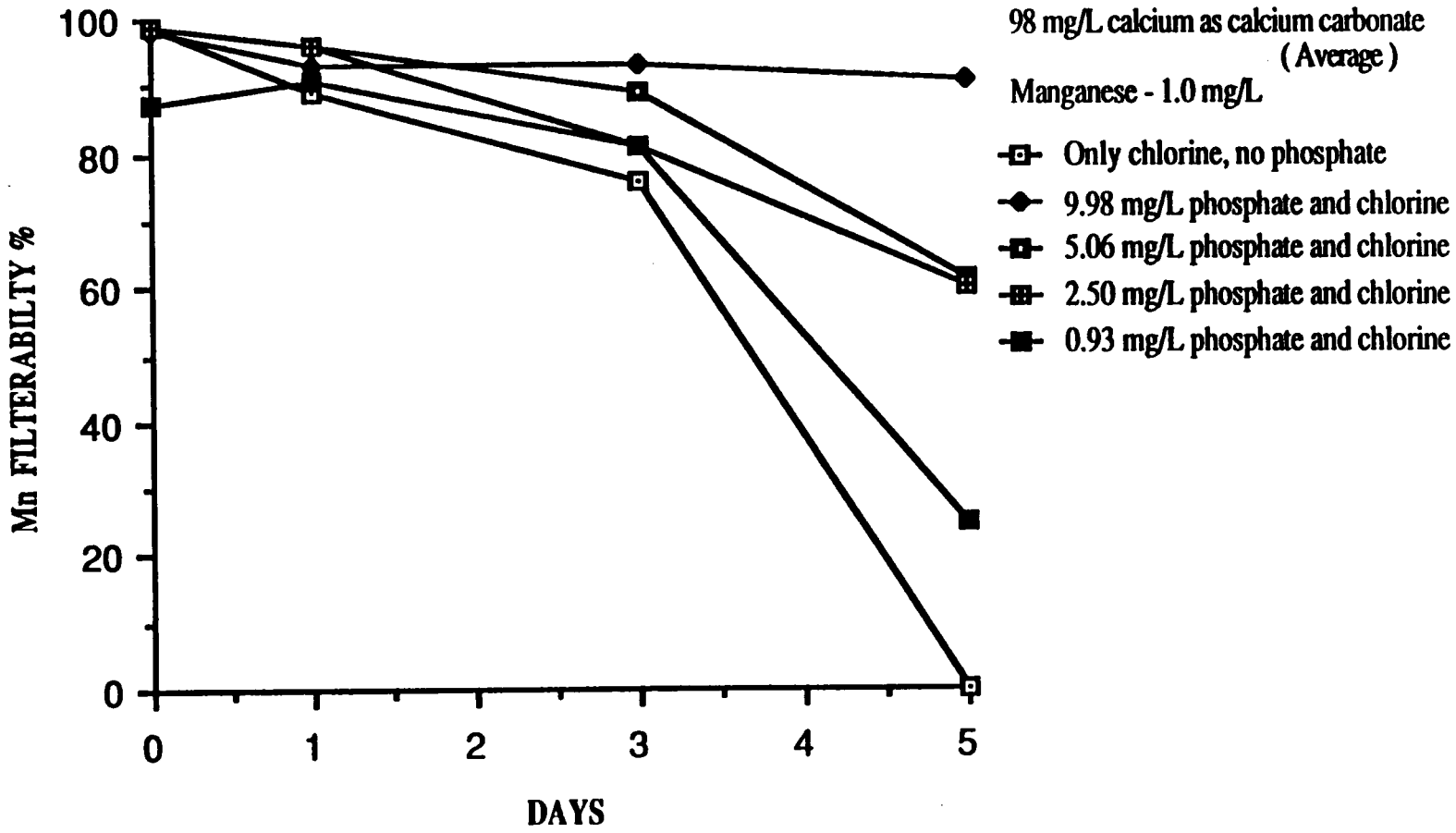


Figure 19. Manganese treatment with polyphosphate D and hypochlorite in the presence of calcium: manganese filterability

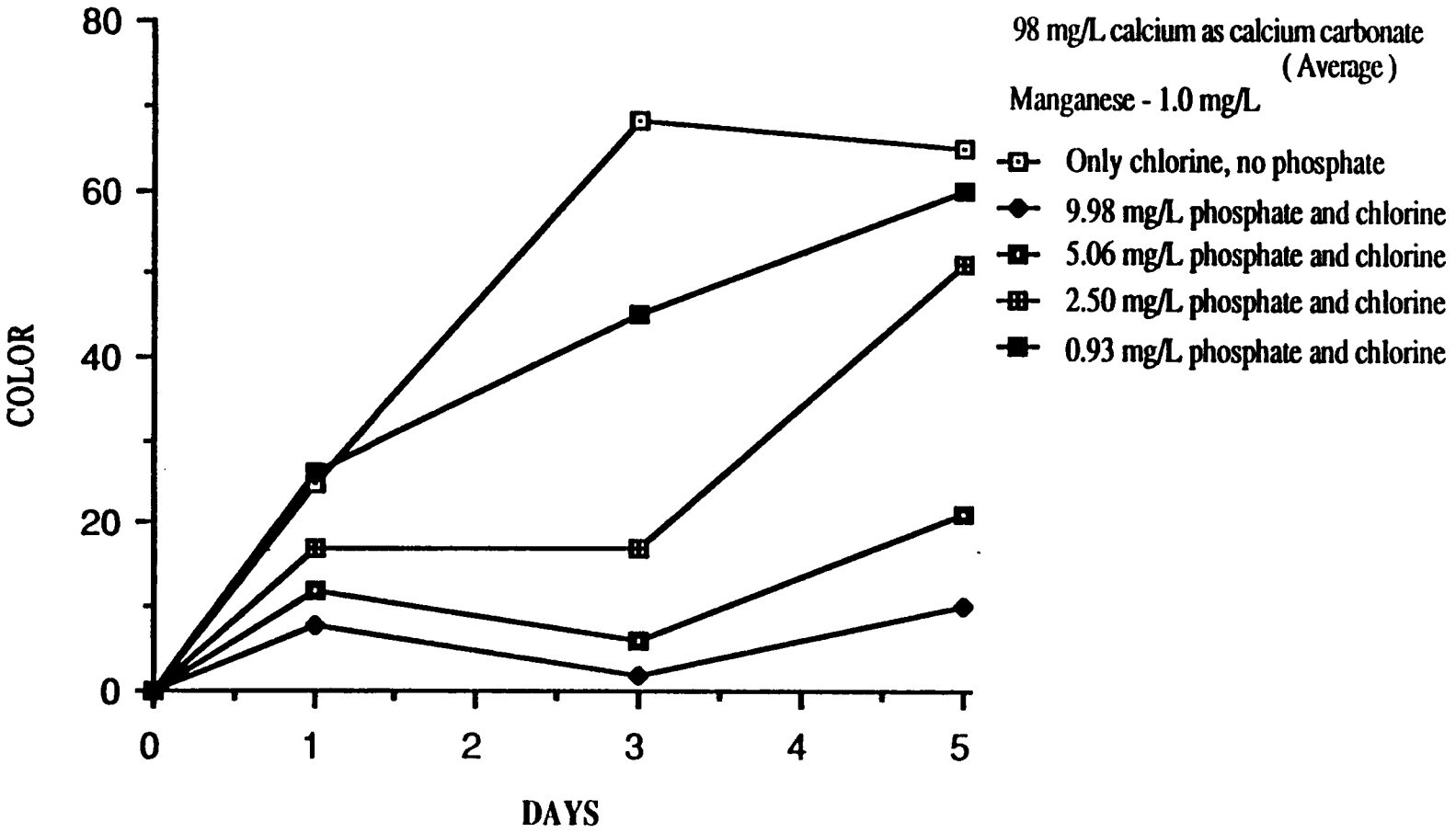


Figure 20. Manganese treatment with polyphosphate D and hypochlorite in the presence of calcium: color

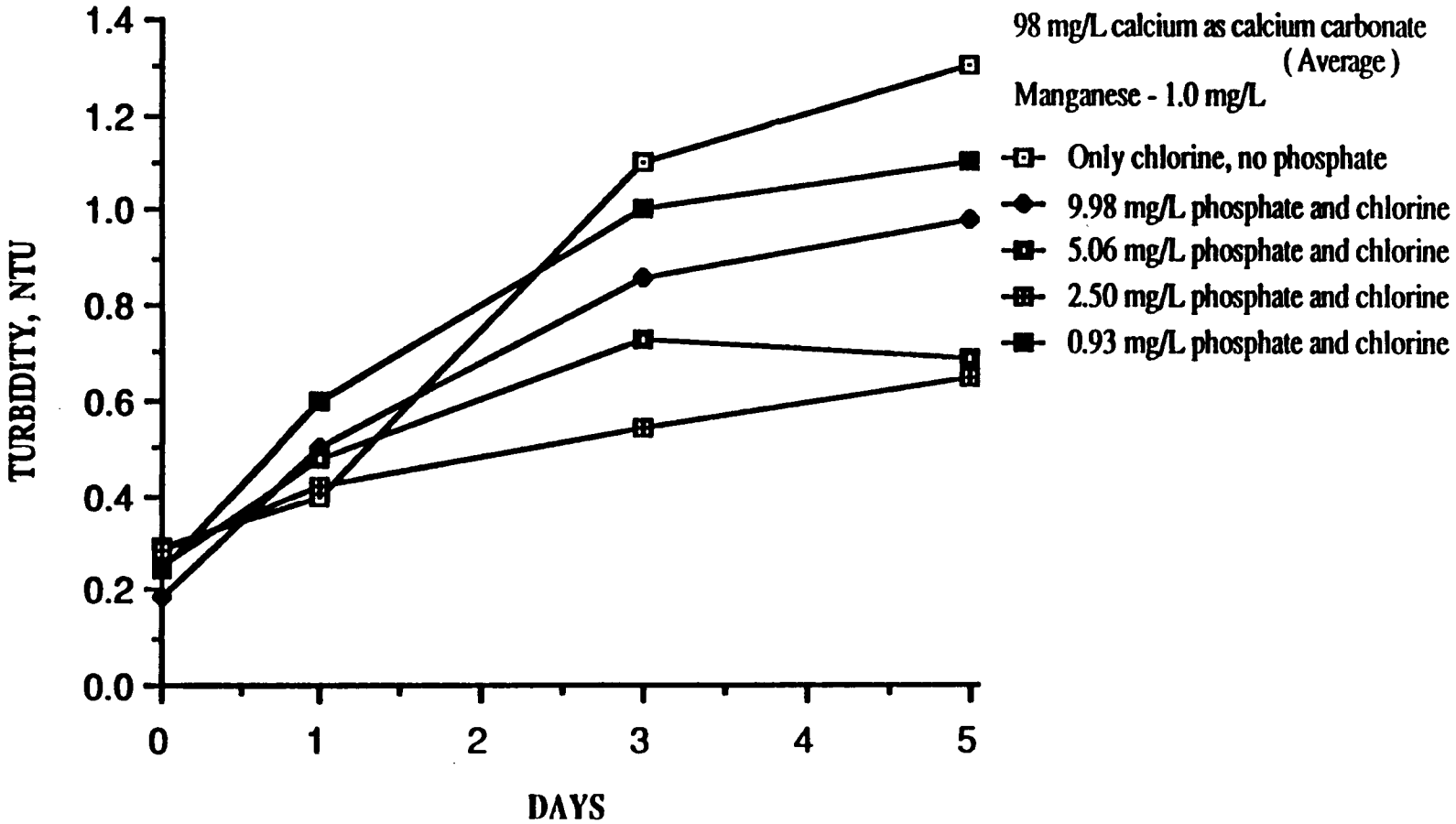


Figure 21. Manganese treatment with polyphosphate D and hypochlorite in the presence of calcium: turbidity

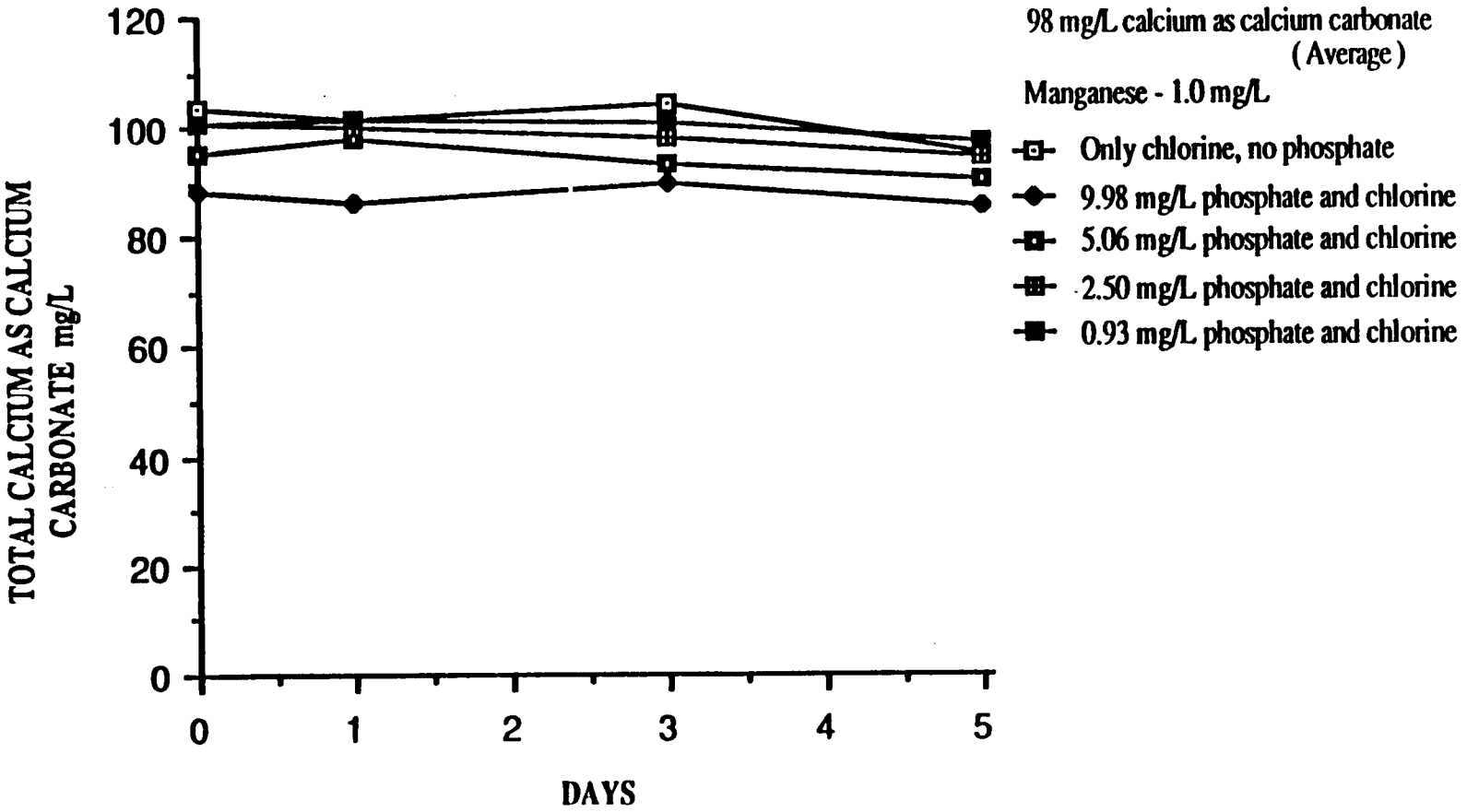


Figure 22. Manganese treatment with polyphosphate D and hypochlorite in the presence of calcium: total calcium

higher filterability (Figure 19) and lower color (Figure 20) correlated with higher polyphosphate dosages. However, the turbidity (Figure 21) appeared to decline with higher polyphosphate dosages (from 0.9 to 2.5 mg/L as total PO_4), and then increase again (from 2.5 to 10 mg/L as total PO_4), due to the formation of a calcium-phosphate precipitate. The lowest turbidity was viewed at a polyphosphate dosage of 2.5 mg/L as total phosphate. In the absence of polyphosphate, low filterability (0% on day 5), high turbidity and high color were observed, due to manganese oxidation and subsequent precipitation.

As seen in Figure 22, the total calcium decreased by about 10% from an initial average calcium concentration of 98 mg/L as $CaCO_3$, indicating that a calcium-phosphate precipitate was formed. However, not much difference was observed in calcium filterability (Figure 23). This indicates that the calcium-phosphate precipitate may have coated the sides of the sample bottle and was not present in samples collected for filterability analysis.

Based on the results shown in Figures 19, 20, and 21, a phosphate dosage of about 6.4 mg/L gave a filterability of 90%, turbidity less than 1.0 NTU and color less than 15 color units for a period of at least three days (see also Section 4.11, Figures 72 and 73). Higher phosphate dosages gave lower color and higher filterability, but higher turbidities. Lower phosphate dosages gave high filterability and lower turbidity, but higher color, with one

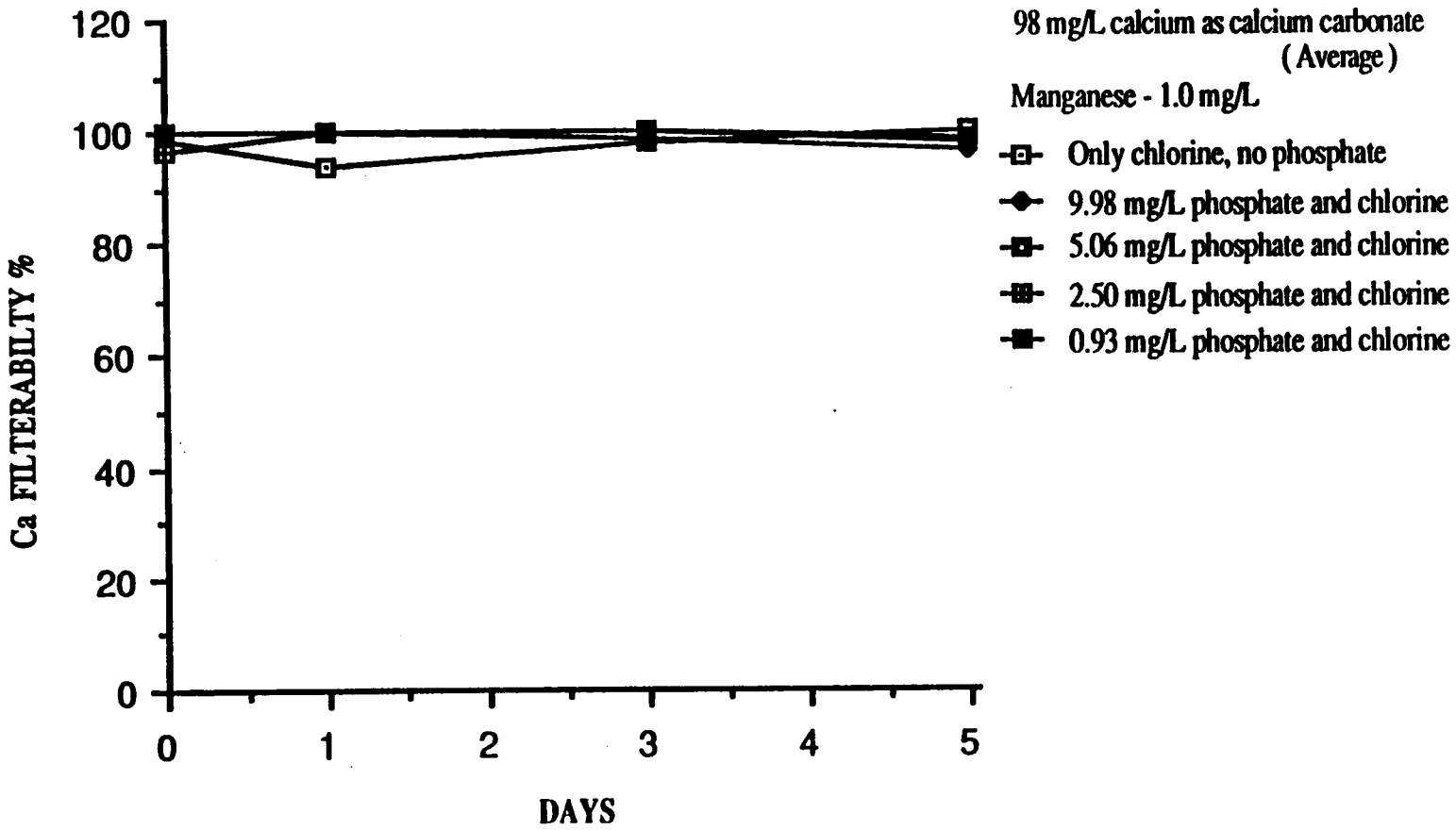


Figure 23. Manganese treatment with polyphosphate D and hypochlorite in the presence of calcium: calcium filterability

exception being a phosphate dosage of 0.9 mg/L which gave high turbidity and high color. In other words, phosphate dosage is inversely correlated to color and directly correlated to turbidity.

Equilibrium modeling was done using MINTEQ to determine the calcium-phosphate precipitate that would form at equilibrium for the conditions in this experiment. Dosages of 2, 4, 5, 7.5, and 10 mg/L total phosphate were used as input for the model. The phosphate species present in the MINTEQ data base include $Ca_5(PO_4)_3OH$ (hydroxyapatite), $MnHPO_4$, Mn_3PO_4, $NaHPO_4^-$, $CaHPO_4(aq)$, $CaPO_4^-$, $CaH_2PO_4^+$, HPO_4^{2-}, H_2PO_4, $H_3PO_4(aq)$, and PO_4^{3-}.

MINTEQ (Figure 24a) predicted that hydroxyapatite would form at certain phosphate dosages for the calcium dosage in this experiment (100 mg/L as $CaCO_3$). Sample MINTEQ results are presented in Table 8. MINTEQ predictions shown in Figures 24 a & b are reasonably consistent with laboratory test results considering the limits of the accuracy of the calculations and the fact that this system is not at equilibrium. Also, MINTEQ cannot be used to predict reaction kinetics. MINTEQ has thermodynamic data for orthophosphates, but does not have data for polyphosphates. This experiment was performed within the pH range of 7-7.6. Figure 24a illustrates that at pH 7, hydroxyapatite would precipitate at phosphate dosages greater than 6.75 mg/L for the conditions in this experiment (100 mg/L as $CaCO_3$). However, hydroxyapatite would precipitate at all phosphate dosages (2 to 10 mg/L) at pH 7.6. Figure

Table 7. Example theoretical speciation

Species	Species concentration-mol/L		
	pH 6	pH 7	pH 8
$NaHCO_3$ added	$3.000X10^{-3}$	$3.000X10^{-3}$	$3.000X10^{-3}$
$CaCl_2$ added	$1.000X10^{-3}$	$1.000X10^{-3}$	$1.000X10^{-3}$
Total PO_4 (P_T)	$1.000X10^{-4}$	$1.000X10^{-4}$	$1.000X10^{-4}$
PO_4^{3-}	$3.997X10^{-12}$	$1.877X10^{-10}$	$2.488X10^{-10}$
HPO_4^{2-}	$6.773X10^{-6}$	$3.111X10^{-5}$	$4.250X10^{-6}$
$H_2PO_4^-$	$8.979X10^{-5}$	$4.070X10^{-5}$	$5.661X10^{-7}$
$H_3PO_{4(aq)}$	$1.107X10^{-8}$	$4.994X10^{-10}$	$6.998X10^{-13}$
OH^-	$7.385X10^{-9}$	$7.419X10^{-8}$	$7.372X10^{-7}$
Ca^{2+}	$9.885X10^{-4}$	$9.413X10^{-4}$	$4.748X10^{-4}$
$CaOH^+$	$1.322X10^{-10}$	$1.244X10^{-9}$	$6.380X10^{-9}$
$CaHCO_3^+$	$6.103X10^{-6}$	$1.503X10^{-5}$	$8.138X10^{-6}$
$CaCO_{3(aq)}$	$3.427X10^{-8}$	$8.403X10^{-7}$	$4.577X10^{-6}$
$CaSO_{4(aq)}$	$1.909X10^{-6}$	$1.769X10^{-6}$	$9.764X10^{-7}$
$CaHPO_{4(aq)}$	$1.857X10^{-6}$	$7.848X10^{-6}$	$5.665X10^{-7}$
$CaPO_4^-$	$4.301X10^{-9}$	$1.826X10^{-7}$	$1.310X10^{-7}$
$CaH_2PO_4^+$	$1.539X10^{-6}$	$6.536X10^{-7}$	$4.689X10^{-9}$
Na^+	$2.999X10^{-3}$	$2.996X10^{-3}$	$2.996X10^{-3}$
$NaCO_3^-$	$1.555X10^{-9}$	$4.067X10^{-8}$	$4.294X10^{-7}$
$NaHCO_{3(aq)}$	$1.209X10^{-6}$	$3.150X10^{-6}$	$3.346X10^{-6}$
$NaSO_4^-$	$1.920X10^{-7}$	$1.898X10^{-7}$	$2.031X10^{-7}$
$NaHPO_4^-$	$2.655X10^{-8}$	$1.198X10^{-7}$	$1.675X10^{-8}$

Table 7. Continued

Species	Species concentration-mol/L		
	pH 6	pH 7	pH 8
Mn^{2+}	$3.813X10^{-28}$	$3.877X10^{-30}$	$3.790X10^{-32}$
Mn^{3+}	$4.938X10^{-31}$	$5.106X10^{-34}$	$4.880X10^{-37}$
Cl^-	$2.000X10^{-3}$	$2.000X10^{-3}$	$2.000X10^{-3}$
$MnCl^+$	$2.300X10^{-30}$	$2.299X10^{-32}$	$2.300X10^{-34}$
$MnCl_{2(aq)}$	$1.073X10^{-33}$	$1.062X10^{-35}$	$1.077X10^{-37}$
$MnCl_3^-$	$9.653X10^{-37}$	$9.558X10^{-39}$	$< 1X10^{-40}$
$MnOH^+$	$5.213X10^{-33}$	$5.236X10^{-34}$	$5.205X10^{-35}$
$MnSO_{4(aq)}$	$6.432X10^{-31}$	$6.364X10^{-33}$	$6.811X10^{-35}$
$MnHCO_3^+$	$4.425X10^{-30}$	$1.164X10^{-31}$	$1.221X10^{-33}$
CO_3^{2-}	$4.858X10^{-8}$	$1.294X10^{-6}$	$1.335X10^{-5}$
HCO_3^-	$9.274X10^{-4}$	$2.439X10^{-3}$	$2.560X10^{-3}$
SO_4^{2-}	$1.790X10^{-5}$	$1.804X10^{-5}$	$1.883X10^{-5}$
HSO_4^-	$1.204X10^{-9}$	$1.197X10^{-10}$	$1.273X10^{-11}$
Solids that have precipitated	Pyrolusite (MnO_2)	Pyrolusite ($MnO_{2(s)}$) Hydroxyapatite $Ca_5(PO_4)_3OH$	Pyrolusite ($MnO_{2(s)}$) Hydroxyapatite $Ca_5(PO_4)_3OH$ Calcite ($CaCO_3$)

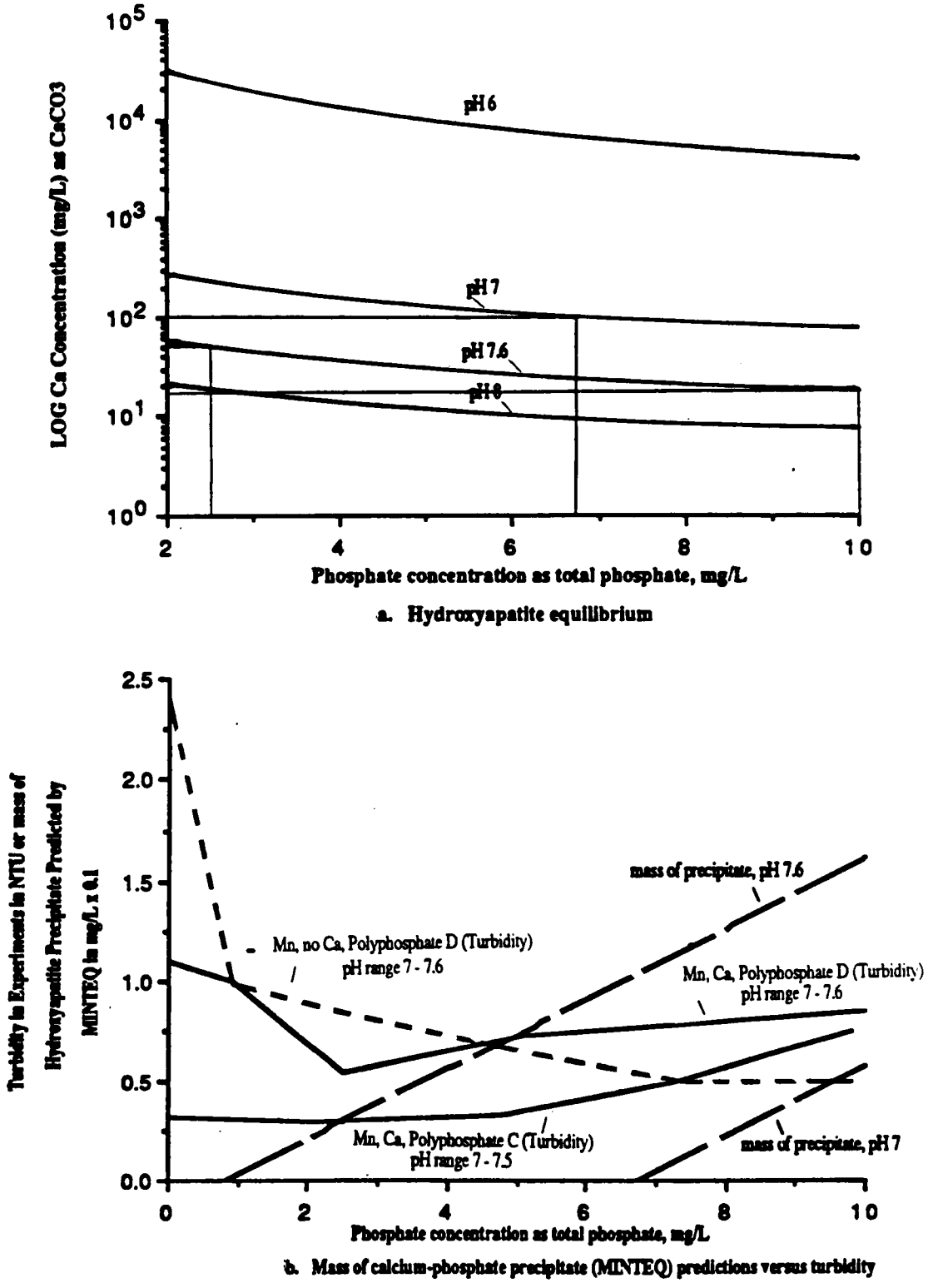


Figure 24. Hydroxyapatite equilibrium

24b shows that both the turbidity and the mass of the calcium-phosphate precipitate increase with the phosphate dosage. In the presence of calcium (100 mg/L as $CaCO_3$), the turbidity decreases at a phosphate dosage of about 2.5 mg/L and then increases at 5 mg/L. Turbidity is even worse at 10 mg/L, whereas in the absence of calcium, the turbidity continues to decrease with increasing polyphosphate dosages. The breakpoint for turbidity lies in the range where calcium-phosphate precipitation should start. If the curve plotting the turbidity in the absence of calcium is added with the calcium-phosphate precipitation curve, then a curve results which shows an initial decrease and then an increase, similar to the trends for the polyphosphates C and D turbidity curves. Although adding curves which represent turbidity (NTU) and mass of calcium-phosphate precipitate (mg/L x 0.1) is not legitimate, it serves for illustrative purposes. Equilibrium for hydroxyapatite is given by the following expression which is part of the MINTEQ data base:

$$Ca_5(PO_4)_3(OH)_{(s)} + H^+ = 5Ca^{2+} + 3PO_4^{3-} + H_2O\ ; \qquad K_{so} = 10^{-38.896}$$

and $$K_{so} = [Ca^{2+}]^5[PO_4^{3-}]^3/[H^+] = 10^{-38.898}$$

4.3.4 Manganese Treatment by Polyphosphate C and Hypochlorite in the Presence of Calcium

Varying dosages of polyphosphate C were tested in this experiment (Table A4 and Figures 25-27). In the previous

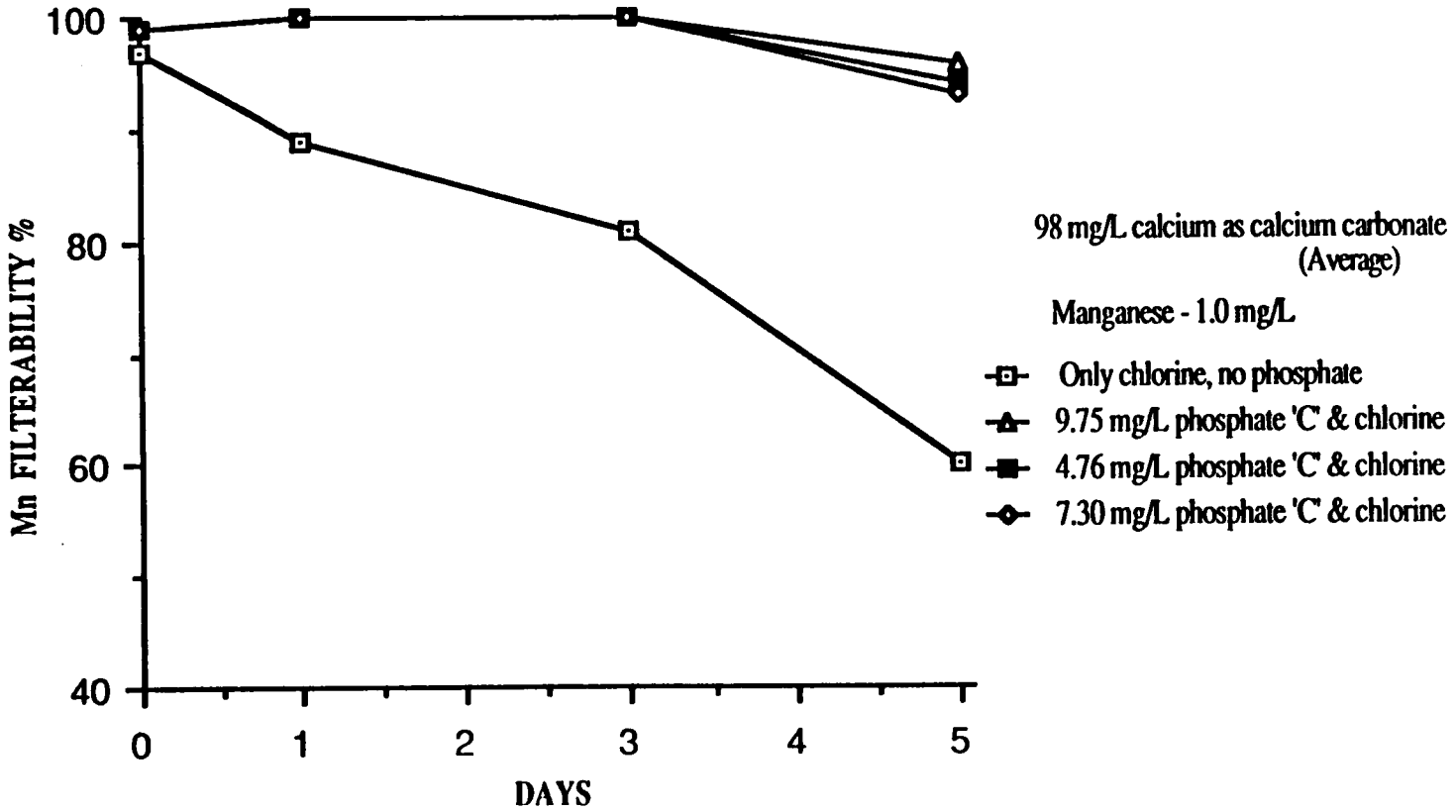


Figure 25. Manganese treatment with polyphosphate C and hypochlorite in the presence of calcium: manganese filterability

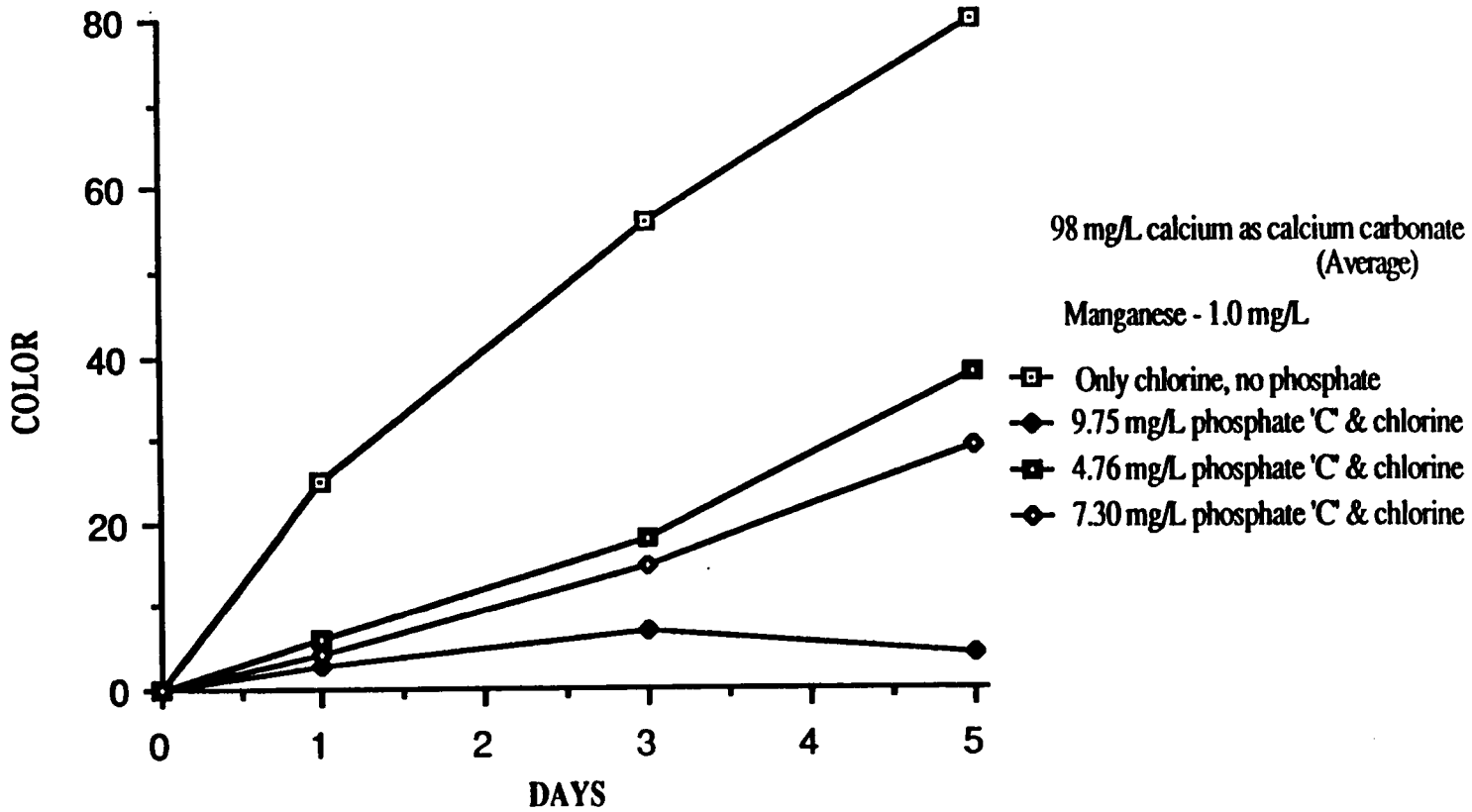


Figure 26. Manganese treatment with polyphosphate C and hypochlorite in the presence of calcium: color

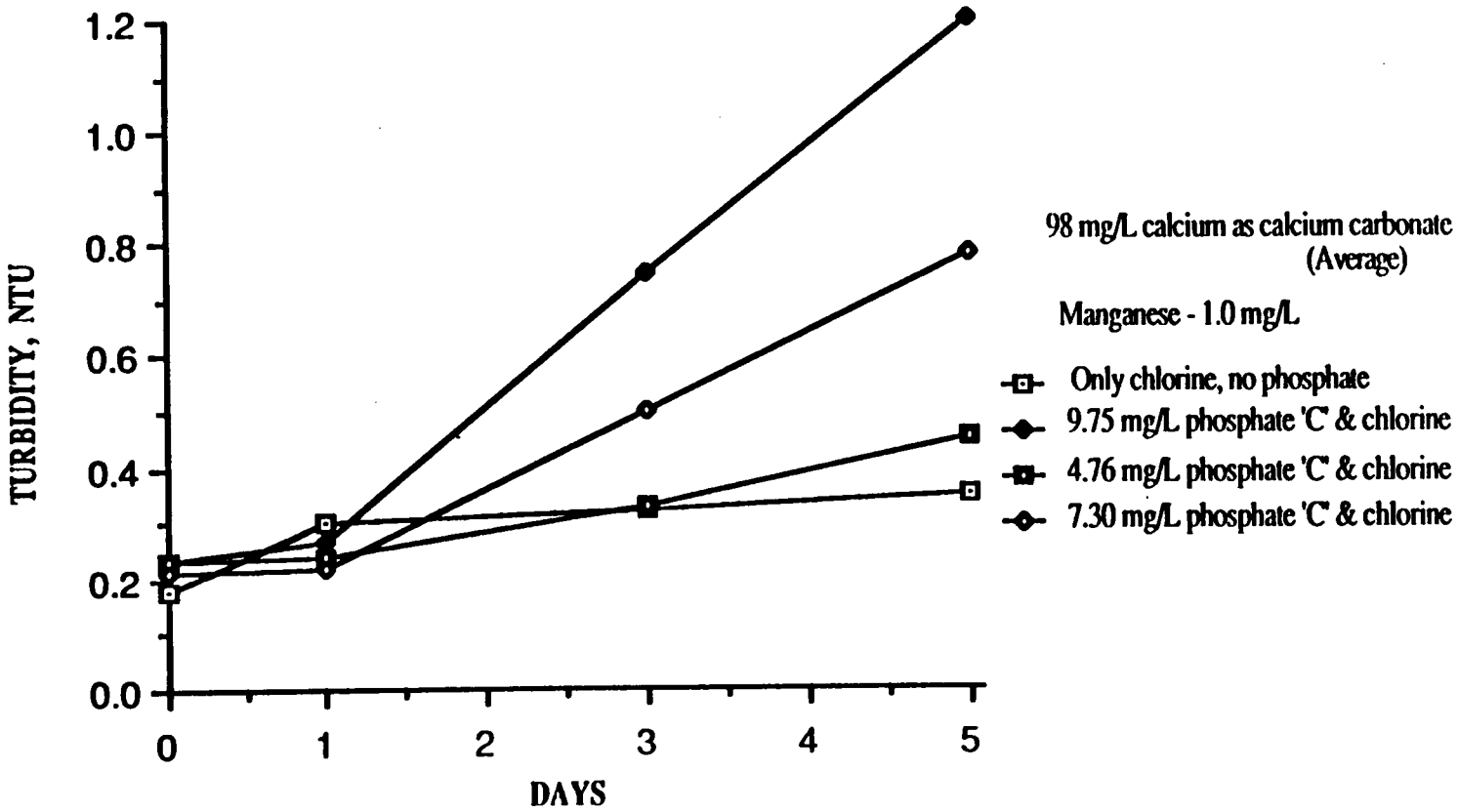


Figure 27. Manganese treatment with polyphosphate C and hypochlorite in the presence of calcium: turbidity

experiment, polyphosphate D was tested and found to be effective in manganese treatment in the presence of hardness for a period of three days, and the optimum phosphate dosage was determined to be 6.4 mg/L as total phosphate (Figures 19-21, also see Section 4.11). However, on day 5, color increased to about 18 color units (Figure 20), which is above the permissible limit of 15 color units. Even though treated water would have passed out of the distribution system within this time period, this experiment tested polyphosphate C to determine if better treatability could be obtained with this particular type of polyphosphate. Figures 25-27 plot the filterability, color and turbidity data shown in Table A4. In general, the trends observed were similar to the previous experiments with calcium present. Higher phosphate dosages yielded higher manganese filterability (Figure 25), lower color (Figure 26), but greater turbidity (Figure 27). A dosage of 10 mg/L as total phosphate gave the maximum turbidity (about 1.2 NTU). The turbidity was slightly lower in this experiment (0.40 NTU) at a dosage of about 6.4 mg/L as total phosphate (day 3) compared to 0.70 NTU observed in the previous experiment with polyphosphate D. However, the color was slightly higher in this experiment (35 color units) on day 5 compared to 18 color units obtained with polyphosphate D in the previous experiment. Manganese filterability was greater than 90% in both experiments. These results indicate that there is no significant difference in manganese treatability between the two polyphosphates. Figures A10-A14 plot the pH, free

chlorine, calcium filterability, total calcium, and total manganese versus time for this experiment.

4.3.5 Comparison of the Manganese Sequestering Ability of Several Polyphosphates and an Orthophosphate with Hypochlorite in the Presence of Calcium

This experiment tested polyphosphates A, B, C and D (Figures 28-30) and an orthophosphate (KH_2PO_4) to identify the phosphate which is most suitable for manganese sequestration. Calcium was added to provide a hardness of 100 mg/L calcium as calcium carbonate. A chlorine residual was maintained for a period of five days, and the pH was adjusted to 7.0 on days of sampling.

The standard deviation (SD) and coefficient of variation (CV) for filterability (Figure 28), turbidity (Figure 29) and color (Figure 30) in this experiment and a quality control experiment which tested replicate bottles (Section 4.7) indicate that there may not be a significant difference between the effectiveness of polyphosphates A, B, C and D (Table 8). However, data for replicates were from the quality control experiment which used polyphosphate A which is a subset of the data for polyphosphates A, B, C, and D. The fact that SD and CV for color and filterability are significantly lower for polyphosphates A, B, C and D than for replicates of polyphosphate A indicate that polyphosphate A may not be a very good control variable. Data from this experiment was chosen for performing statistical analysis, as all the polyphosphates (A, B, C and D) were

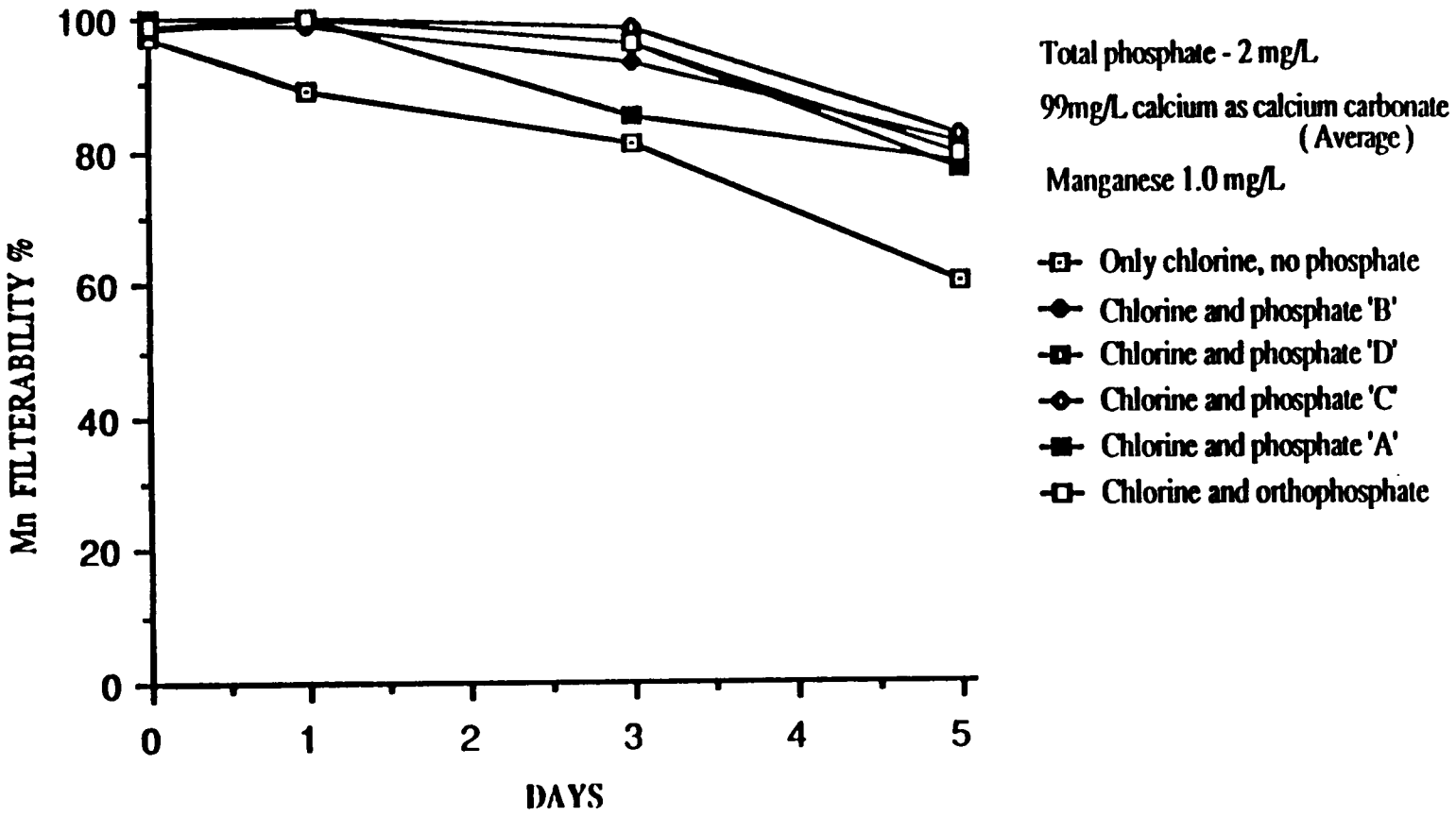


Figure 28. Side-by-side comparison of the manganese sequestering ability of several polyphosphates and an orthophosphate with hypochlorite: manganese filterability

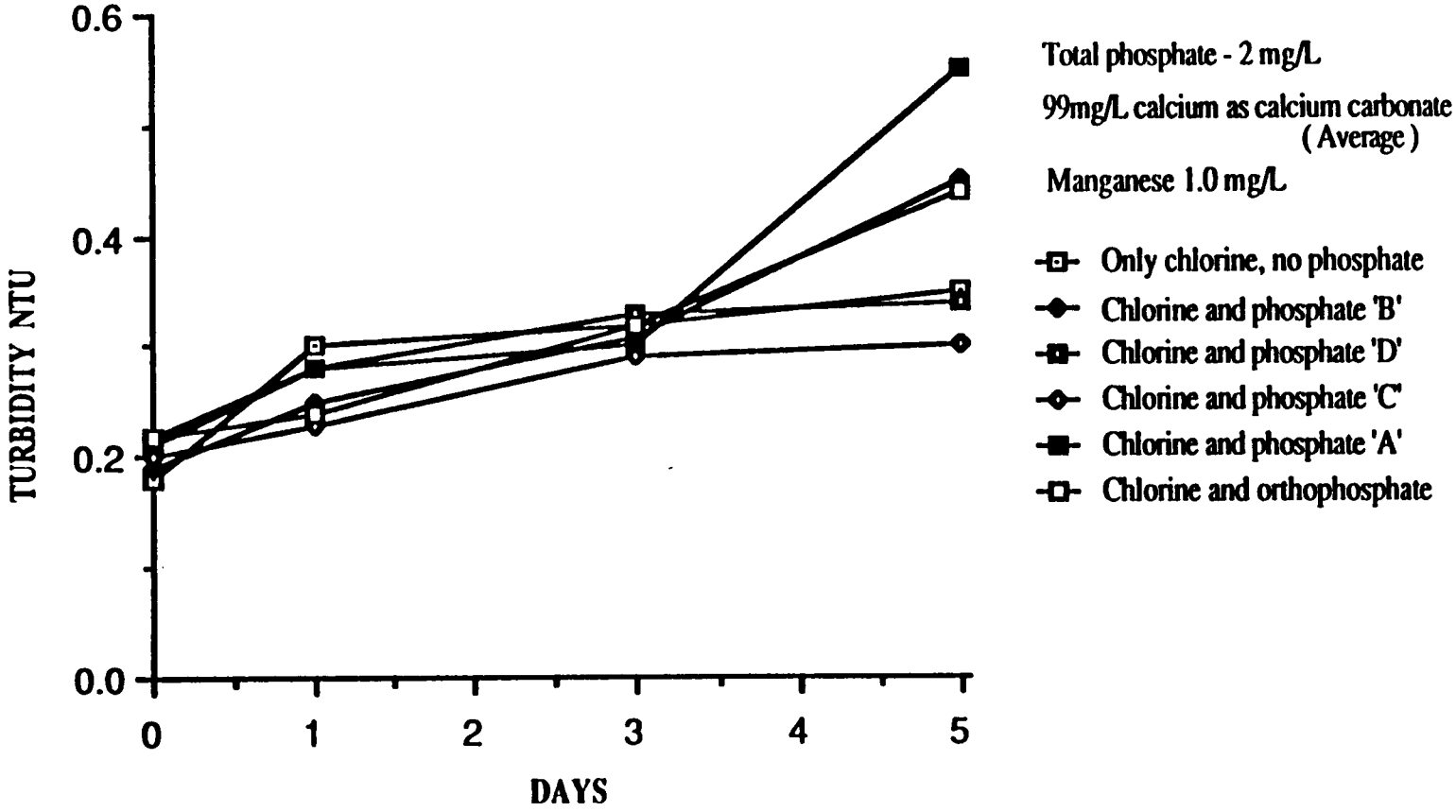


Figure 29. Side-by-side comparison of the manganese sequestering ability of several polyphosphates and an orthophosphate with hypochlorite: turbidity

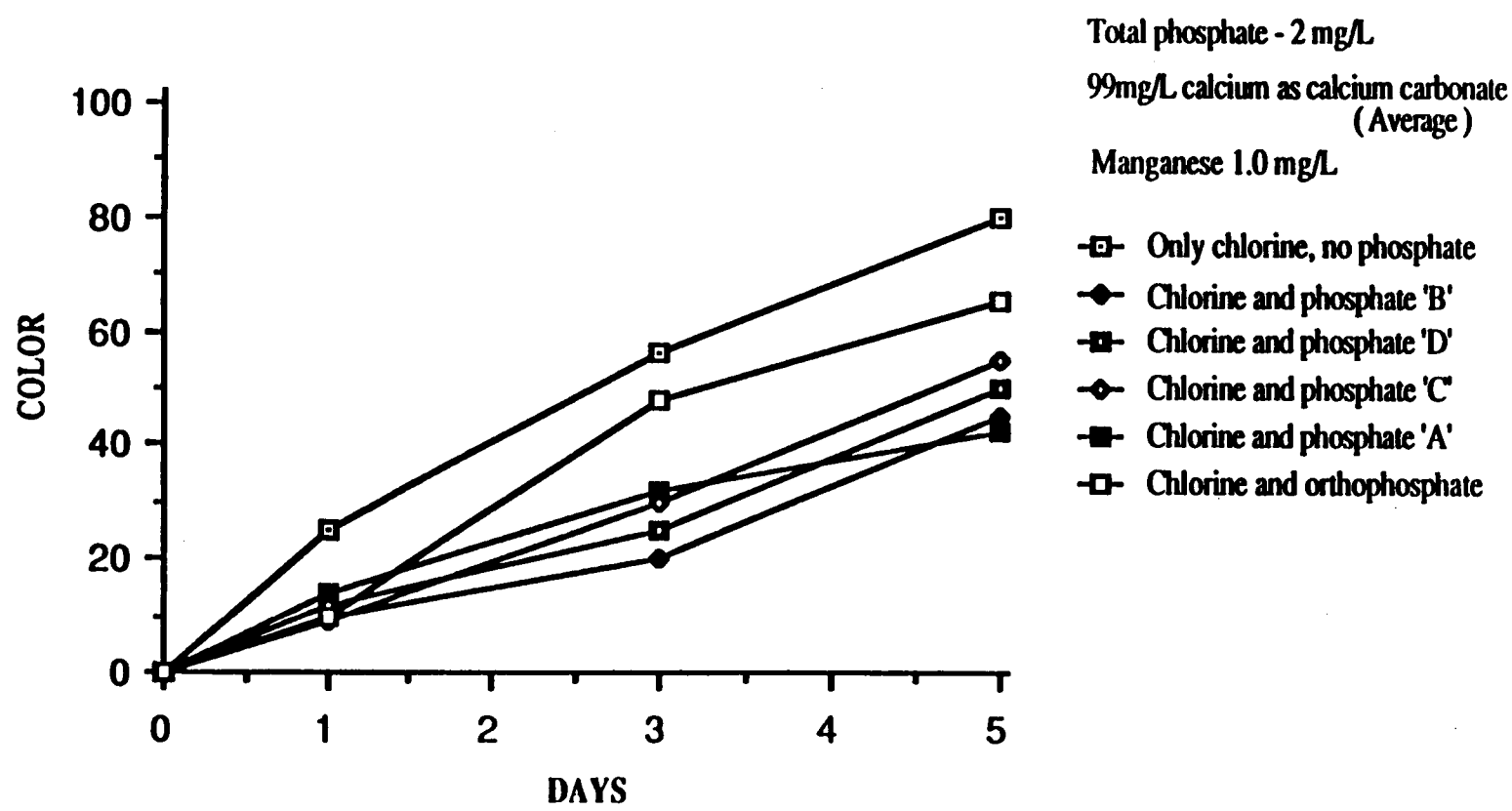


Figure 30. Side-by-side comparison of the manganese sequestering ability of several polyphosphates and an orthophosphate with hypochlorite: color

tested at a constant phosphate dosage in the same experiment, compared to other experiments reported in Sections 4.3.3 and 4.3.4 which are from separate experiments testing polyphosphate C and D dosage effects. Since this research had multiple goals (Section 1.5), sufficient data to perform a better statistical analysis and arrive at a firm conclusion on the effectiveness of the various polyphosphates was not available. Hence, future studies should test replicates of several polyphosphates (in addition to the four polyphosphates tested in this research) to perform a more detailed statistical analysis. Figures A15-A19 in the appendix show the pH, free Cl_2, total and filterable Ca, and total Mn for this experiment.

Table 8. Statistical calculations

Statistics	Filt. replicates	Filt. A, B, C,D	Turbidity replicates	Turbidity A, B, C, D	Color replicates	Color A, B, C, D
MEAN (DAY 0)	100	99	0.13	0.21	0	0
SD (DAY 0)	0.58	0.95	0.02	0.01	0	0
CV % (DAY 0)	0.58	0.96	11.28	6.19	0	0
MEAN (DAY 1)	98	99	0.42	0.31	0	11
SD (DAY 1)	0.58	0.50	0.03	0.02	0	2.22
CV % (DAY 1)	0.59	0.50	5.95	6.45	0	19.70
MEAN (DAY 3)	93	93	0.74	0.31	6	27
SD (DAY 3)	5.03	5.72	0.04	0.02	5.29	5.38
CV % (DAY 3)	5.39	6.15	4.87	5.48	88	20
MEAN (DAY 5)	90	80	0.64	0.41	15	48
SD (DAY 5)	7	2.38	0.06	0.11	25	5.72
CV % (DAY 5)	7.77	2.99	9.38	26.8	60	12
MEAN (average)	95	93	0.48	0.31	8	22
SD (average)	3.30	2.38	0.03	0.04	5.07	3.33
CV % (average)	3.58	2.65	7.87	11.23	37	13

4.3.6 Correlation Between Polyphosphate Characteristics and Treatment Success

Several commercially available polyphosphates and an orthophosphate (KH_2PO_4) were compared in this research. The characteristics of the phosphates as given by the manufacturers (92, 105) and available from previous work by other researchers (87) are given in Table 9 and 10. Table 9 contains data from the studies of Reed et al. (87) on the reversion rate of polyphosphates A, B and D. Polyphosphate C was not tested in Reed et al.'s studies. The significance of the reversion rate and its effects on the sequestration process were discussed in Section 2.8. Table 10 indicates that the molecular weight and the orthophosphate percentage of the total phosphate were different for each polyphosphate type. This ratio indicates the amount of polyphosphate which is present in the polymeric form. Even though characteristics of the polyphosphates were different, no significant difference in manganese treatability was observed (Figures 28-30) when these polyphosphates were used.

Table 9. Reversion rates of polyphosphates in %/day (87)

Polyphosphate	%/day
A	6.69
B	7.00
D	13.42

Table 10. Other characteristics of Polyphosphates

Polyphosphate	Form	%PO4	% orthophosphate (as % of total PO4)	Molecular Weight
A	Liquid	23%	32%	1785
B	Solid	81%	27%	5098
C	Liquid	34%	36%	331
D	Liquid	72%	36%	5408

4.3.7 Effects of pH on Manganese Treatability by Polyphosphates and Hypochlorite

In all of the earlier experiments, pH was adjusted to 7 on days of sampling. To observe the effects of pH on manganese treatability, an additional experiment was run adjusting pH levels to pH 6, 7, and 8 on days of sampling (Figures 31-33). The maximum drift in pH between days of sampling was about 0.55 units. Hence, it would be more appropriate to state that this experiment was performed at pH ranges of 6.0-6.3, 7.0-7.55, and 7.85-8.1. Data for this experiment are shown in appendix Table A5. Polyphosphate A was used in this experiment, and calcium was added to provide a hardness of 100 mg/L as calcium carbonate. A free chlorine residual was maintained continually throughout the experiment. As indicated by filterability (Figure 31), turbidity (Figure 32) and color (Figure 33), best treatability was obtained at pH 6. At pH 6 on day 5,

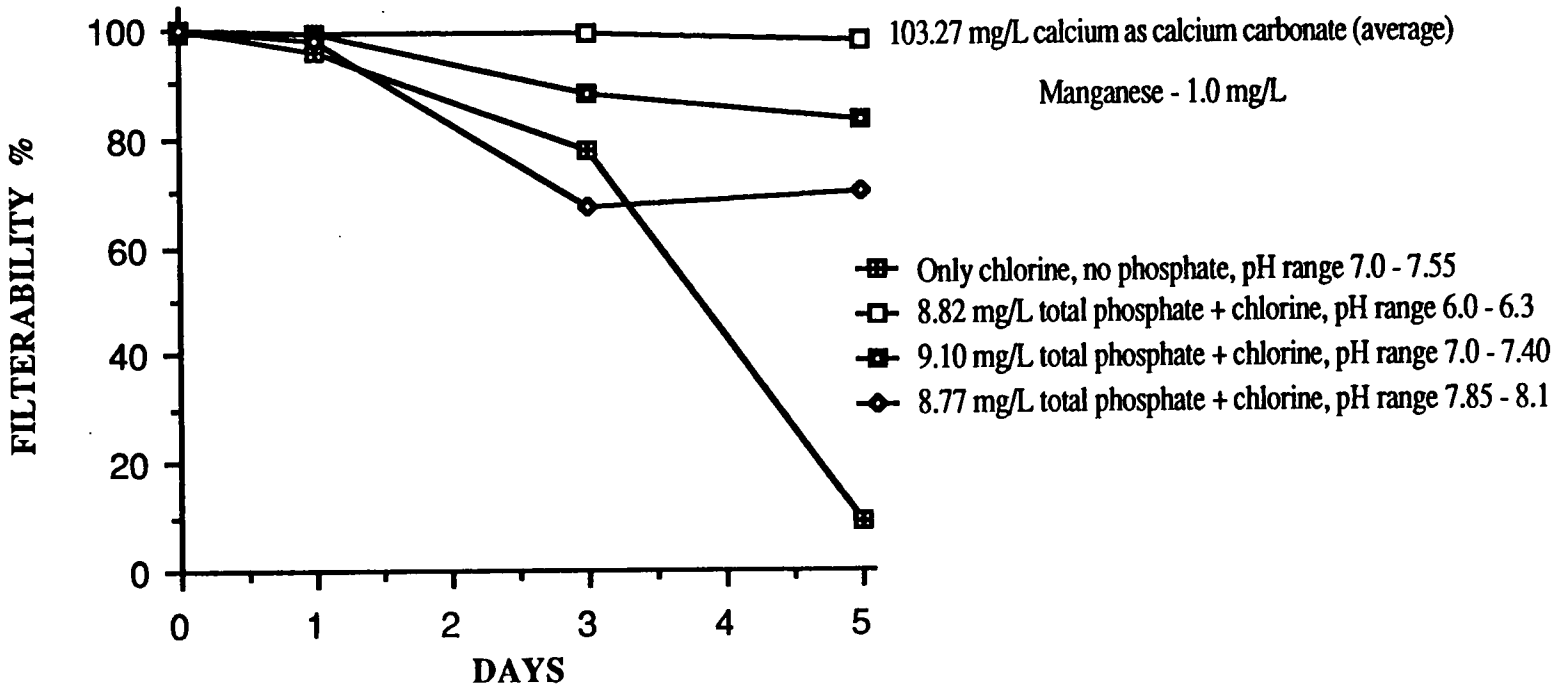


Figure 31. pH effects on manganese treatment by polyphosphate and hypochlorite: manganese filterability

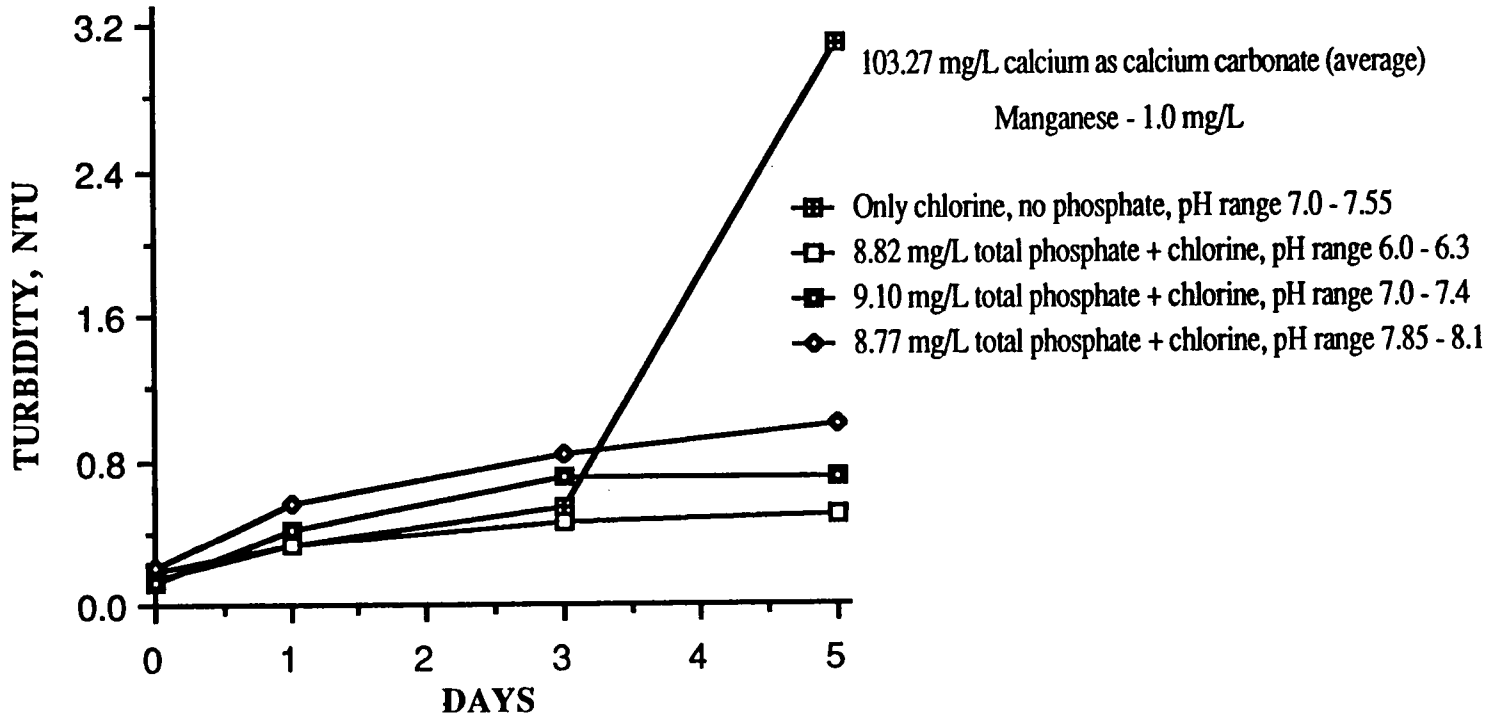


Figure 32. pH effects on manganese treatment by polyphosphate and hypochlorite: turbidity

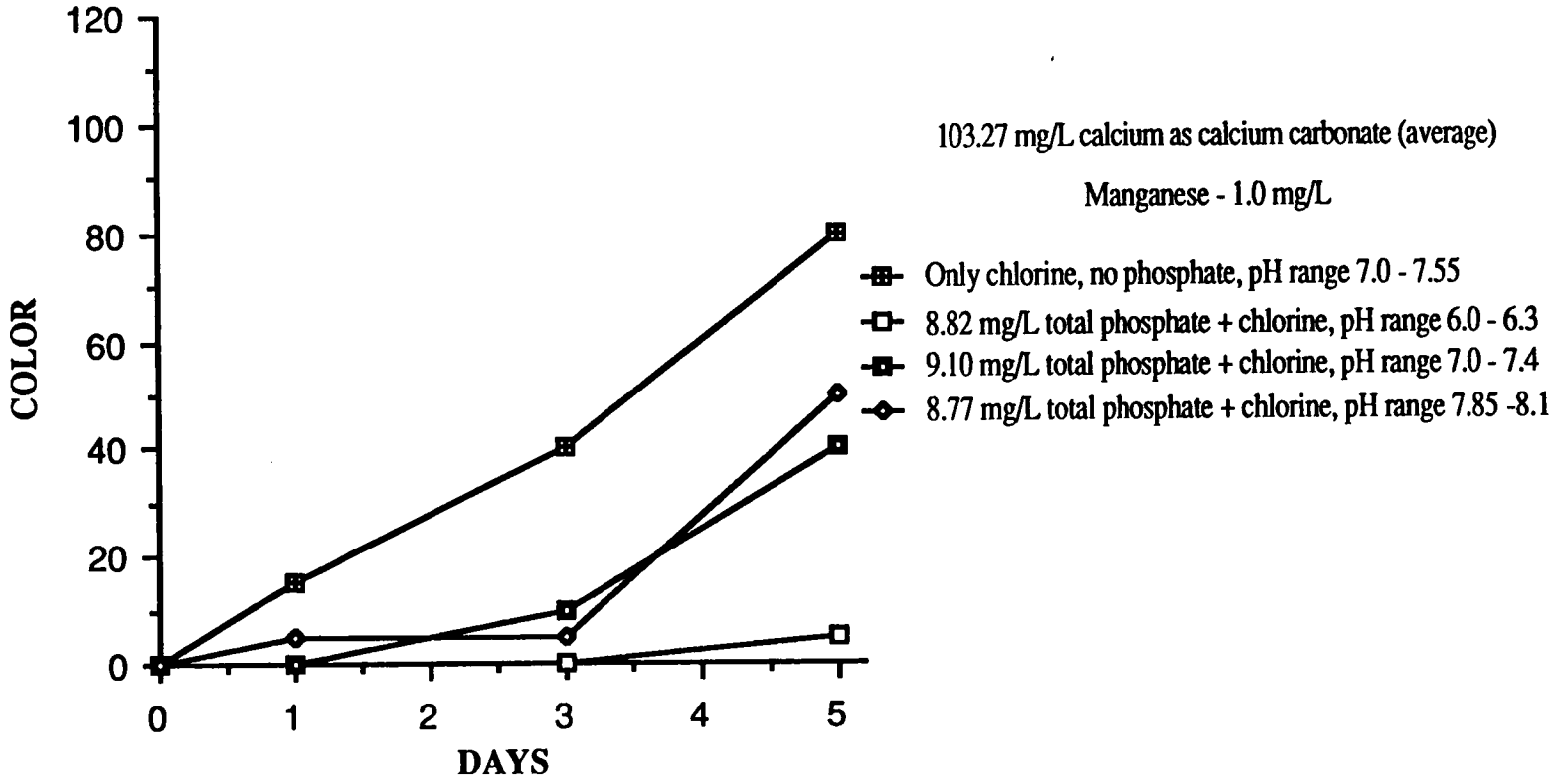


Figure 33. pH effects on manganese treatment by polyphosphate and hypochlorite: color

filterability was 98%, turbidity was 0.5 NTU and color was equal to 5 units. The desired manganese treatability was obtained for a period of three days at pH 7. On day 5 at pH 7.0, filterability decreased to less than 90% and increase in color was noticed. Even though the decline in filterability and increase in color was more significant at pH 8.0 than at pH 7 on day 5, significant decrease in total manganese was observed on day 5 for both pH 7 and pH 8 (Figure 34), indicating that manganese precipitation took place. However, it is estimated that the treated water would have passed through the distribution system within three days. Figures A20 and A21 show the pH and free chlorine in this experiment. Bottles were again dosed with hypochlorite on day 1 to maintain a free chlorine residual throughout the period of this experiment.

As Figure 35 illustrates, the decrease in manganese treatability with increasing pH (Figure 31-34) is due to an increase in the degree of manganese oxidation at higher pH levels. Inhibition of oxidation of manganese could be the cause for the observed reduction in color (better treatability) at a lower pH, as color was always found to correlate with the degree of manganese oxidation (Figure 33). Also, presence of more manganese in the soluble form as Mn^{2+} could be one of the reasons for the observed high filterabilities through a 0.1 micron filter (Figure 31) and lower turbidities (Figure 32) in the treated water, as manganese was added in this experiment as Mn^{2+} and was not oxidized (Figure 35) even on

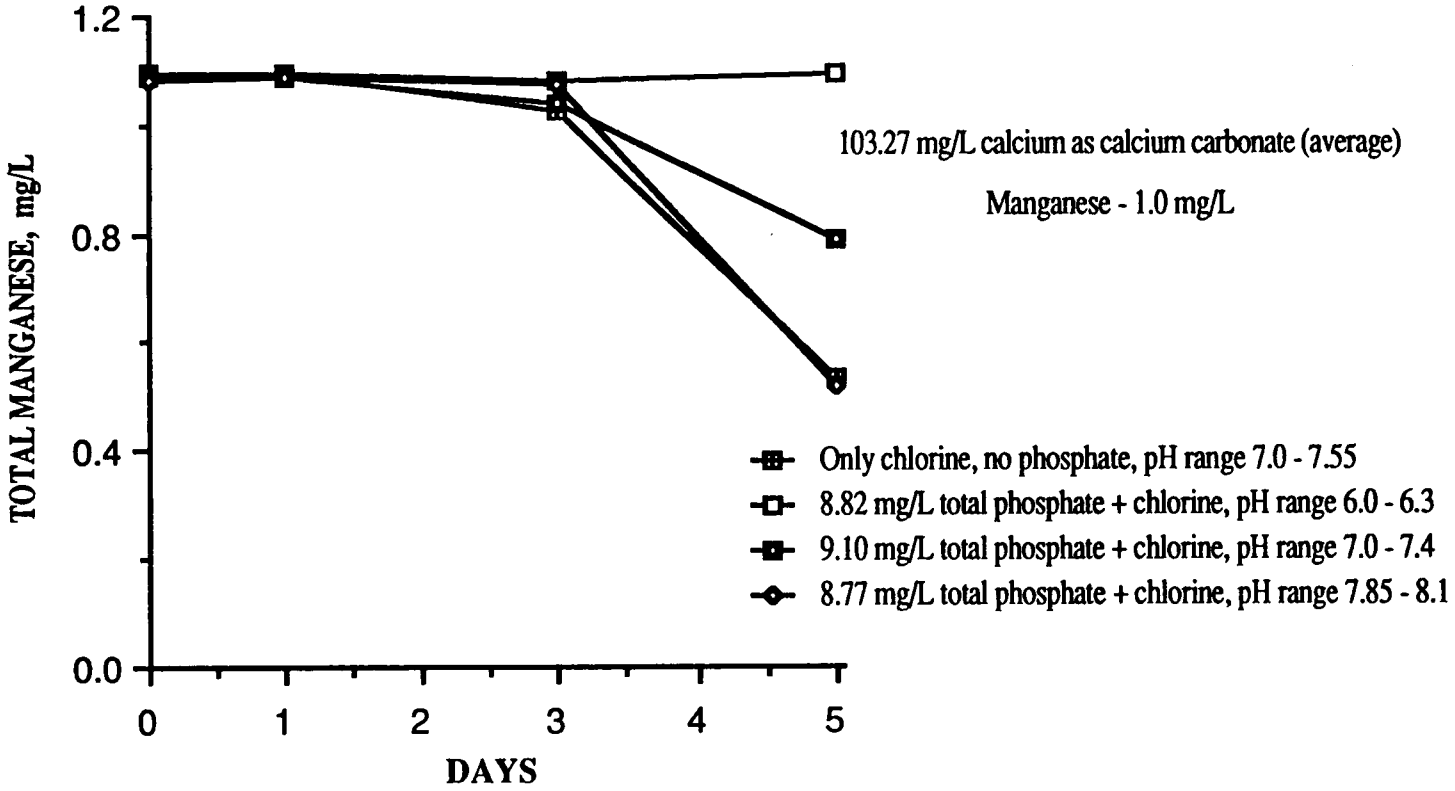


Figure 34. pH effects on manganese treatment by polyphosphate and hypochlorite: total manganese

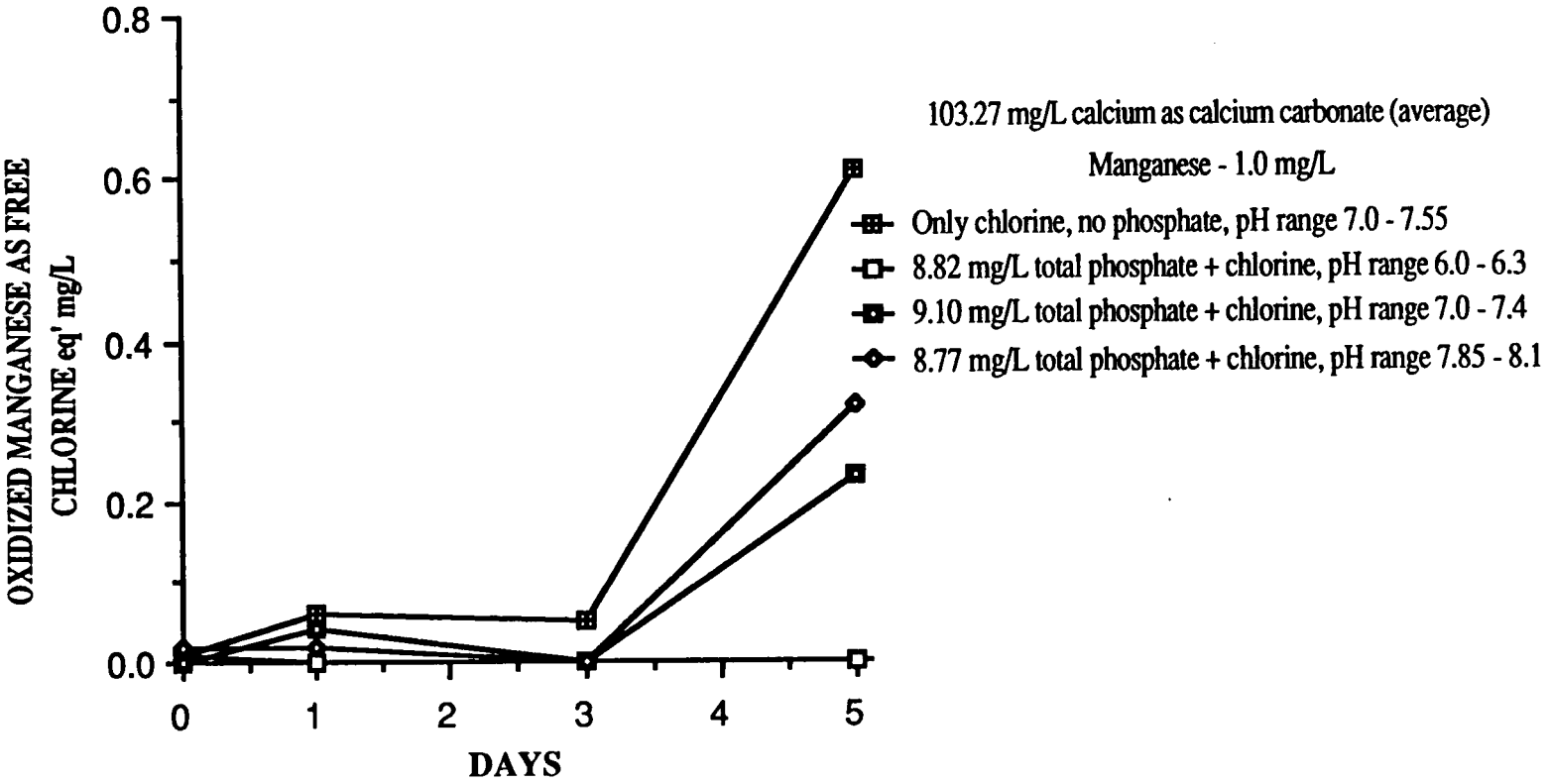


Figure 35. pH effects on manganese treatment by polyphosphate and hypochlorite: oxidized manganese

day 5 at lower pH levels. Increase in the degree of manganese oxidation at higher pH levels can be explained by the following equilibrium calculations for manganese oxidation by hypochlorite:

$OCl^- + 2H^+ + 2e^-$ <——> $Cl^- + H_2O$ $E^o = +1.72V$

$Mn^{2+} + 2H_2O$ <——> $MnO_2(s) + 4H^+ + 2e^-$ $E^o = -1.23V$

$Mn^{2+} + OCl^- + H_2O$ <——> $MnO_2(s) + 2H^+ + Cl^-$ $E^o = +0.49V$

where E^o is the standard electrode potential in volts. The standard state free energy change for this reaction is

$\Delta G^o = -n^oFE^o$

where n^o = the number of electrochemical gram equivalents per gram mole exchanged during the reaction

F = Faraday's constant (23.06 kcal/volt)

Hence, ΔG^o = -22.60 Kcal/mole

Free energy changes for conditions other than the standard state are given by $\Delta G = \Delta G^o + 2.303\ RT\ \log Q_r$

for 20°C, RT = $[(1.986 \times 10^{-3})kcal/(^oK)(mole)] \times 293^oK = 0.58$

$\Delta G = \Delta G^o + 1.34\ \log Q_r$

where the reaction quotient Q_r has the same form as the equilibrium constant, but pertains to nonequilibrium conditions

$Q_r = [Cl^-][H^+]^2/[Mn^{2+}][OCl^-]$

For conditions in this experiment ($CaCl_2$ = $1x10^{-3}$ moles or 100 mg/L as calcium carbonate, manganese = $2x10^{-5}$ moles or 1 mg/L, and OCL^- = $4.7x10^{-5}$ or 2.4 mg/L),

at pH 7

$$\Delta G = \Delta G^o + 1.34 \log [2x10^{-3}][10^{-7}]^2/[2x10^{-5}][4.7x10^{-5}]$$

$$= -22.60 - 10.28 = -32.88 \text{ kcal}$$

At pH 8,

$$\Delta G = \Delta G^o + 1.34 \log [2x10^{-3}][10^{-8}]^2/[2x10^{-5}][4.7x10^{-5}]$$

$$= -22.6 - 12.96 = -35.56 \text{ kcal}$$

The free energy change for oxidation increases with increasing pH, which implies that the thermodynamic spontaneity of manganese oxidation by hypochlorite and thus the degree of manganese oxidation also increases.

In this experiment, higher turbidity was noticed at pH 7 and 8 (due to the formation of a calcium phosphate precipitate) than at pH 6. MINTEQ was used to predict the total phosphate and calcium concentrations at which hydroxyapatite (a calcium-phosphate precipitate which is thermodynamically favored) would form at pH 6, 7, and 8. These results are illustrated in Figure 24 of Section 4.3.3. From the figure it is evident that better treatment can be obtained at pH 6, as hydroxyapatite precipitation will not take place at the

normal calcium concentrations in most ground waters at pH 6 but may at pH 7 and 8.

4.3.8 Summary: Polyphosphate/Hypochlorite Method

Results of experiments on manganese treatment by the polyphosphate/hypochlorite method support the conclusion that this method can be used in manganese sequestration. High filterability and low turbidity and color were observed in these experiments in the absence of hardness. In the presence of hardness, turbidity increased with the polyphosphate dosage. The maximum turbidity was observed to be about 1.2 NTU (Figure 27) at a phosphate dosage of 10 mg/L (Polyphosphate C) and a hardness of 100 mg/L calcium as calcium carbonate which were the highest calcium concentration and phosphate dosage tested. However, at a lower phosphate dosage of 7.3 mg/L (Polyphosphate C), turbidity decreased to about 0.5 NTU (which is below the standard of 1.0 NTU) and high filterability (Figure 25) as well as low color (Figure 26) was observed for a period of three days (Section 4.11). No significant difference was observed between the effectiveness of the various polyphosphates used, but orthophosphate performed poorly compared to polyphosphates.

As already documented in Section 4.3.1 and 4.3.7, either manganese was in an unoxidized form (Figure 12) or very little manganese was oxidized at pH 6 and 7 (Figure 35), as polyphosphates retarded the oxidation of manganese by hypochlorite. At pH 8, manganese was oxidized and high color was

produced on day 3 (Figure 33). However, even at pH 8, low discoloration could be maintained for a period of at least one day. From these results, it is evident that inhibition of manganese oxidation is an important mechanism by which polyphosphates sequester manganese when used with hypochlorite.

4.4 POLYPHOSPHATE/CHLORINE DIOXIDE METHOD

In order to observe differences in manganese oxidation and treatment in the presence of a stronger oxidant (which may also be used by utilities for disinfection purposes), an experiment was run substituting chlorine dioxide for hypochlorite. Chlorine dioxide was produced in the laboratory by reacting sodium chlorite ($NaClO_2$) with concentrated sulfuric acid according to standard methods (APHA et. al. 1985). Results of the polyphosphate/chlorine dioxide method of manganese treatment are discussed in the following section.

4.4.1 Comparison of the Manganese Sequestering Ability of Several Polyphosphates in the Presence of Calcium

Data from Table A6 which are reproduced in Figures 36-38 show the results of an experiment performed at pH 7, to compare the effectiveness of different polyphosphates with chlorine dioxide. Calcium was added in this experiment to provide a hardness of 115 mg/L calcium as calcium carbonate. The pH was adjusted to 7.0 on days when the samples were taken. Polyphosphates A and C

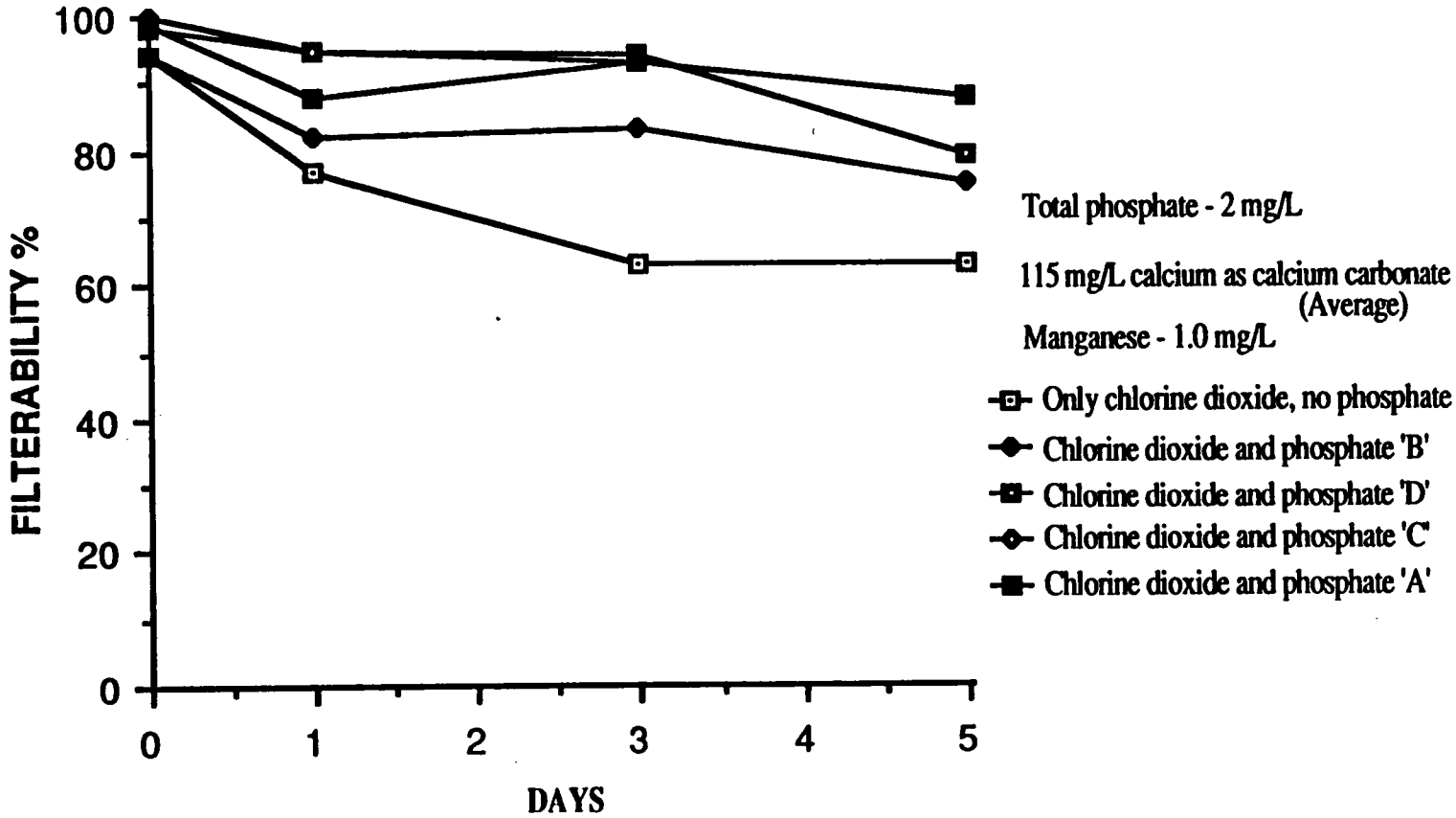


Figure 36. Side-by-side comparison of the manganese sequestering ability of several polyphosphates and chlorine dioxide in the presence of calcium: manganese filterability

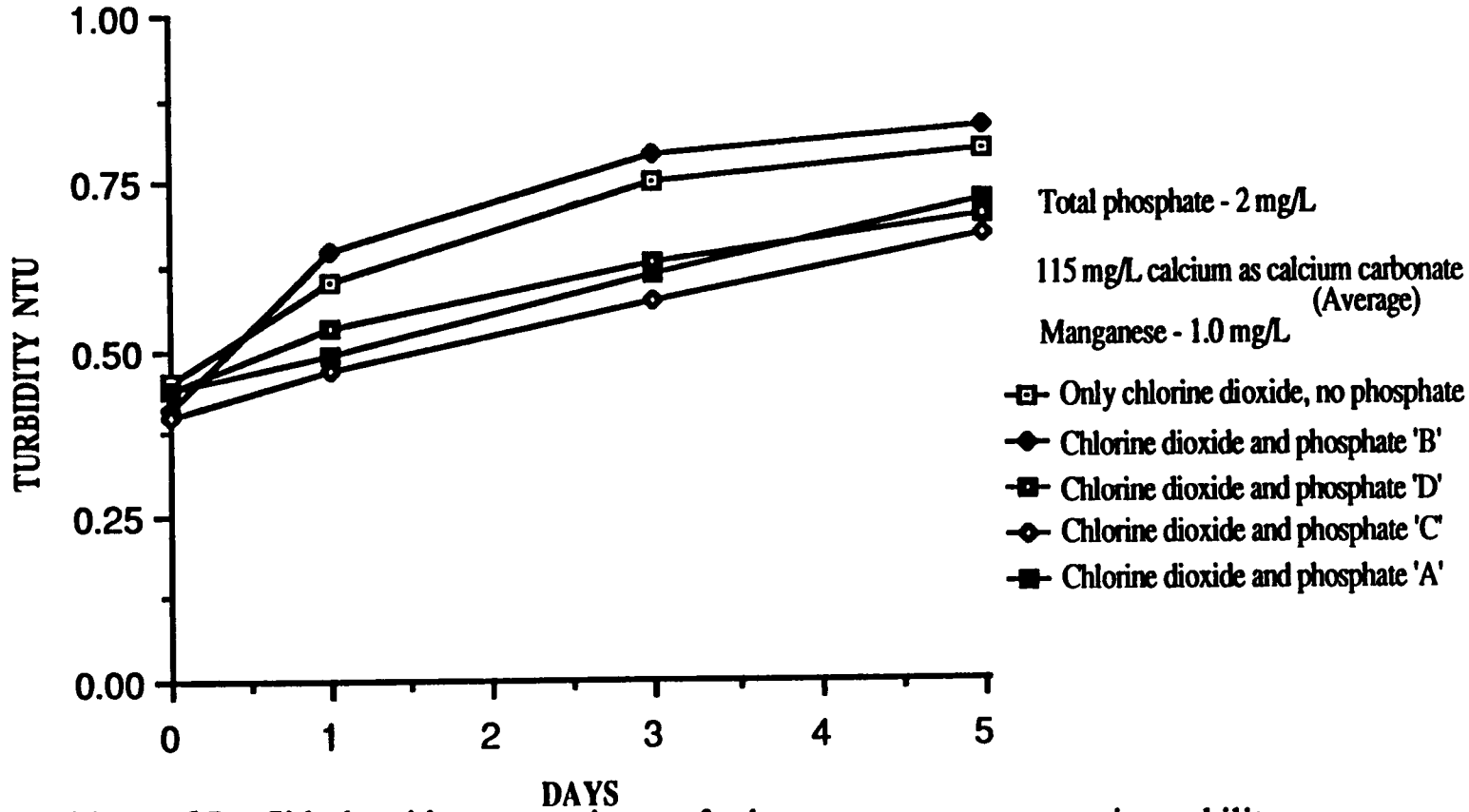


Figure 37. Side-by-side comparison of the manganesesequestering ability of several polyphosphates and chlorine dioxide in the presence of calcium: turbidity

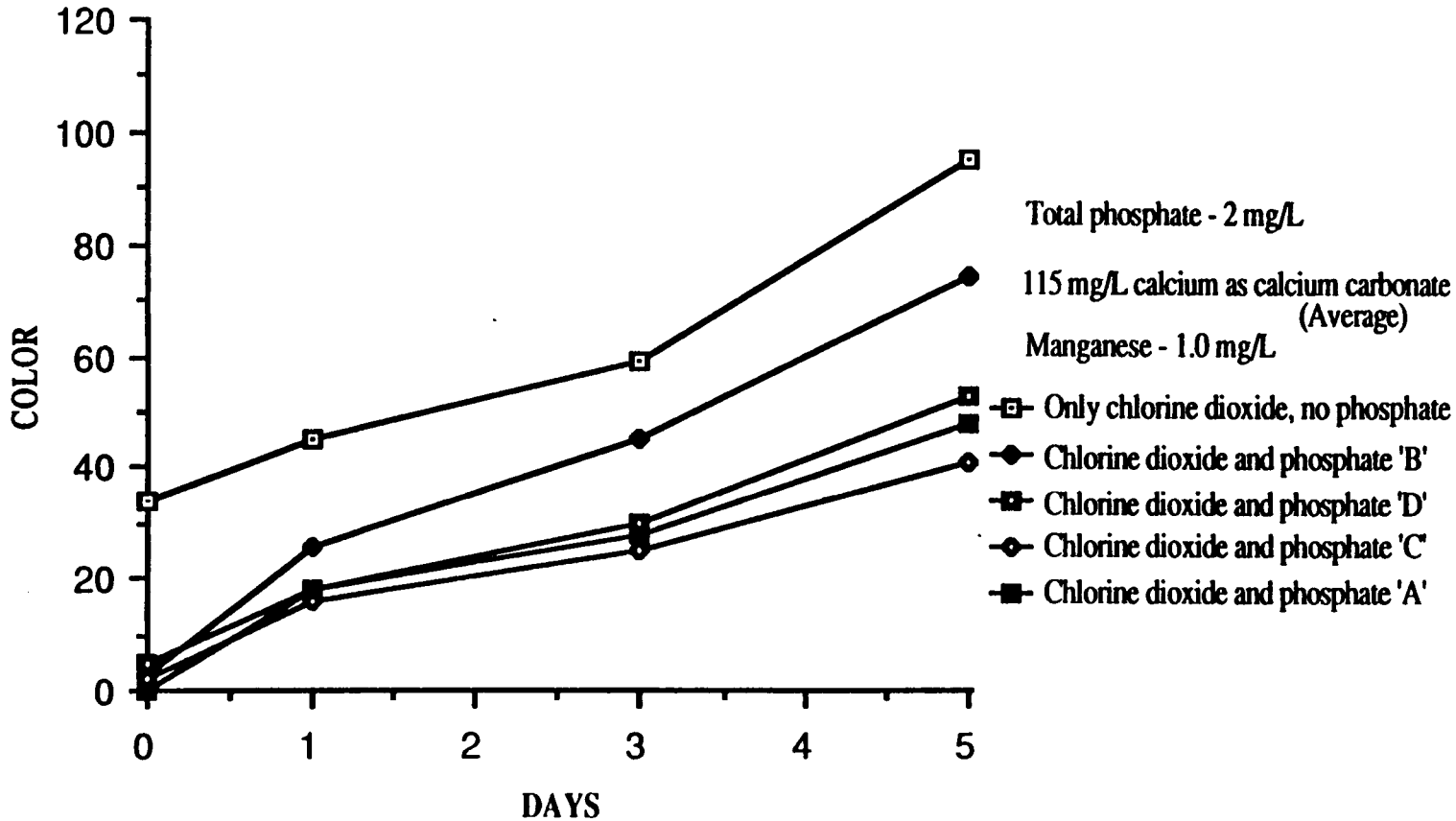


Figure 38. Side-by-side comparison of the manganese sequestering ability of several polyphosphates and chlorine dioxide in the presence of calcium: color

performed equally well in this experiment, and high manganese filterability (Figure 36) and low turbidity (Figure 37) were obtained. However, color (Figure 38) was greater than the permissible limit of 15 color units on day 3, about 28 units for type A and 25 units for polyphosphate C. The poorest performing polyphosphate (type B) gave a color of 45 units on day 3, turbidity of 0.79 NTU and low filterability (83%). Filterability dropped to less than 63% in the absence of polyphosphates, and color and turbidity were 59 units and 0.75 NTU respectively. All treated bottles showed a visible red-orange color. The color observed in this experiment indicates that the polyphosphate/chlorine dioxide method is not suitable for manganese sequestration. Figures A22 and A23 plot the pH and total manganese in this experiment.

4.4.2 Manganese Treatment with Polyphosphate D and Chlorine Dioxide in the Absence of Calcium

In this experiment, polyphosphate D was selected for further study to identify methods to improve treatment by the polyphosphate/chlorine dioxide method (Figures 39-43). The effectiveness of two different polyphosphate dosages and various dosages of chlorine dioxide were tested in the absence of calcium. One set of bottles was dosed at 2 mg/L phosphate, and the other set was dosed at 10 mg/L as total phosphate. Chlorine dioxide dosage varied from 0.5 mg/L to 2.0 mg/L in each set of bottles. The pH was adjusted to 7.0 on days when samples were taken. Ultrafiltration

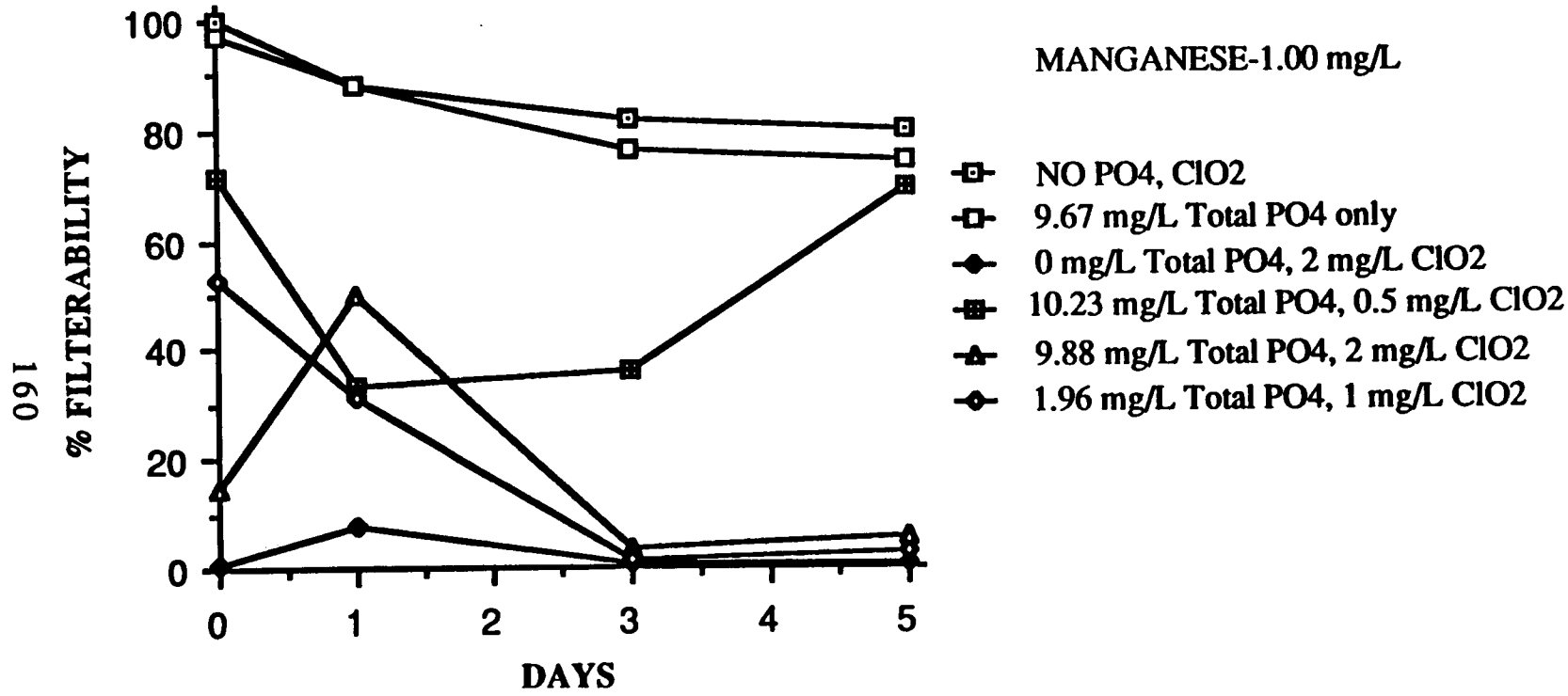


Figure 39. Manganese treatment with polyphosphate D and chlorine dioxide in the absence of calcium: ultrafiltration

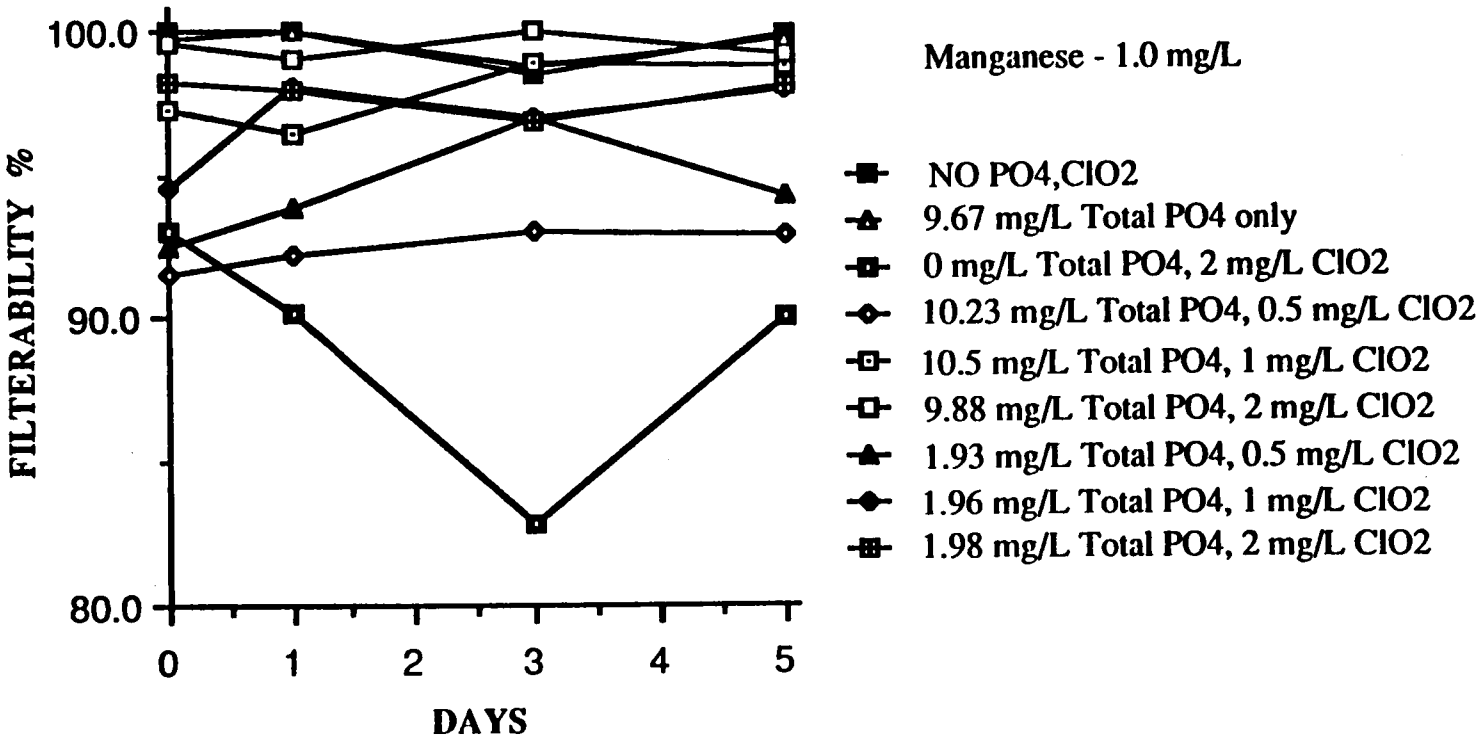


Figure 40. Manganese treatment with polyphosphate D and chlorine dioxide in the absence of calcium: manganese filterability

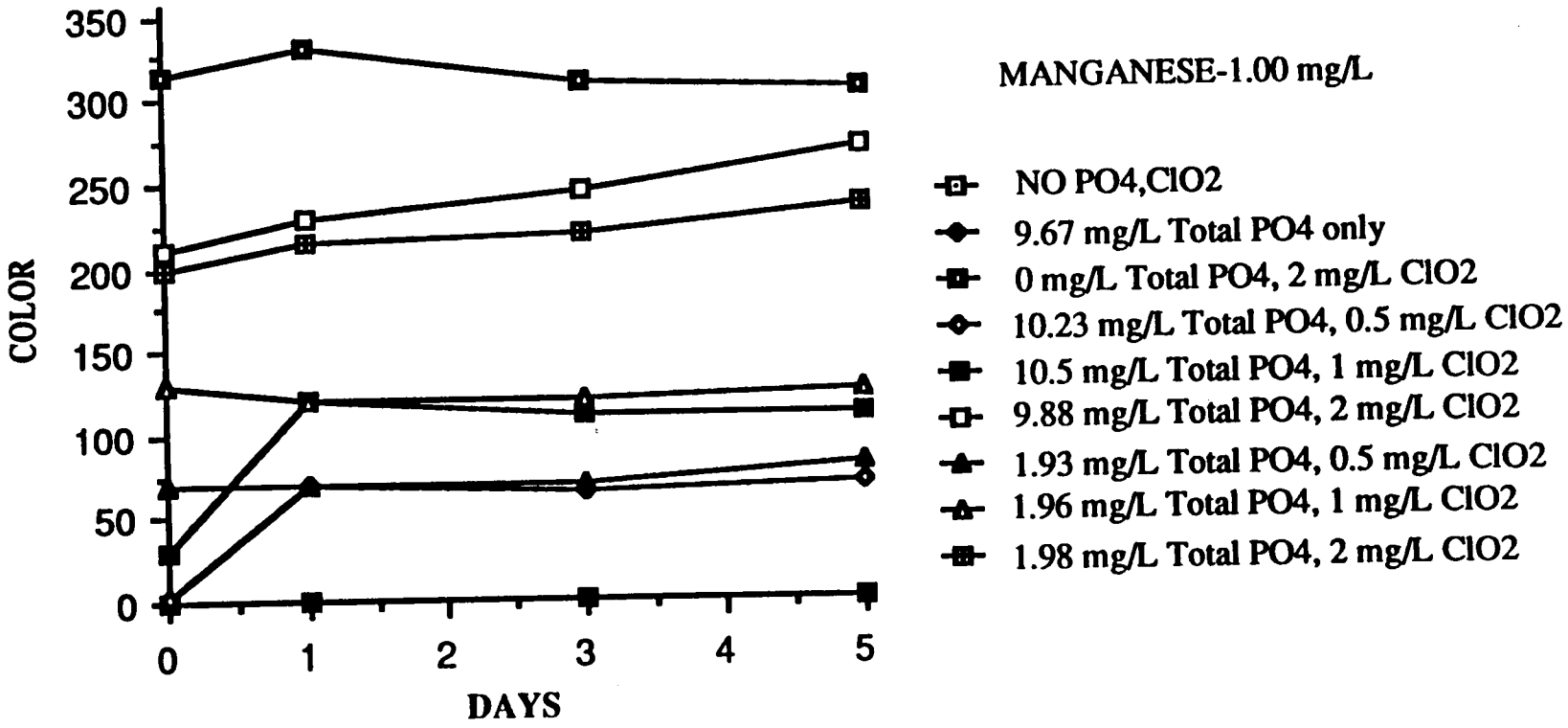


Figure 41. Manganese treatment with polyphosphate D and chlorine dioxide in the absence of calcium: color

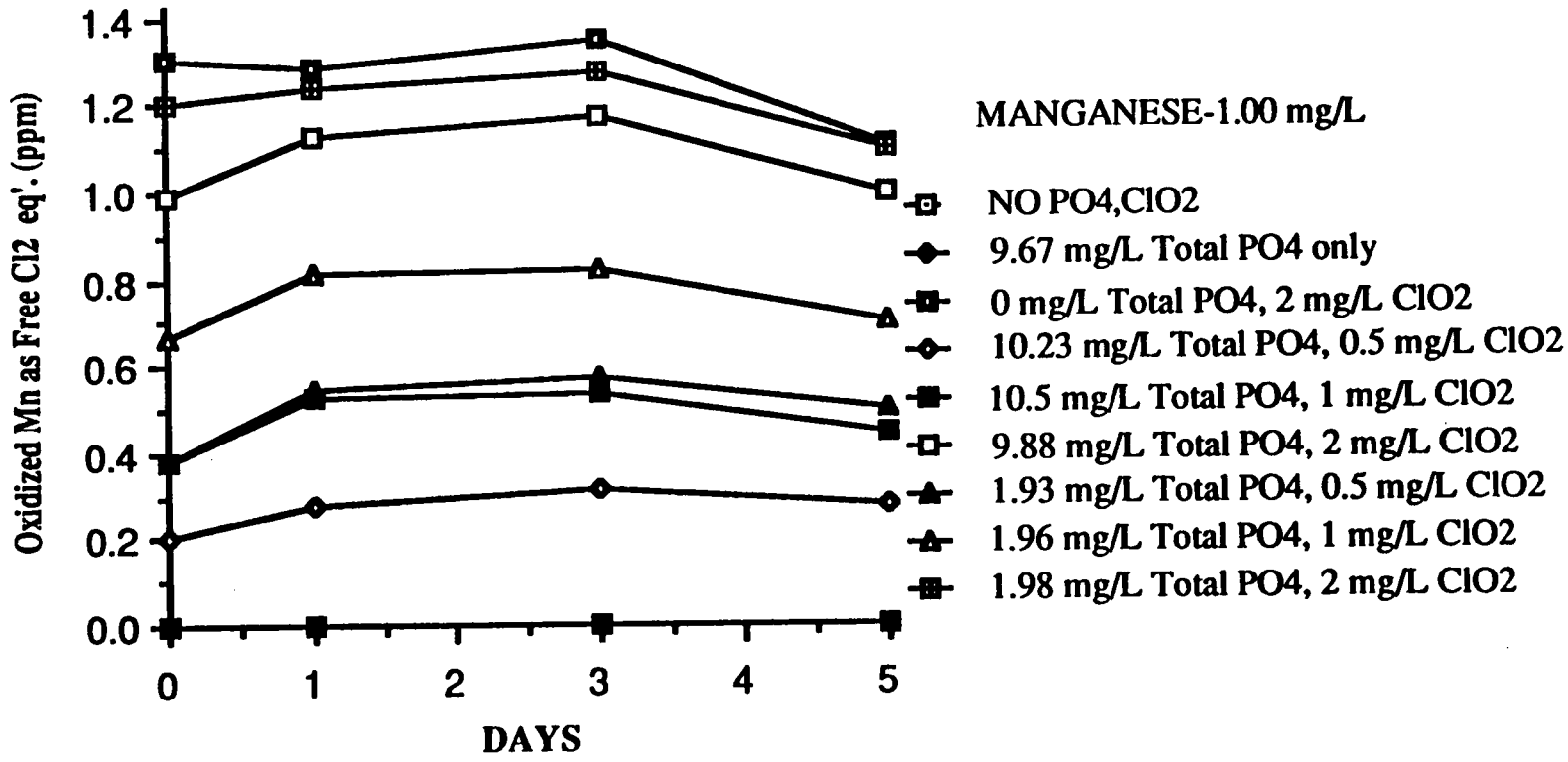


Figure 42. Manganese treatment with polyphosphate D and chlorine dioxide in the absence of calcium: oxidized manganese

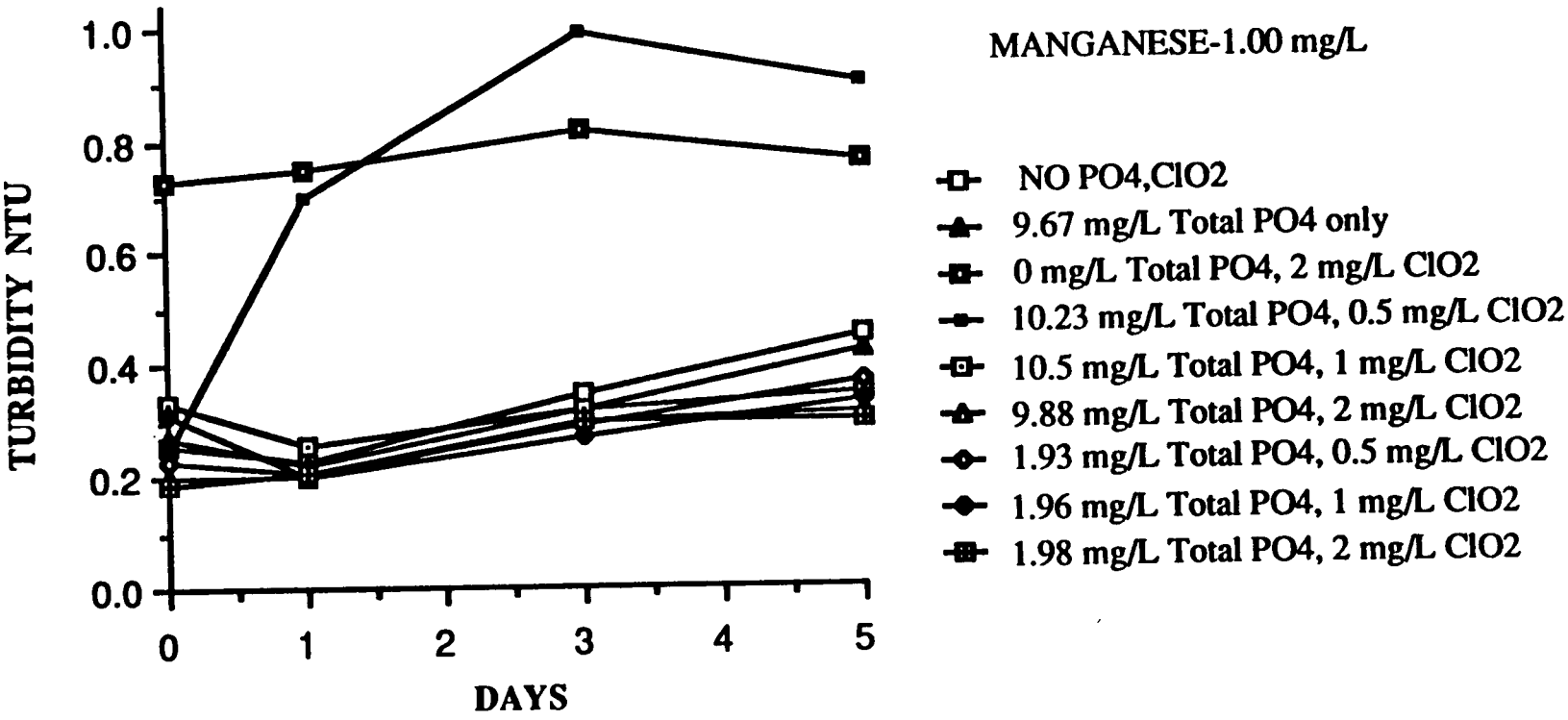


Figure 43. Manganese treatment with polyphosphate D and chlorine dioxide in the absence of calcium: turbidity

(Figure 39), microfiltration (Figure 40), color (Figure 41), oxidized manganese (Figure 42), and turbidity studies (Figure 43) were done in this experiment. Data for this experiment is given in appendix Table A7.

Not much difference in turbidity or filterability through a 0.1 micron filter (Figure 40) was observed between the various treated bottles except for one bottle which showed an exceptionally high turbidity (10 mg/L total phosphate, 0.5 mg/L chlorine dioxide). The most significant variables in this experiment were observed to be the color and degree of manganese oxidation. Color and the degree of manganese oxidation increased with the chlorine dioxide dosage (at a constant polyphosphate dosage) and decreased with polyphosphate dosage (at a constant chlorine dioxide dosage). In other words, the chlorine dioxide dosage directly correlated with color and the degree of manganese oxidation, whereas the polyphosphate dosage inversely correlated with color and the degree of manganese oxidation. At a constant polyphosphate dosage, a twofold increase in chlorine dioxide dosage caused a significant increase in the color and concentration of oxidized manganese (Table 11). At a constant chlorine dioxide dosage (only for 0.5 and 1.0 mg/L), a fivefold increase in the polyphosphate dosage caused a significant decrease in concentration of oxidized manganese and color (Table 12), implying that polyphosphates inhibited manganese oxidation to a certain extent, though not completely as in earlier experiments (Sections 4.3.1) with polyphosphate and hypochlorite.

Table 11. Relationship between phosphate dosage, oxidized manganese and color on day 0

Total PO_4 mg/L	ClO_2 dosage mg/L	oxidized manganese mg/L as free Cl_2 eq'.	color units
10.23	0.50	0.18	3
10.50	1.00	0.35	30
9.88	2.00	0.90	210
1.93	0.50	0.35	70
1.96	1.00	0.58	130
1.98	2.00	1.05	200

Table 12. Relationship between chlorine dioxide dosage, manganese oxidation and color on day 0

Total PO_4 mg/L	ClO_2 dosage mg/L	oxidized manganese mg/L as free Cl_2 eq'.	color units
1.93	0.5	0.35	70
10.23	0.5	0.18	3
1.96	1.0	0.58	130
10.50	1.0	0.35	30
1.98	2.0	1.05	200
9.88	2.0	0.90	210

The data in Table 11 show a direct correlation between the degree of manganese oxidation and color. Bottles in which manganese was oxidized to a larger extent always gave higher color The dependence of color on the degree of manganese oxidation in this experiment indicates that the high discoloration produced is due to the oxidation of manganese by chlorine dioxide.

Ultrafiltration analysis was done in this experiment with a 200,000 MW cut off ultrafilter to study the effect of polyphosphate dosage on manganese particle size. This study was only intended to give a relative comparison between treated bottles and not necessarily the actual particle size. Further, the MW cut offs cannot be directly related to the particle size since there is a range of pore sizes within a filter. Also, the cut-off rating is derived from experiments on organic species. However, assuming an organic species density of 1.5 gm/cm^3, the average pore diameter for the ultrafilter was estimated as 0.0075 microns.

Results of ultrafiltration studies are shown in Figure 39. At a constant dosage of 10 mg/L as total phosphate, particle size increased with increasing chlorine dioxide dosages. For example, at a dosage of 0.5 mg/L of chlorine dioxide, filterability through the 200,000 MW cut-off ultrafilter (nominal pore size approximately 0.0075 micron) was about 72%, implying that 28% of the particles had a size greater than 0.0073 microns whereas at a higher chlorine dioxide dosage of 2 mg/L manganese filterability declined rapidly to

15%. These results are shown in Table 13. Table 13 illustrates that filterability correlated with manganese oxidation and color.

A decrease in filterability was accompanied by an increase in the degree of manganese oxidation and color. This indicates that manganese oxidation resulted in the formation of colloidal particles which caused high discoloration and adversely affected treatment. No significant difference in manganese filterability (filterability > 90%) was observed among the treated bottles when 0.1 micron filters were used in filterability analysis (Figure 40), which indicates that these particles were smaller than 0.1 microns and therefore passed through the filter. When chlorine dioxide alone was present, filterability through 0.1 micron filters decreased to less than 90% and filterability through ultrafilters decreased to 0.5%.

Table 13. Relationship between manganese filterability through 200,000 MW ultrafilter, manganese oxidation and color on day 0

Total PO_4 mg/L	ClO_2 dosage mg/L	Filterability percentage	oxidized manganese mg/L as free Cl_2 eq'.	color unit
0	0	100	0	0
9.67	0	97	0	0
10.23	0.5	72	0.18	3
1.96	1.0	53	0.58	130
9.88	2.0	15	0.90	210
0	2.0	0.50	1.15	315

In this experiment, the best treatment (high filterability, low color and low turbidity) was obtained in the absence of chlorine dioxide. Even though polyphosphate inhibited manganese oxidation to a certain extent when chlorine dioxide was added to the other bottles, most of the manganese was oxidized and produced high color. High color was observed in all the bottles (including the bottle containing only chlorine dioxide and no phosphate) except the bottles to which chlorine dioxide was not added (Figure 41). But since disinfection is a minimum treatment requirement for utilities, it would not be possible to add polyphosphate alone without a disinfecting (oxidizing) agent in actual facilities or completely eliminate any sequestrant addition, as some form of oxidant has to be added for bacterial control. Hence, even though good treatability was obtained in the absence of chlorine dioxide, this factor does not have any practical application in water treatment. Figures A24 and A25 show the pH and total manganese in this experiment for informational purposes.

4.4.3 Manganese Treatment with Polyphosphate A and Chlorine Dioxide in the absence of Calcium

Since poor manganese treatability was obtained with polyphosphate D in the previous experiment, a similar experiment was run using polyphosphate A (Figures 44-48 and Table A8) to determine if better manganese treatment can be obtained with this polyphosphate type. Chlorine dioxide and polyphosphate A dosage effects were studied in this experiment.

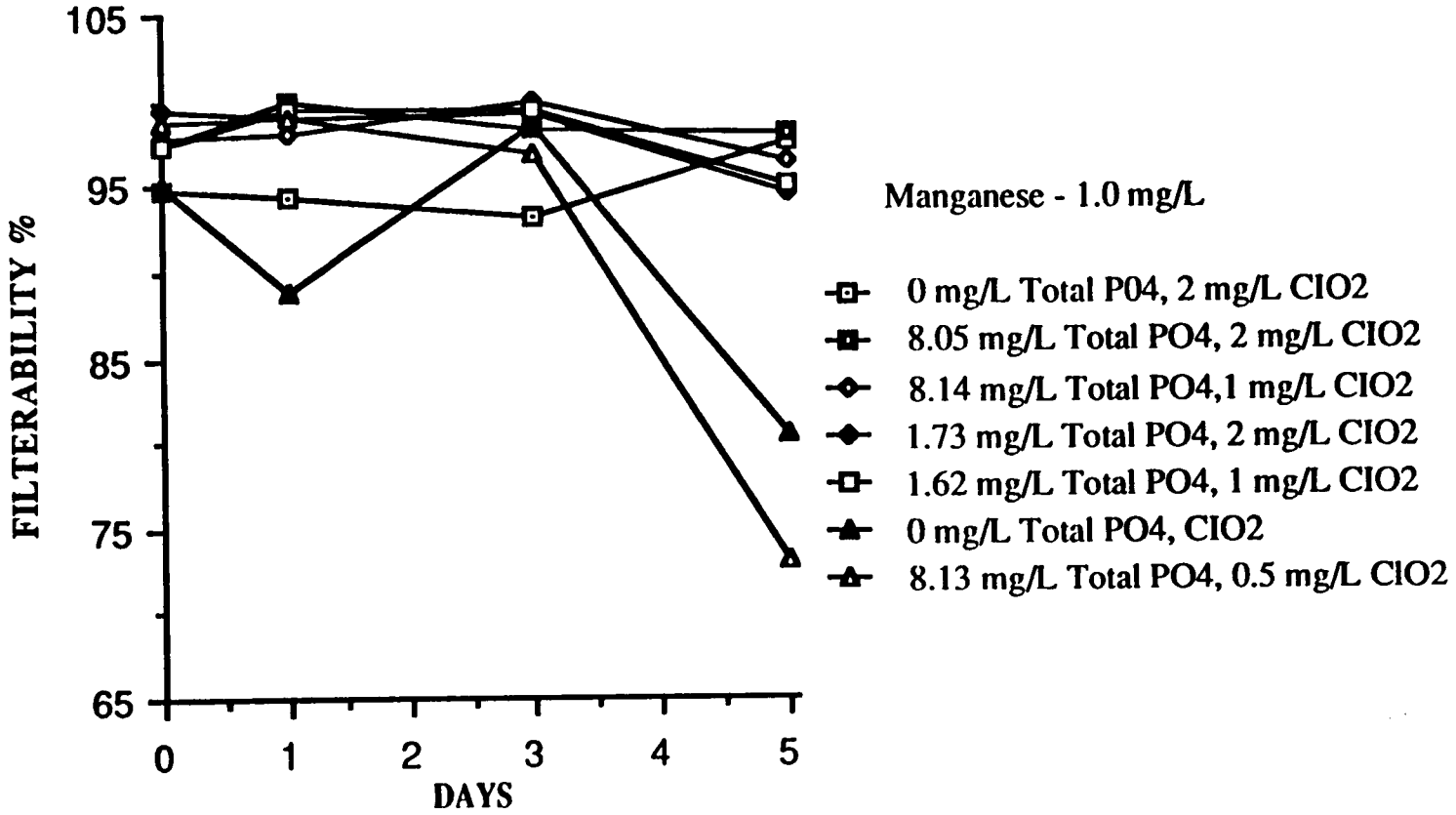


Figure 44. Manganese treatment with polyphosphate A and chlorine dioxide in the absence of calcium: manganese filterability

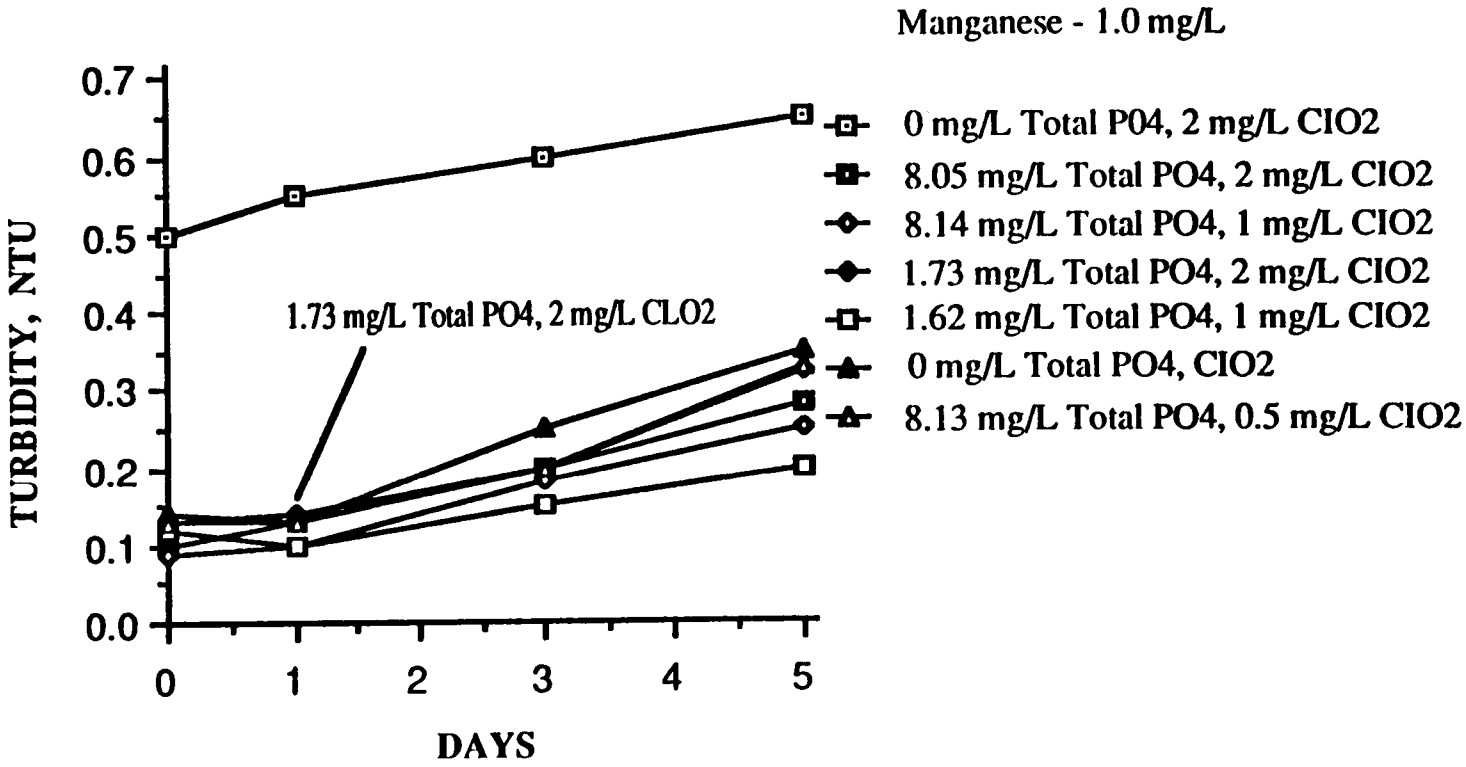


Figure 45. Manganese treatment with polyphosphate A and chlorine dioxide in the absence of calcium: turbidity

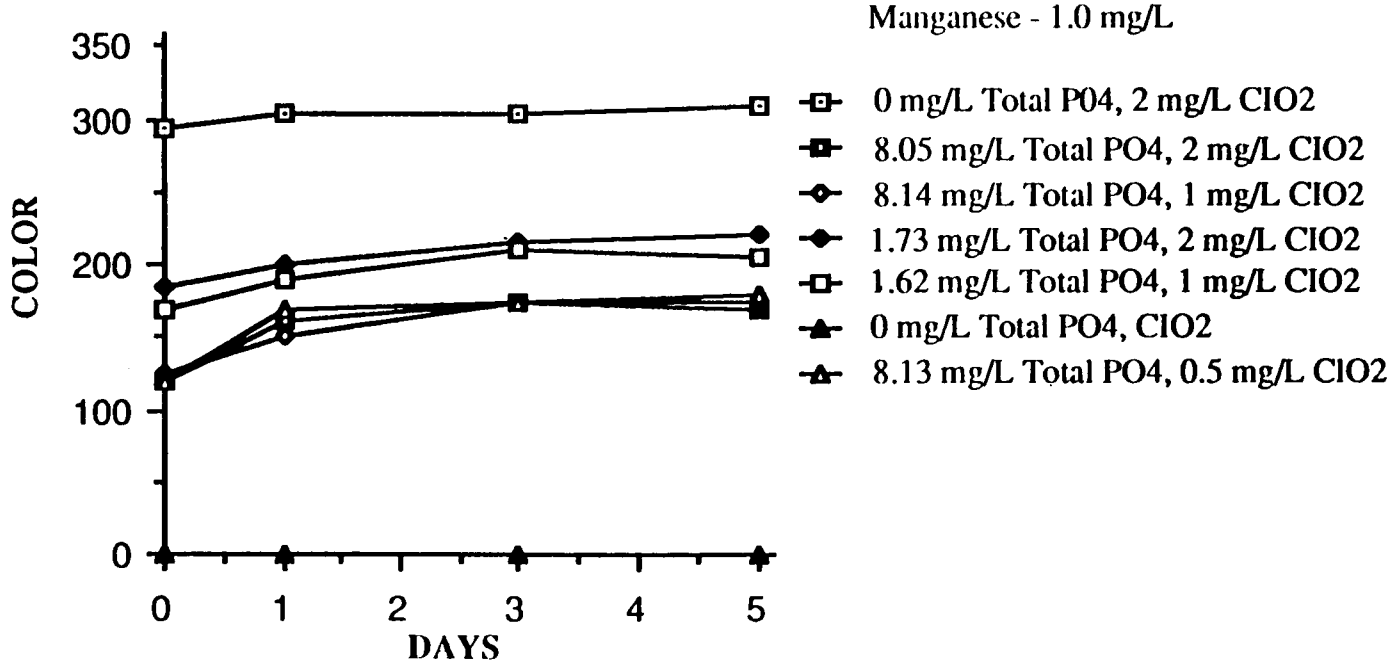


Figure 46. Manganese treatment with polyphosphate A and chlorine dioxide in the absence of calcium: color

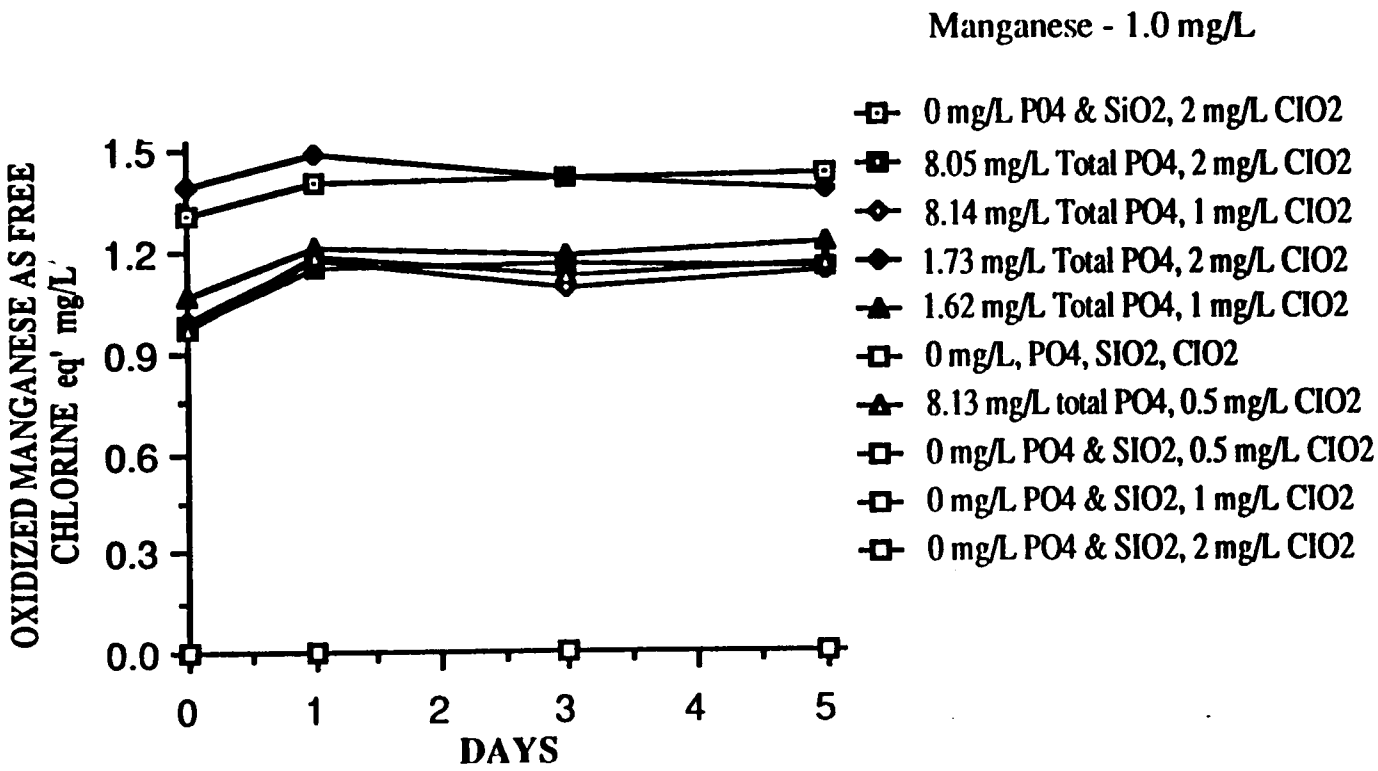


Figure 47. Manganese treatment with polyphosphate A and chlorine dioxide in the absence of calcium: oxidized manganese

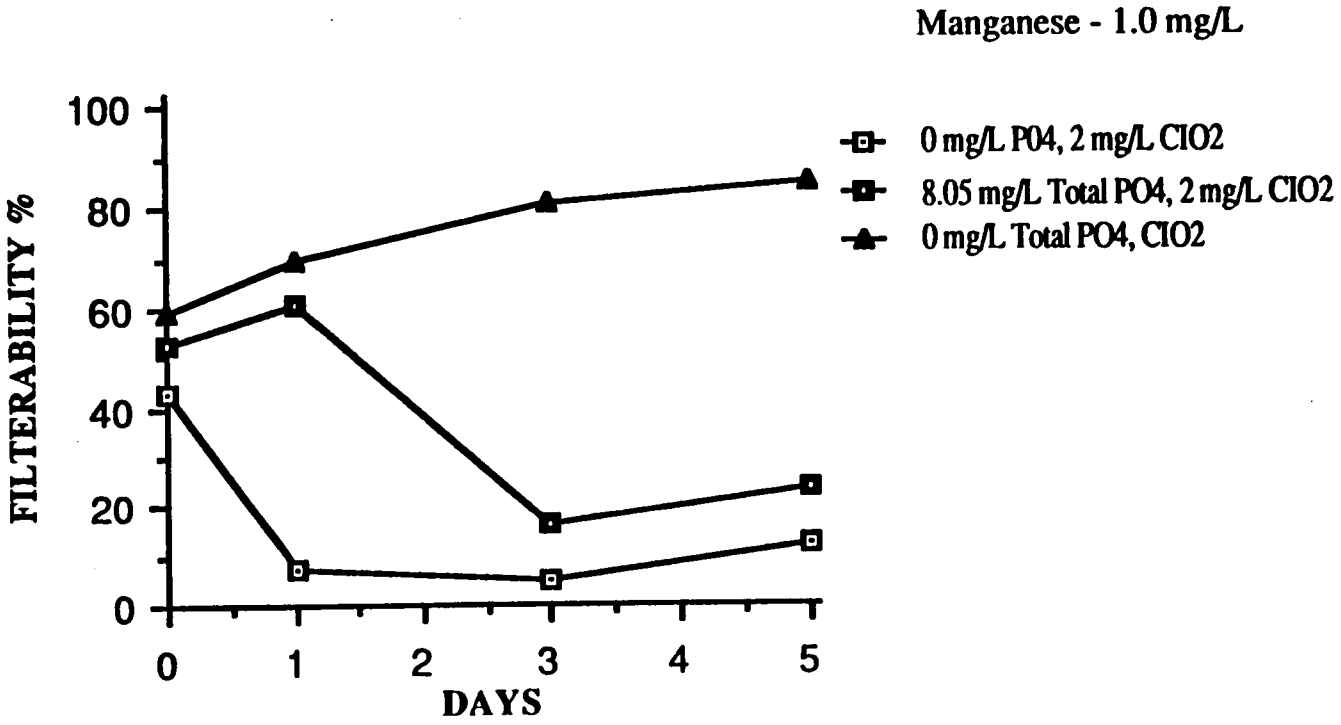


Figure 48. Manganese treatment with polyphosphate A and chlorine dioxide in the absence of calcium: ultrafiltration

No significant difference in manganese filterability (Figure 44), turbidity (Figure 45), color (Figure 46), oxidized manganese (Figure 47) and ultrafiltration analysis (Figure 48) using a 200,000 MW cut-off ultrafilter was observed compared to the previous experiment. The high discoloration produced indicates that manganese oxidation by disinfectants/oxidants has to be inhibited as in the polyphosphate/hypochlorite method to successfully sequester manganese, and thus achieve the dual purposes of disinfection and manganese sequestration. Figures A26 and A27 show the results for total manganese and pH in this experiment.

Results obtained in this experiment (4.4.3) and the previous one testing polyphosphate D (4.4.2) conflict with an early experiment (Section 4.4.1). For example, the color measured in these experiments (4.4.2 and 4.4.3) was much higher than the measured color in the earlier experiment (4.4.1). In order to address this concern, the effect of polyphosphate shelf-life on the color produced was tested in a later experiment to determine if this could account for the conflicting results. These results are discussed in Section 4.6. In the following section, further studies to compare the effectiveness of polyphosphates C and D are discussed.

4.4.4 Manganese Treatment with Polyphosphate C and Chlorine Dioxide in the Absence of Calcium

Since polyphosphates A and D yielded poor results in previous experiments, polyphosphate C was tested in this experiment

to determine if manganese treatability can be improved with this particular polyphosphate type. Also, this experiment was intended to verify conflicting results in the extent of discoloration observed between the experiments discussed in Section 4.4.2 and 4.4.3 and an earlier experiment (Section 4.4.1). One bottle containing polyphosphate D was also included to compare the effectiveness of polyphosphate C with polyphosphate D. Results of this experiment were similar to the previous experiments (4.4.2 and 4.4.3). Poor manganese treatability was observed, and no significant difference in manganese treatability was noticed between the various polyphosphate types. However, results obtained were significantly different from the earlier experiment explained in Section 4.4.1 in which low discoloration was noticed. High color, about 100 color units was produced in all the bottles and most of the manganese was oxidized in these bottles. Since oxidized manganese analysis was not performed in the earlier experiment reported in Section 4.4.1, greater credence is given to the more recent experiments (4.4.2, 4.4.3, and 4.4.4) in which this analysis was performed. Results for filterability, turbidity, color, oxidized manganese, total manganese and pH are shown in Figures 49-52, A28 and A29 and Table A8. Figure 49 shows some scatter in filterability data. For example, filterability for the control bottle (0 mg/L total PO_4 and ClO_2) increased on day 3 after an initial decrease on day 1. This trend may be due to the mixing which could cause the flocs to tear apart. Breaking up of these flocs could cause higher filterabilities after an initial decrease, as they may not subsequently flocculate. This trend

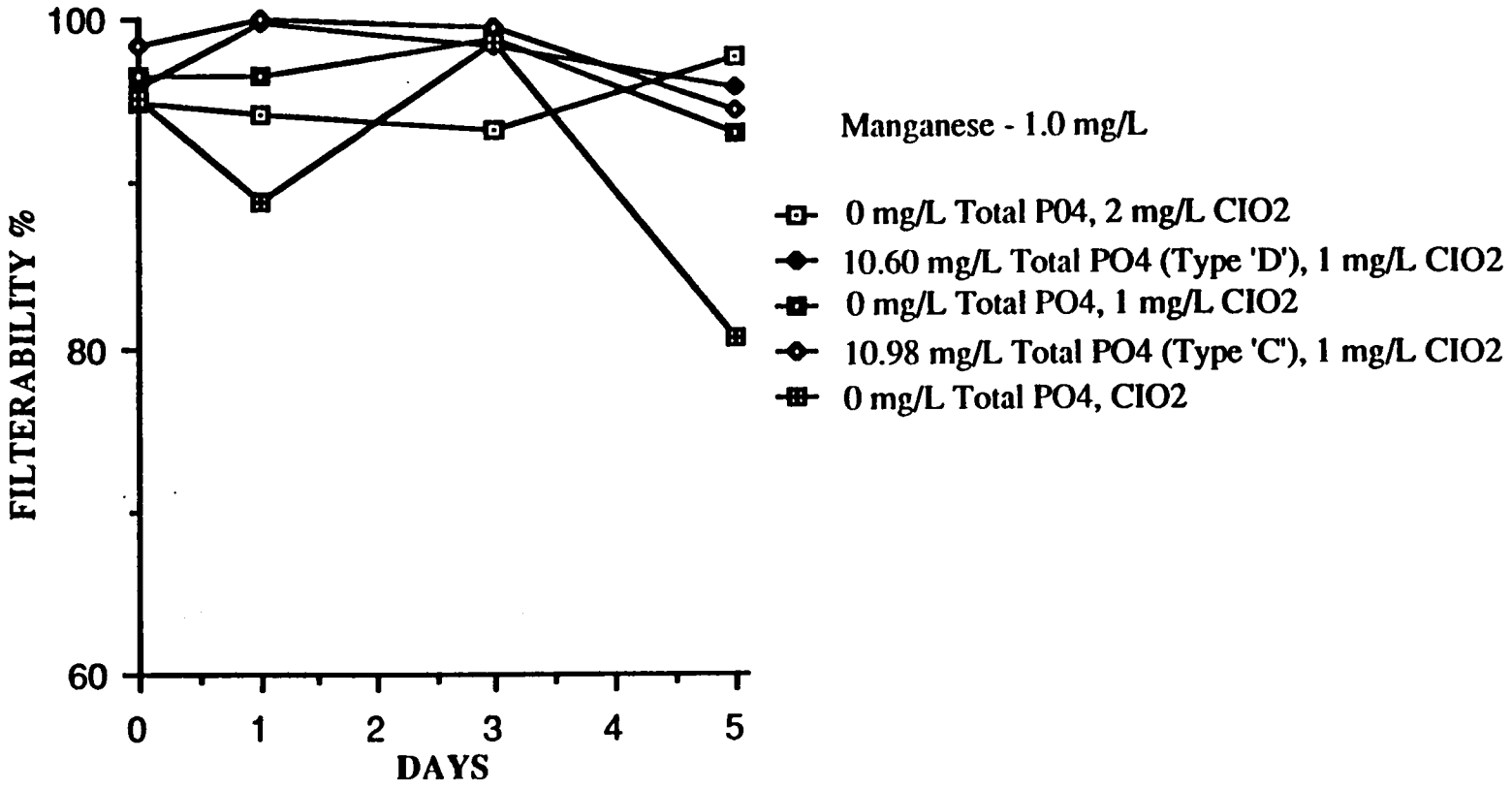


Figure 49. Manganese treatment with polyphosphate C and chlorine dioxide in the absence of calcium: manganese filterability

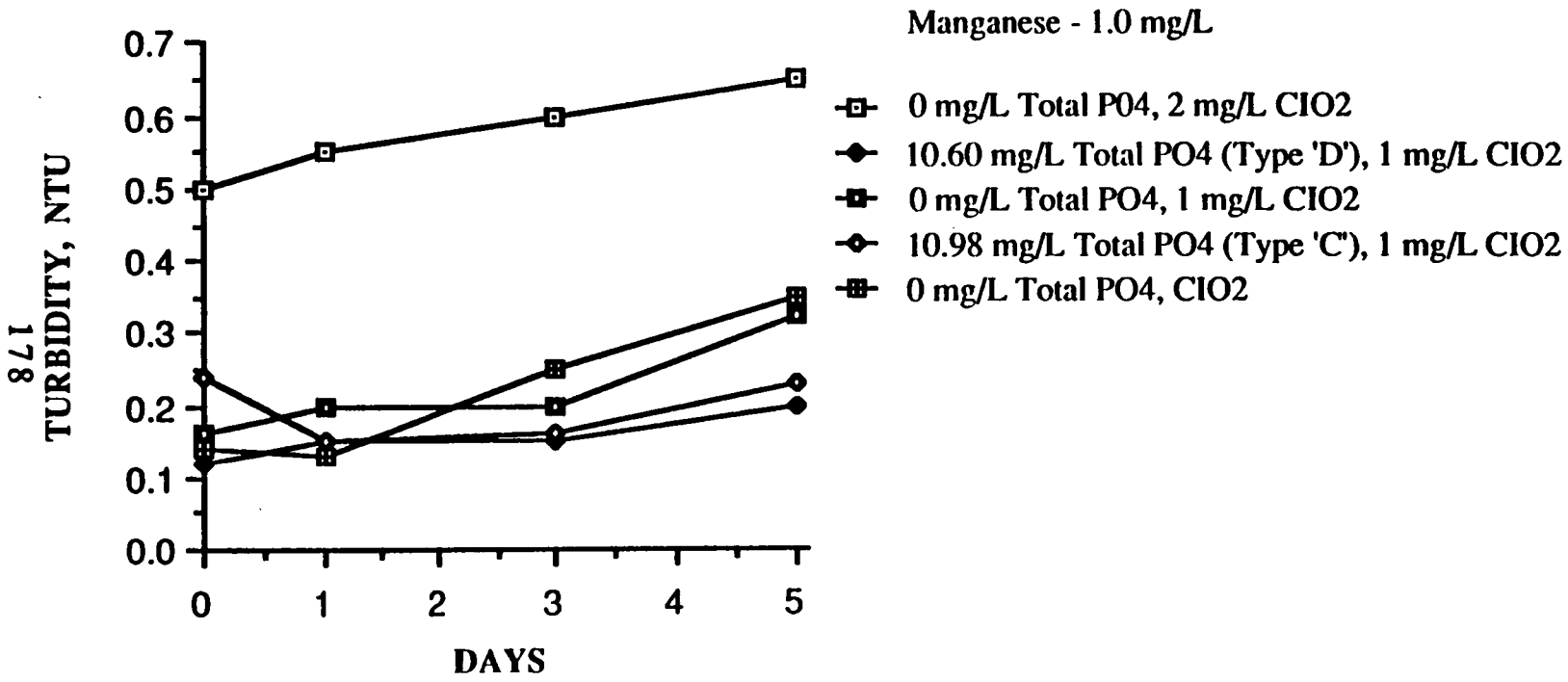


Figure 50. Manganese treatment with polyphosphate C and chlorine dioxide in the absence of calcium: turbidity

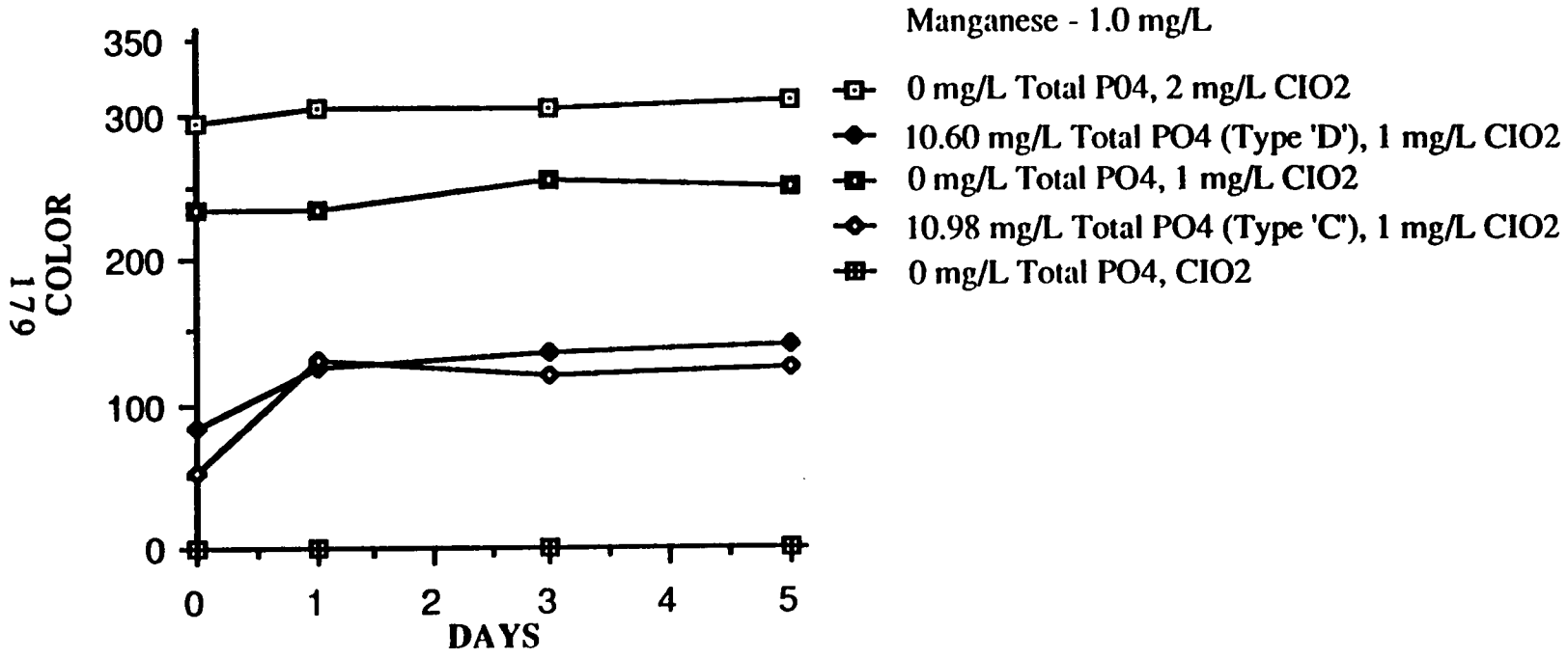


Figure 51. Manganese treatment with polyphosphate C and chlorine dioxide in the absence of calcium: color

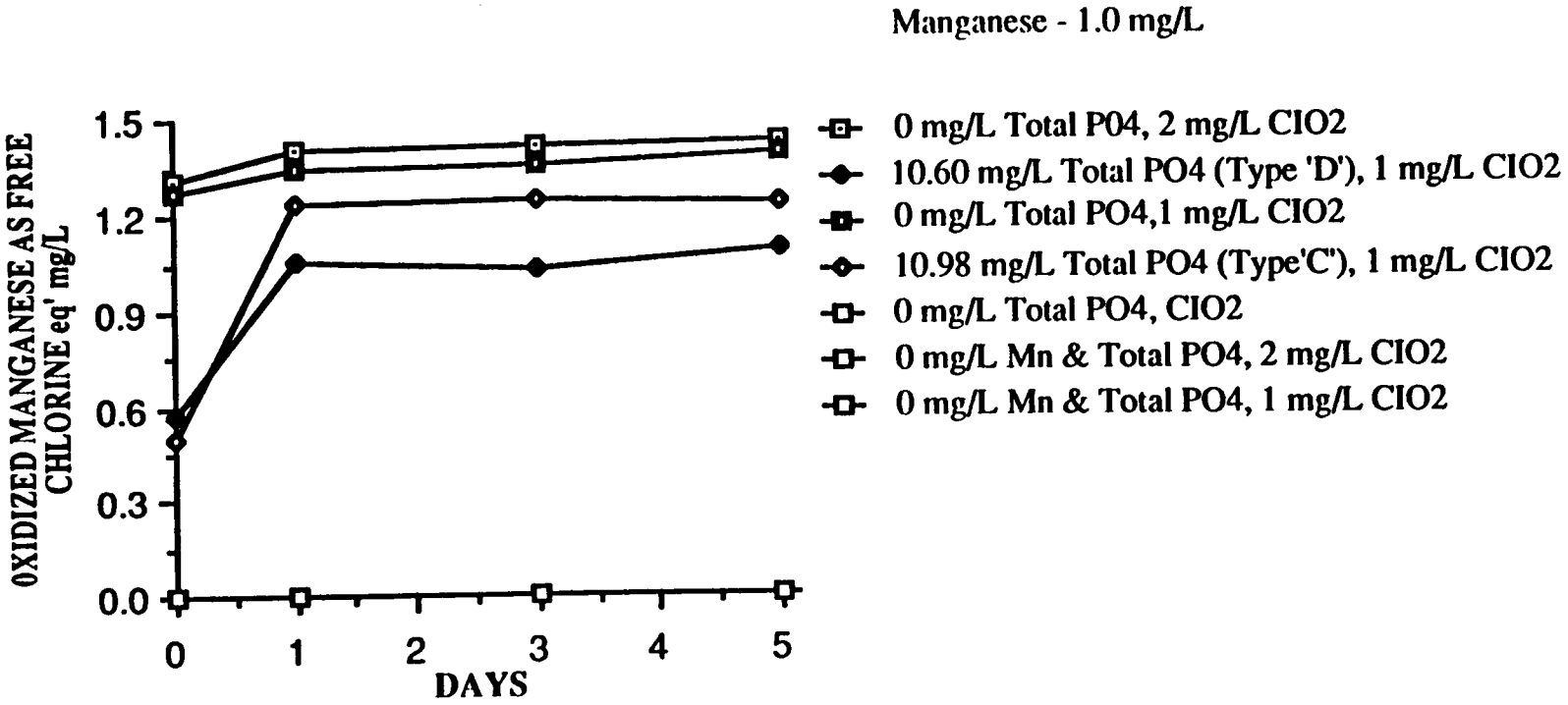


Figure 52. Manganese treatment with polyphosphate C and chlorine dioxide in the absence of calcium: oxidized manganese

could have also been caused by experimental error.

4.5 MANGANESE TREATMENT WITH POLYPHOSPHATE AND SILICATE IN CONJUNCTION

Since previous studies in this research using the silicate/chlorine dioxide method as well as the polyphosphate/chlorine dioxide method did not yield successful results (Section 4.2.1 and 4.4.1-4.4.4), the sequestering ability of silicates and polyphosphates in conjunction were tested. Studies using polyphosphate and silicates in conjunction were also recommended by Robinson and Ronk, who observed poor manganese treatability when silicates alone were used. Results of this experiment are discussed next.

4.5.1 Manganese Treatment by Polyphosphate 'A' and Silicate in Conjunction with Chlorine Dioxide in the Absence of Calcium

In this experiment, polyphosphate A and silicate were used in conjunction to test their ability to sequester manganese with chlorine dioxide. Results of these studies were compared with manganese treatability when polyphosphate A alone was added by running a control bottle containing polyphosphate A. Manganese filterability was studied using both 0.1 micron filters and 200,000 MW cut-off ultrafilters. Data for this experiment are given in appendix Table A8. Similar results were obtained in this experiment for manganese filterability (Figure 53), turbidity (Figure 54), color

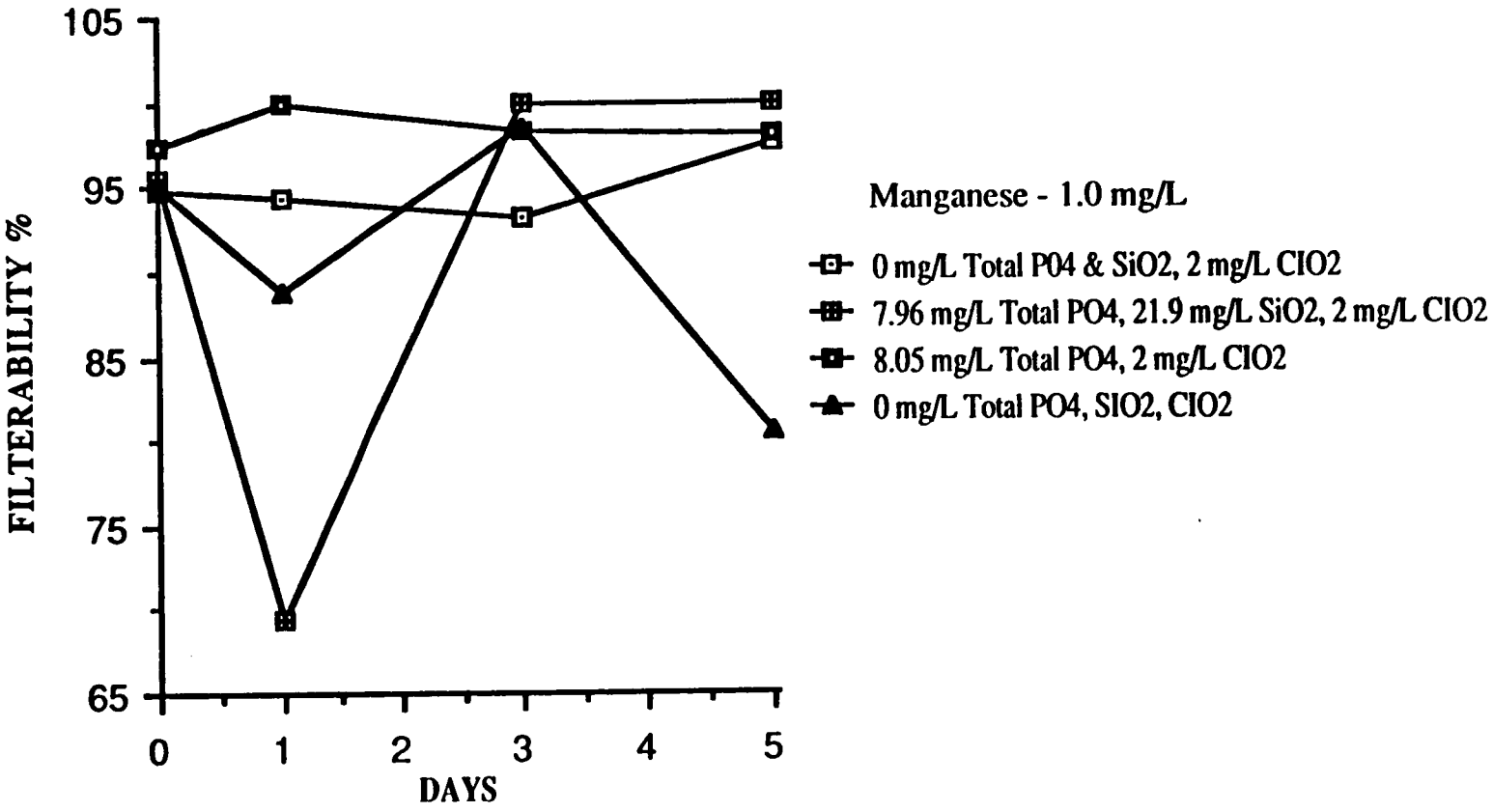


Figure 53. Manganese treatment by polyphosphate A and silicate in conjunction with chlorine dioxide in the absence of calcium: manganese filterability

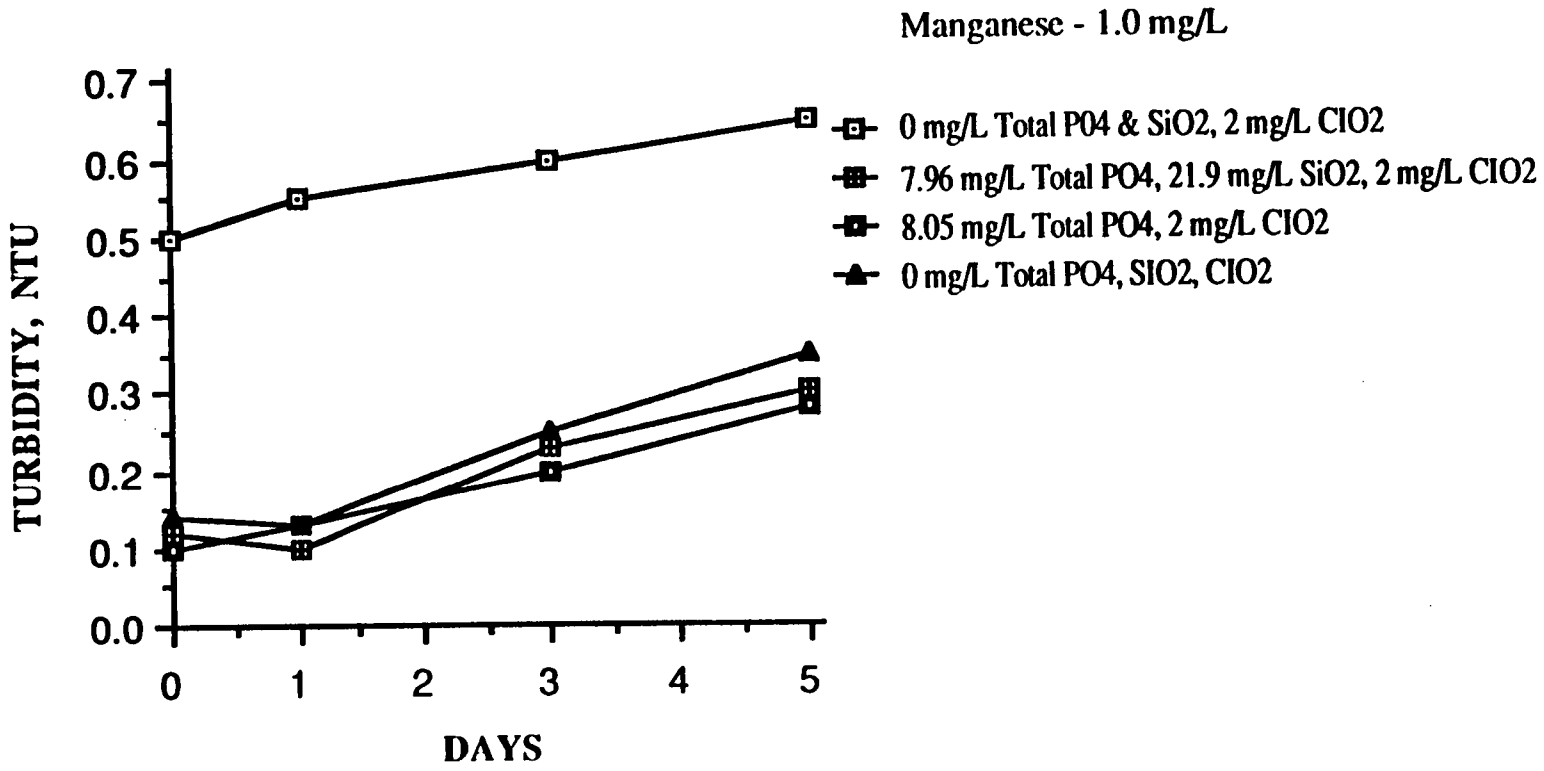


Figure 54. Manganese treatment by polyphosphate A and silicate in conjunction with chlorine dioxide in the absence of calcium: turbidity

(Figure 55), and oxidized manganese (Figure 56) as in the previous experiment. Ultrafiltration analysis (Figure 57) using a 200,000 MW cut-off ultrafilter showed better manganese filterability when polyphosphate and silicate were added in conjunction. However, manganese was oxidized to a much larger extent in the presence of polyphosphate and silicate than in the presence of polyphosphate alone (Figure 56), indicating that silicate may have catalyzed manganese oxidation. Figures A30 and A31 plot the total manganese and pH versus time in this experiment.

4.6 EFFECT OF SHELF LIFE ON MANGANESE TREATMENT WITH POLYPHOSPHATE AND CHLORINE DIOXIDE

As already documented in the previous sections, some conflicting results were seen between the experiments reported in Sections 4.4.2 to 4.4.5 and an earlier experiment (Section 4.4.1). The major difference was in the amount of color produced. Comparing Figure 39 with Figures 41, 46, 51 and 55, it is evident that higher color was produced in later experiments than in the first one. Since this difference was rather unexpected, it was hypothesized that a specific variable such as shelf life could have caused this difference in results. Since chemical manufacturers typically do not give the shelf life for their products, it was determined that a study of this variable might provide some explanation for the difference in results. The experiments reported in Section 4.4.1, 4.4.2 and 4.4.3 to 4.4.5 were performed on 10-15-87, 4-3-88 and 5-3-88 respectively.

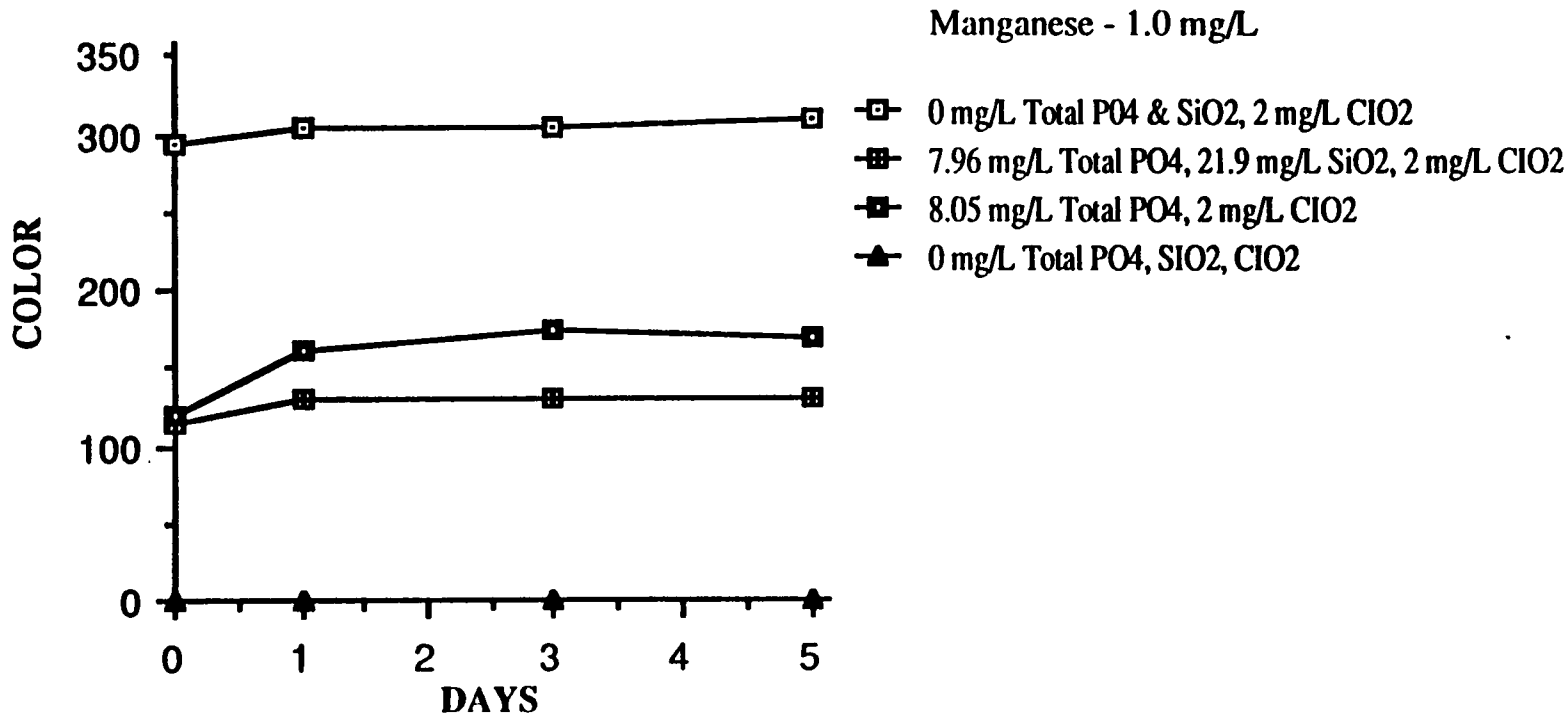


Figure 55. Manganese treatment by polyphosphate A and silicate in conjunction with chlorine dioxide in the absence of calcium: color

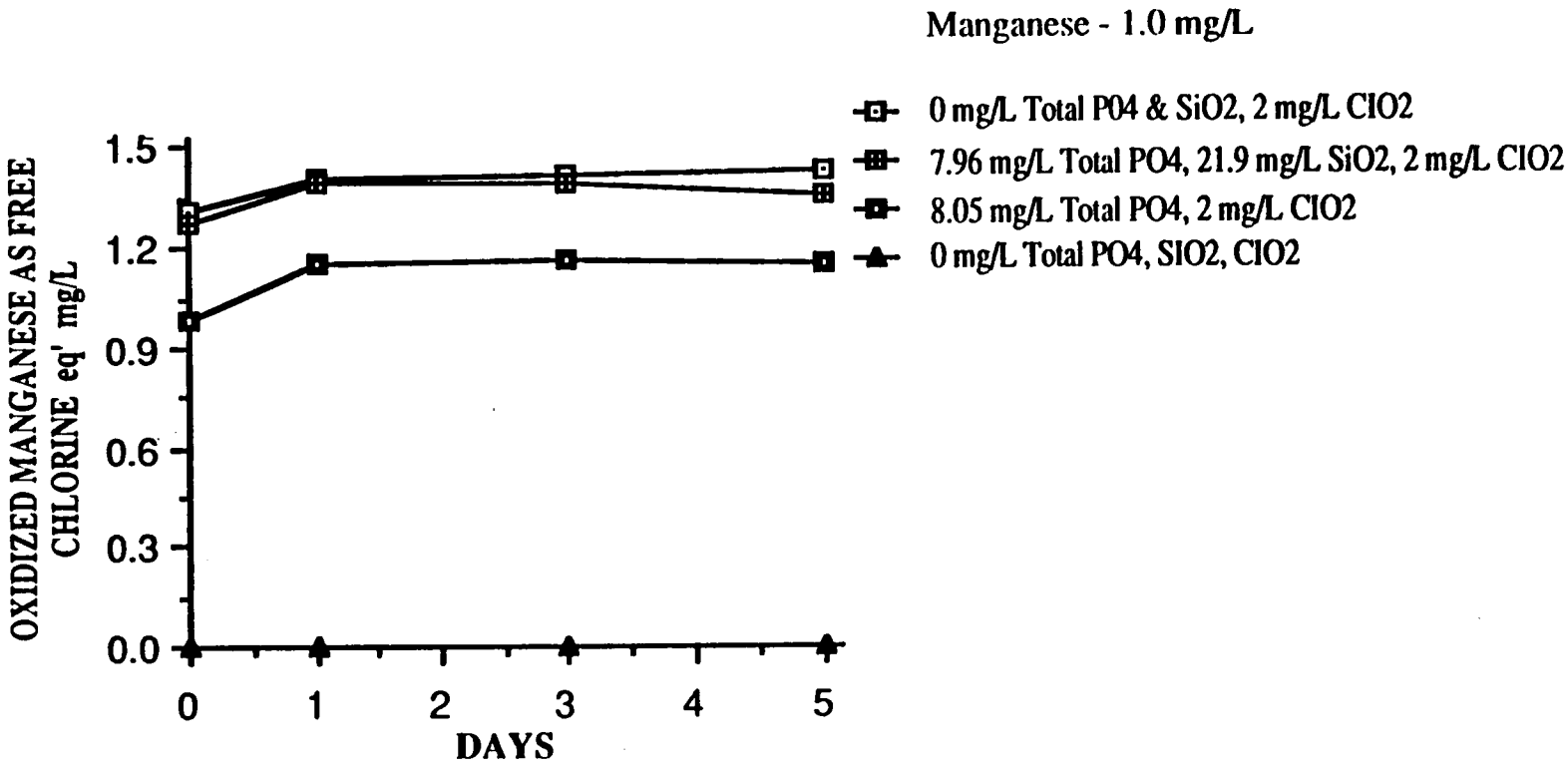


Figure 56. Manganese treatment by polyphosphate A and silicate in conjunction with chlorine dioxide in the absence of calcium: oxidized manganese

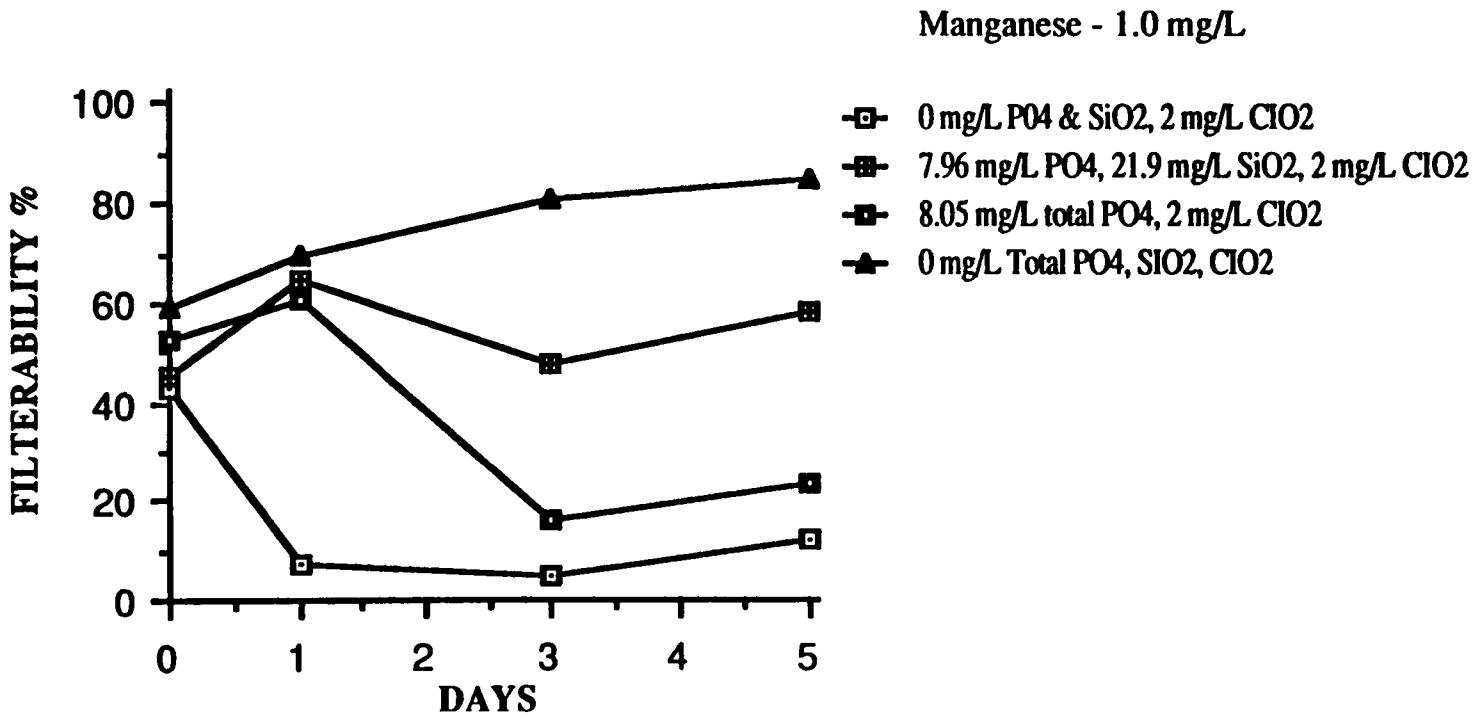


Figure 57. Manganese treatment by polyphosphate A and silicate in conjunction with chlorine dioxide in the absence of calcium: ultrafiltration

By the time the later experiments were performed, the polyphosphate stocks were over seven months old. In order to test the effect of aging on manganese treatability by polyphosphates, new samples of polyphosphates A, C and D were procured and the experiment was repeated to determine if shelf life would account for conflicting results. Results of this experiment are presented in Table 14 and discussed in the following paragraphs.

High filterability, high color and low turbidity (Table 14) were obtained in this experiment with polyphosphate D and no significant improvement in manganese treatability was observed compared to earlier experiments which used older polyphosphates (Section 4.4.2). However color, which was the most significant variable, was much less when new samples of polyphosphate A and C were used compared to older polyphosphates, possibly due to slow polyphosphate depolymerization with time (41). Aulenbach (2) stated that depolymerization decreases the effectiveness of polyphosphates. Even though the color produced in this experiment using newly purchased polyphosphates was much lower than in previous experiments (Sections 4.4.2 to 4.4.5), the measured color (red-orange) was several times the standard (15 color units). Hence, even though fresher polyphosphates improved manganese treatability by the polyphosphate/chlorine dioxide method, the improvement was not great enough to allow this method to achieve acceptable results, and therefore, it must be concluded that the polyphosphate/chlorine dioxide method will not be suitable for

Table 14. Effect of shelf-life on manganese treatment by polyphosphate and chlorine dioxide

Jar #	Pre-dosage			Post-dosage			Dosage			Day 0	
	pH	Turb[a]	D.O.[b]	pH	Turb	D.O.	PO_4[c]	SiO_2[d]	ClO_2[e]	Color[f]	Color[g]
10	7.0	0.35	<0.1	7.2	0.65	<0.1	0	0	1.0	175	180
20[A]	7.0	0.25	<0.1	6.9	0.30	<0.1	10	0	1.0	50	50
30[C]	7.0	0.23	<0.1	7.1	0.35	<0.1	10	0	1.0	5	145
40[A]	7.0	0.25	<0.1	7.2	0.34	<0.1	10	0	1.0	55	50
50[C]	7.0	0.25	<0.1	7.1	0.32	<0.1	10	0	1.0	0	155
60[D]	7.0	0.27	<0.1	7.1	0.34	<0.1	10	0	1.0	75	125
70[B]	7.0	0.25	<0.1	7.3	0.33	<0.1	10	0	1.0	70	65
80[O]	7.0	0.28	<0.1	7.2	0.35	<0.1	10	0	1.0	80	108
90[C]	7.0	0.29	<0.1	7.25	0.34	<0.1	10	10	1.0	15	120
100[A]	7.0	0.25	<0.1	7.1	0.39	<0.1	10	10	1.0	30	39
110[D]	7.0	0.28	<0.1	7.3	0.34	<0.1	10	10	1.0	50	85
120[B]	7.0	0.29	<0.1	7.2	0.38	<0.1	10	10	1.0	30	55
130	7.0	0.30	<0.1	7.6	0.41	<0.1	0	20	1.0	90	85
140	7.0	0.27	<0.1	7.9	0.40	<0.1	0	40	1.0	45	50

[a] Turbidity units in NTU
[b] Dissolved oxygen in mg/L
[c] Polyphosphate dosage in mg/L as total PO_4
[d] Silicate dosage in mg/L as SiO_2
[e] ClO_2 concentration in mg/L
[f] Initial color after treatment
[g] Color after 80 minutes
A, B, C, D Polyphosphate types
O Orthophosphate

manganese treatment. However, these results are different from Henry's results (documented in Section 2.3 of the literature review), as older polyphosphates performed better than newer ones in his experiments (41). Hence, further research is recommended to determine the effect of shelf-life on manganese treatability.

4.7 QUALITY CONTROL VERIFICATION OF POLYPHOSPHATE/CHLORINE DIOXIDE AND POLYPHOSPHATE/HYPOCHLORITE METHODS

Separate experiments were run to verify the reproducibility of the results of the experiments testing the polyphosphate/chlorine dioxide and polyphosphate/hypochlorite methods of manganese treatment. These experiments were run concurrently with the experiment testing pH effects on manganese treatability by the polyphosphate/hypochlorite method (Section 4.3.7). Figures 58-62 show the results of this verification. Data for this experiment are given in Table A9. Three sets of bottles (total of nine bottles) were run in this experiment, and each set had three identical bottles (triplicates). Hypochlorite alone was added to one set, polyphosphate and hypochlorite were added to the second set, and polyphosphate and chlorine dioxide were added to the third set. Samples were adjusted to pH 7.0 on sampling days. A free chlorine residual was maintained continually in this experiment. Samples were filtered through 0.1 micron filters (Figure 58) and 200,000 MW and 1000 MW cut off ultrafilters (Figure 59), and turbidity (Figure 60), color (Figure 61), and oxidized manganese (Figure 62) were measured.

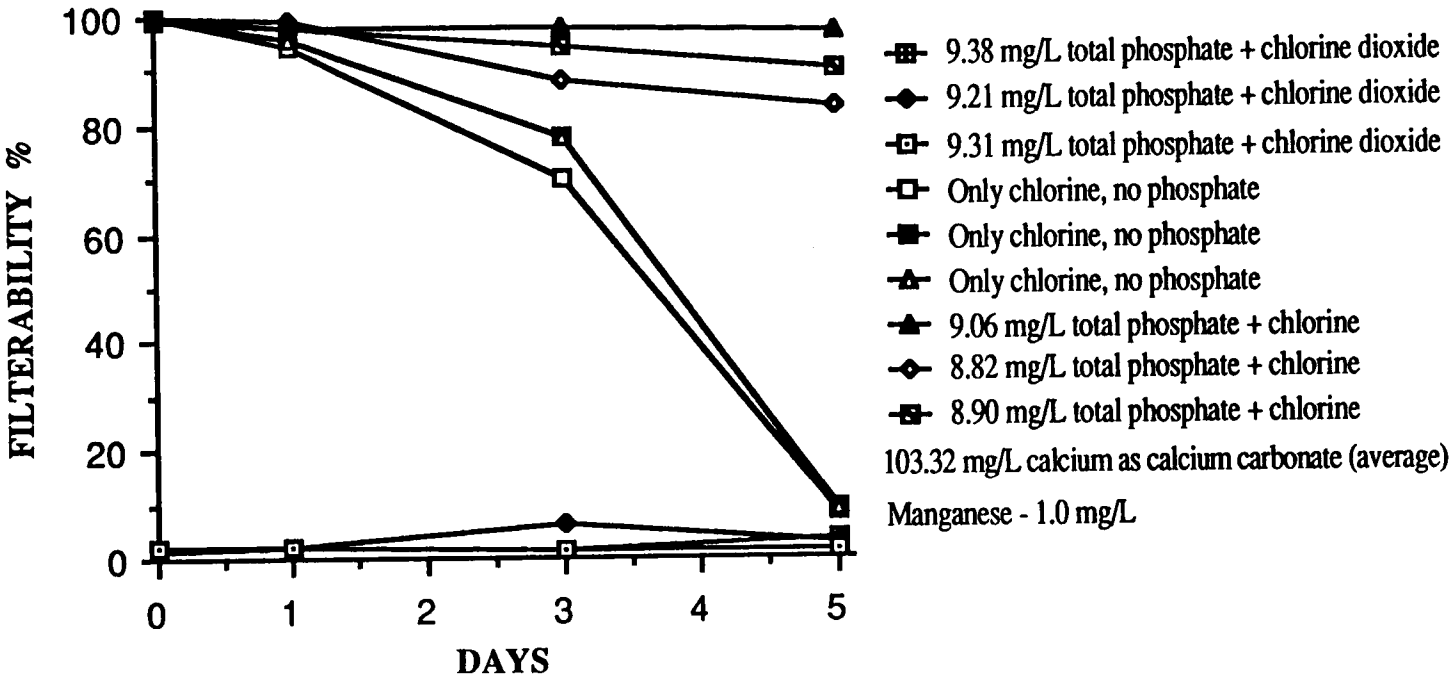


Figure 58. Quality control verification of polyphosphate/chlorine dioxide and polyphosphate/hypochlorite methods: manganese filterability

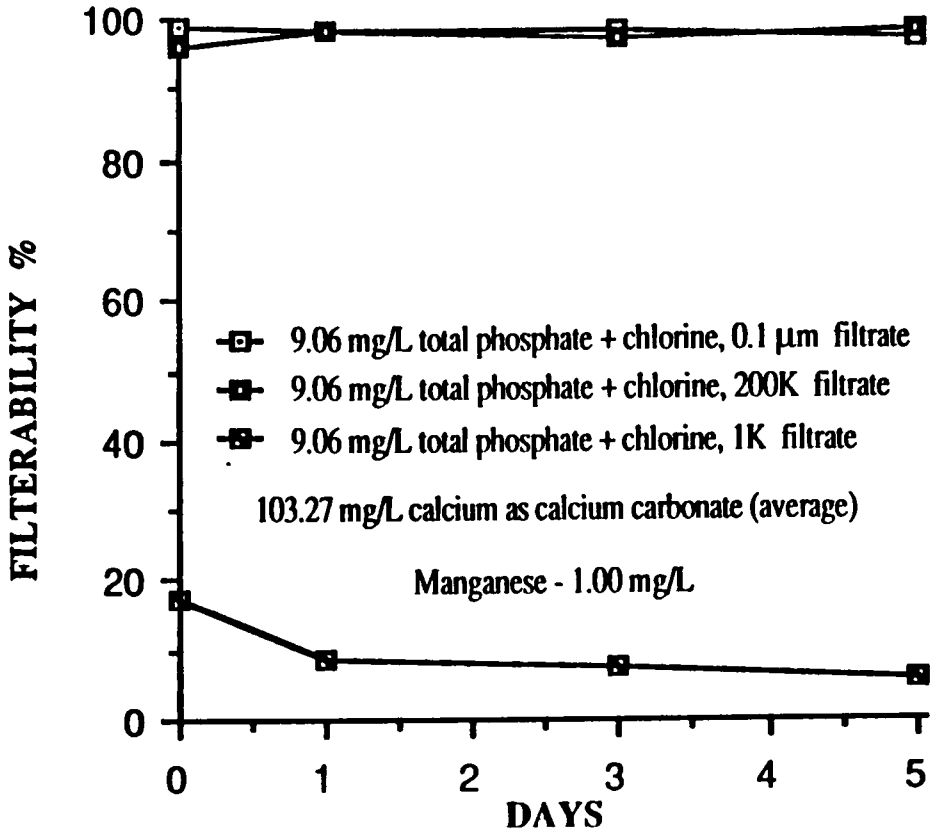


Figure 59. Quality control verification of polyphosphate/chlorine dioxide and polyphosphate/hypochlorite methods: manganese filterability (ultrafiltration and microfiltration)

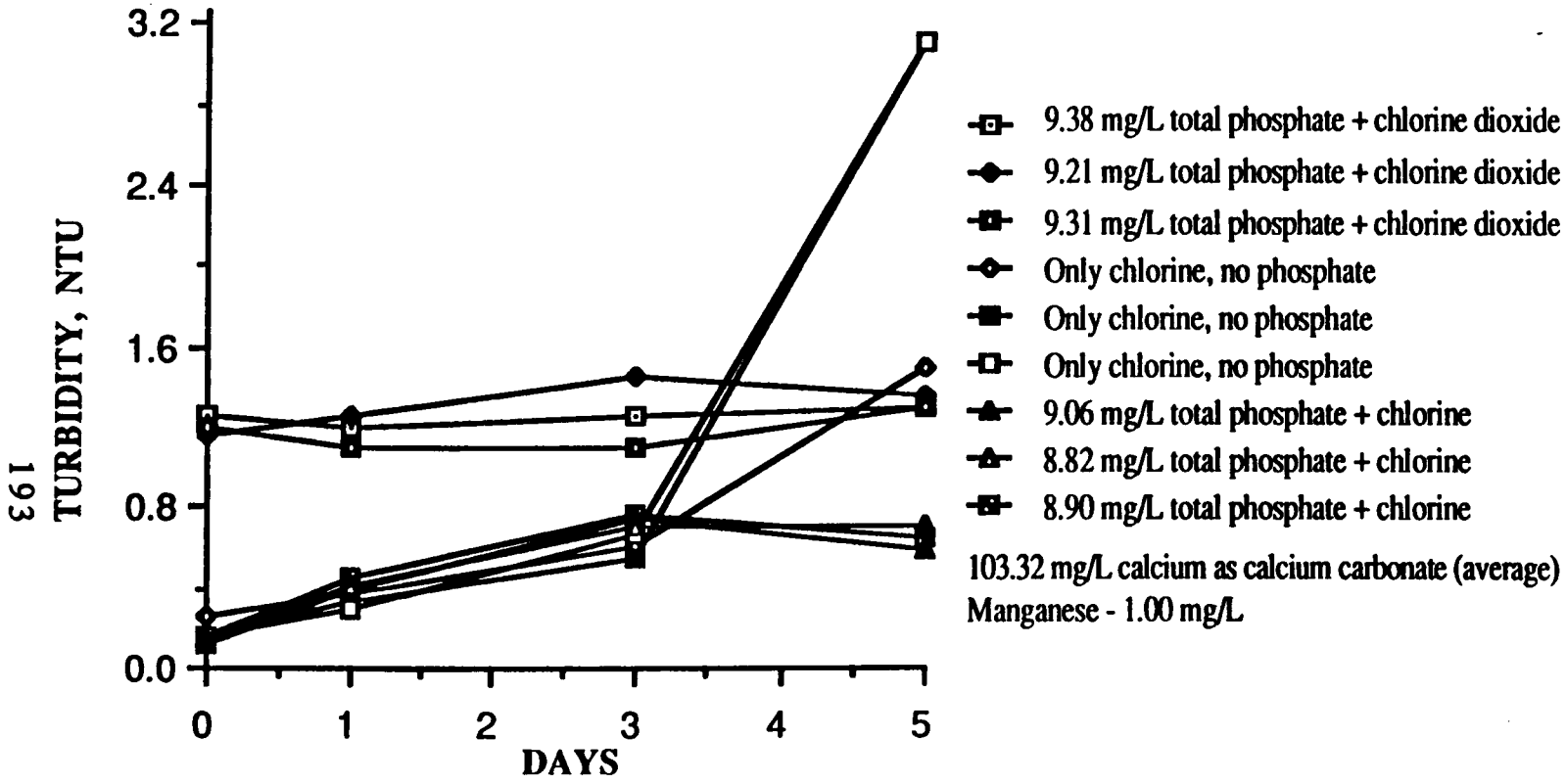


Figure 60. Quality control verification of polyphosphate/chlorine dioxide and polyphosphate/hypochlorite methods: turbidity

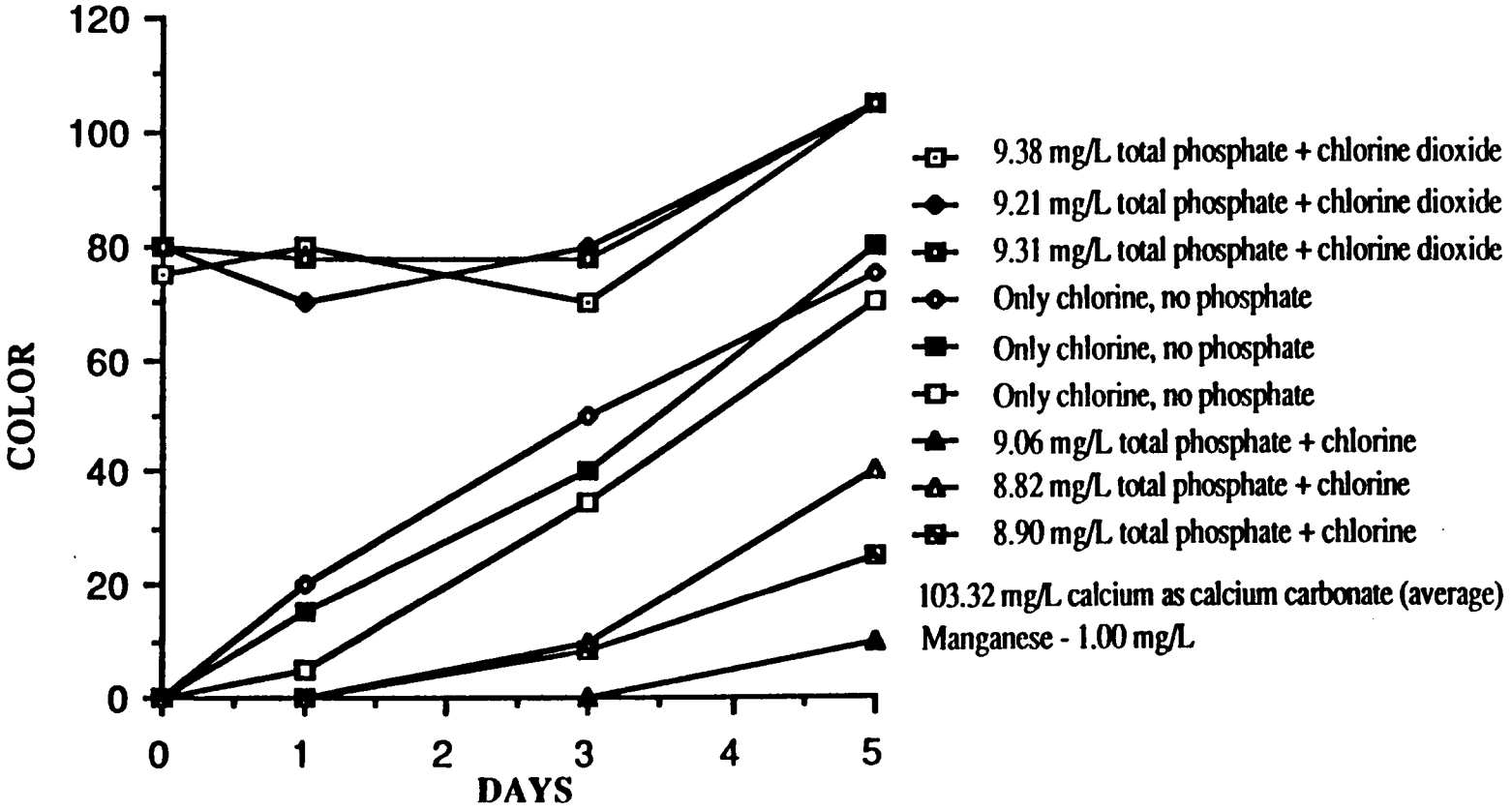


Figure 61. Quality control verification of polyphosphate/chlorine dioxide and polyphosphate/hypochlorite methods: color

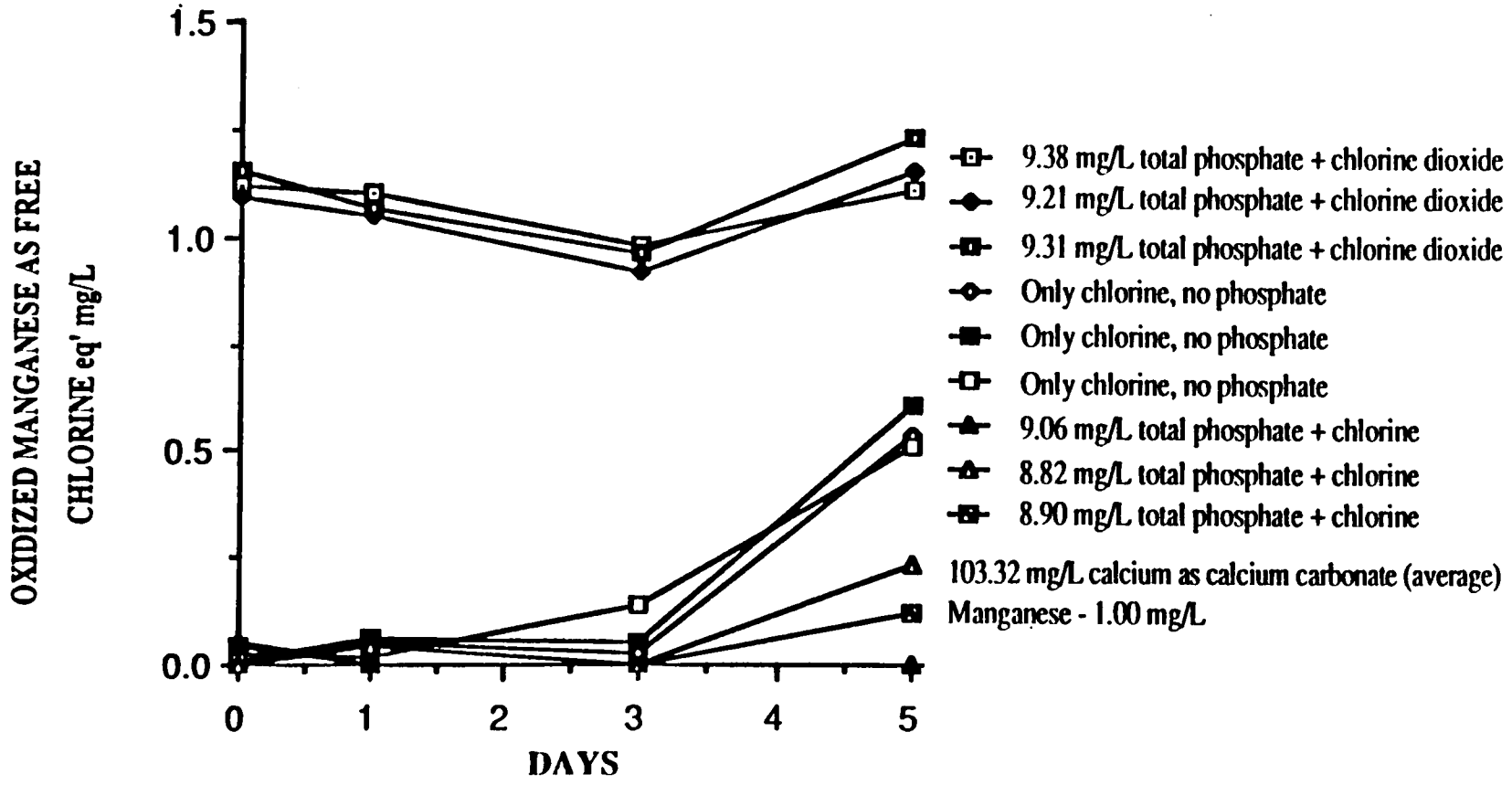


Figure 62. Quality control verification of polyphosphate/chlorine dioxide and polyphosphate/hypochlorite methods: oxidized manganese

Reasonably consistent results for filterability (Figure 58), color (Figure 61), turbidity (Figure 60), and concentration of oxidized manganese (Figure 62) were obtained for replicate bottles. Only the control bottle showed a significant difference in turbidity (about 1.6 NTU) between the two other bottles on day 5. As in earlier experiments, high color was produced in bottles dosed with polyphosphate and chlorine dioxide. Color was significantly lower and within the permissible limits for color at least for a period of 3 days when dosed with polyphosphate and hypochlorite. As Figure 59 illustrates for the polyphosphate hypochlorite method, filterability through a 200,000 MW (0.0073 micron pore size) ultrafilter and 0.1 micron filter gave about 100% filterability, and less than 10% of the manganese passed through a 1000 MW ultrafilter (pore size 0.0013 micron). Poor filterability through the 1000 MW cut-off ultrafilter (Figure 59) indicates that about 90% of the manganese may be present as a complex with the polyphosphate when manganese is treated by polyphosphate and hypochlorite.

A sharp increase in turbidity from about 0.6 NTU on day 3 to 3.1 NTU on day 5 was noticed when polyphosphates were absent (Figure 60). This could be due to oxidation of manganese by hypochlorite and subsequent precipitation of manganese oxides. Figure 62 illustrates that significant manganese oxidation occured between day 3 and day 5. The increase is turbidity may also be due

to an increase in the particle size of manganese particulates (due to flocculation) as shown by declining filterability from day 3 to day 5 (Figure 58). Since turbidity varies directly as the cube of the particle radius, a small increase in the particle size may cause a significant increase in turbidity. Figures A32-A34 show the pH, free chlorine and total manganese for this experiment.

4.8 MANGANESE CONCENTRATION AS A FUNCTION OF pE-pH

To understand the degree of manganese oxidation that would take place in the presence of hypochlorite and chlorine dioxide as well as other oxidants, pE-pH calculations were done to determine the manganese concentration as a function of pH and pE. pE, analogous to the pH expression for proton (hydrogen-ion) activity, is a measure of the oxidizing or reducing tendency of a solution. pE can be used as a master variable for graphical presentation of the following redox equilibria.

The oxidation of Mn^{2+} to manganese dioxide is given by the following expression.

$$Mn^{2+} + 2H_2O \quad <\!\!\longrightarrow \quad MnO_2(s) + 4H^+ + 2e^- \qquad E^o = -1.23V$$

The equilibrium constant k for this expression can be found from the equation $k = \exp(n^oFE^o/RT)$

where n^o = the number of electrochemical gram equivalents per gram mole exchanged during the reaction

F = Faraday's constant (23.06 kcal/volt)

for 20°C, RT = $[(1.986 \times 10^{-3})$kcal/(°K)(mole)] x 293°K

$k = \exp[2(23.06)(-1.23)/(1.986 \times 10^{-3})293^{o}k]$

ln k = -97.83

log k = -97.83/2.3 = -42.48.

Now, for the equilibrium expression

$Mn^{2+} + 2H_2O \longleftrightarrow MnO_2(s) + 4H^+ + 2e^-$ $\quad E^o = -1.23V$

the equilibrium constant $k = \{H^+\}^4\{e^-\}^2/\{Mn^{2+}\}$.

Taking logarithm on both sides

$\log k = \log \{[H^+\}^4/\{Mn^{2+}\} + 2 \log \{e^-\}$

$1/2 \log k - 1/2 \log \{H^+\}^4/\{Mn^{2+}\} = \log \{e^-\} = -pE$, as $pE = - \log \{e^-\}$

$-pE = 1/2 \log k + 1/2 \log \{Mn^{2+}\}/\{H^+\}^4$

or $pE = -1/2 \log k - 1/2 \log \{Mn^{2+}\}/\{H^+\}^4$

$pE = 21.24 - 1/2 \log \{Mn^{2+}\}/\{H^+\}^4$ (Since log k = -42.48) __ (1)

From this equation (which is plotted for various pH and pE values in Figure 63) the concentration of manganese that would exist as Mn^{2+} at various pE and pH levels can be determined.

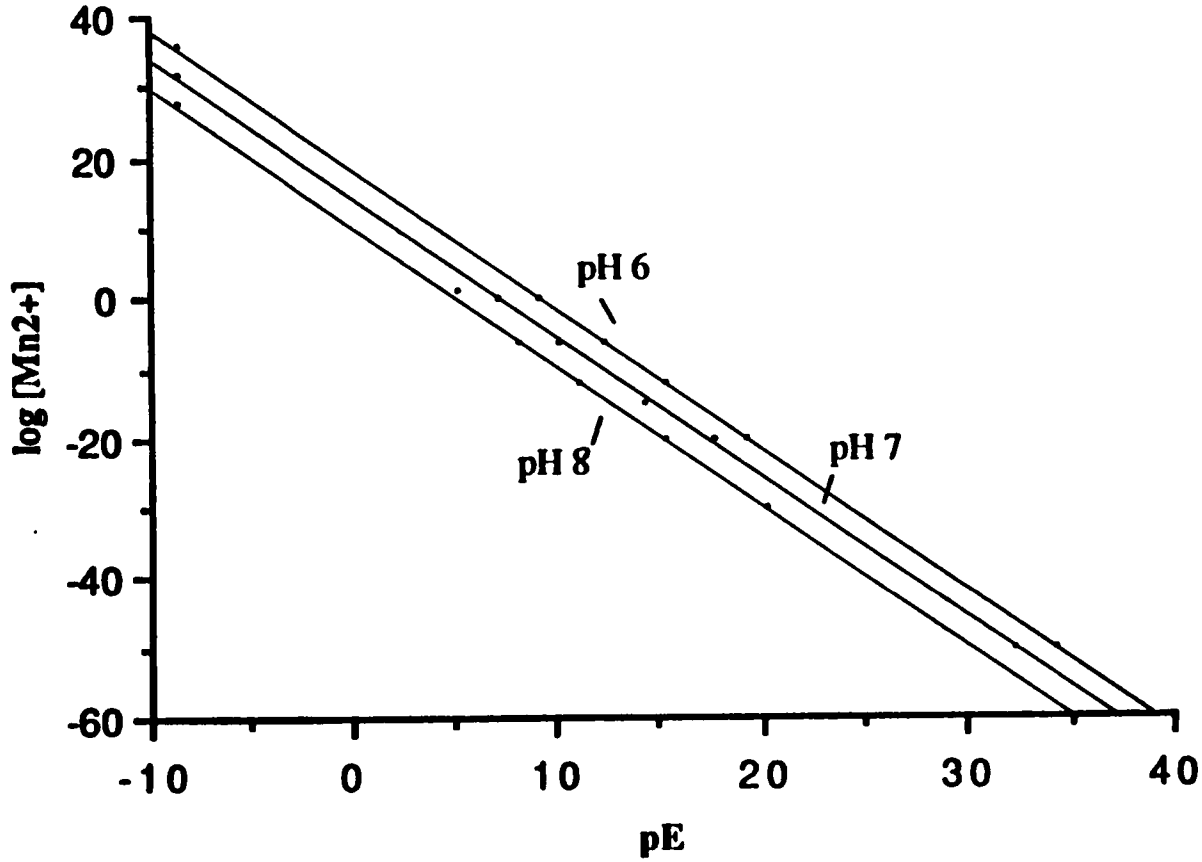


Figure 63. Equilibrium Mn^{2+} concentration as a function of pE and pH

The pE for conditions in which manganese is oxidized by hypochlorite or chlorine dioxide can be found from the following equilibrium reactions for chlorine dioxide and hypochlorite:

$ClO_2 + 4H^+ + 5e^- \longleftrightarrow Cl^- + 2H_2O \quad E^o = +4.405\ V \quad (2)$

$OCl^- + 2H^+ + 2e^- \longleftrightarrow Cl^- + H_2O \quad E^o = +1.72V \quad (3)$

The equilibrium constant k for equation (2) can be found again from the equation $k = \exp(n^oFE^o/RT)$

$k = \exp[5(23.06)(4.405)/(1.986 \times 10^{-3})293^ok]$

$\ln k = 872.83$

$\log k = 872.83/2.303 = 379.$

Now, for the equilibrium expression

$ClO_2 + 4H^+ + 5e^- \longleftrightarrow Cl^- + 2H_2O$

equilibrium constant $k = \{Cl^-\}/\{H^+\}^4\{ClO_2\}\{e^-\}^5$

Taking logs on both sides as before and simplifying, it can be shown that

$pE = 75.8 - 1/5 \log \{ClO_2\}\{H^+\}^4/\{Cl^-\}$

For a concentration of $ClO_2 = 1.48 \times 10^{-5}$ M (1 mg/L), $Cl^- = 2x10^{-3}$ M (corresponding to 100 mg/L $CaCl_2$ as $CaCO_3$) and pH = 7,

$pE = 69.80.$

Similarly for equation (3), $k = \{Cl^-\}/\{OCl^-\}\{H^+\}^2$

and pE = 21.80 at pH 7, for $OCl^-=4.7x10^{-5}$ M (2.40 mg/L) and $Cl^-=2x10^{-3}$ M (when $CaCl_2$ concentration is 100 mg/L as $CaCO_3$)

The concentration of manganese that would be present as Mn^{2+} at equilibrium can be determined from Figure 63 and/or equation (1) for these pE values when hypochlorite or chlorine dioxide are used as the oxidants. Coordinates for plotting Figure 63 are given in Table A10 in the appendix. According to Figure 63, the maximum concentration of manganese that could exist as Mn^{2+} at pH 7 when hypochlorite is used as the oxidant is about 10^{-35} moles/L, i.e. essentially none which would also be true if chlorine dioxide were the oxidant. However, when polyphosphates are present, this oxidation will be retarded as mentioned previously.

4.9 ANALYSES OF PRECIPITATES

X-ray diffraction analysis (Figure 64) was performed to identify the solid phase formed upon oxidation of 1 mg/L of manganese by chlorine dioxide. An average calcium concentration of about 100 mg/L was present in these samples. The polyphosphate dosage was 10 mg/L as total phosphate. The sample was prepared for x-ray diffraction by filtering bottles dosed with chlorine dioxide and polyphosphate through 0.1 micron filters. The precipitate retained on the filters was dried and ground with a mortar and pestle, and an elutriated slide was prepared prior to analysis.

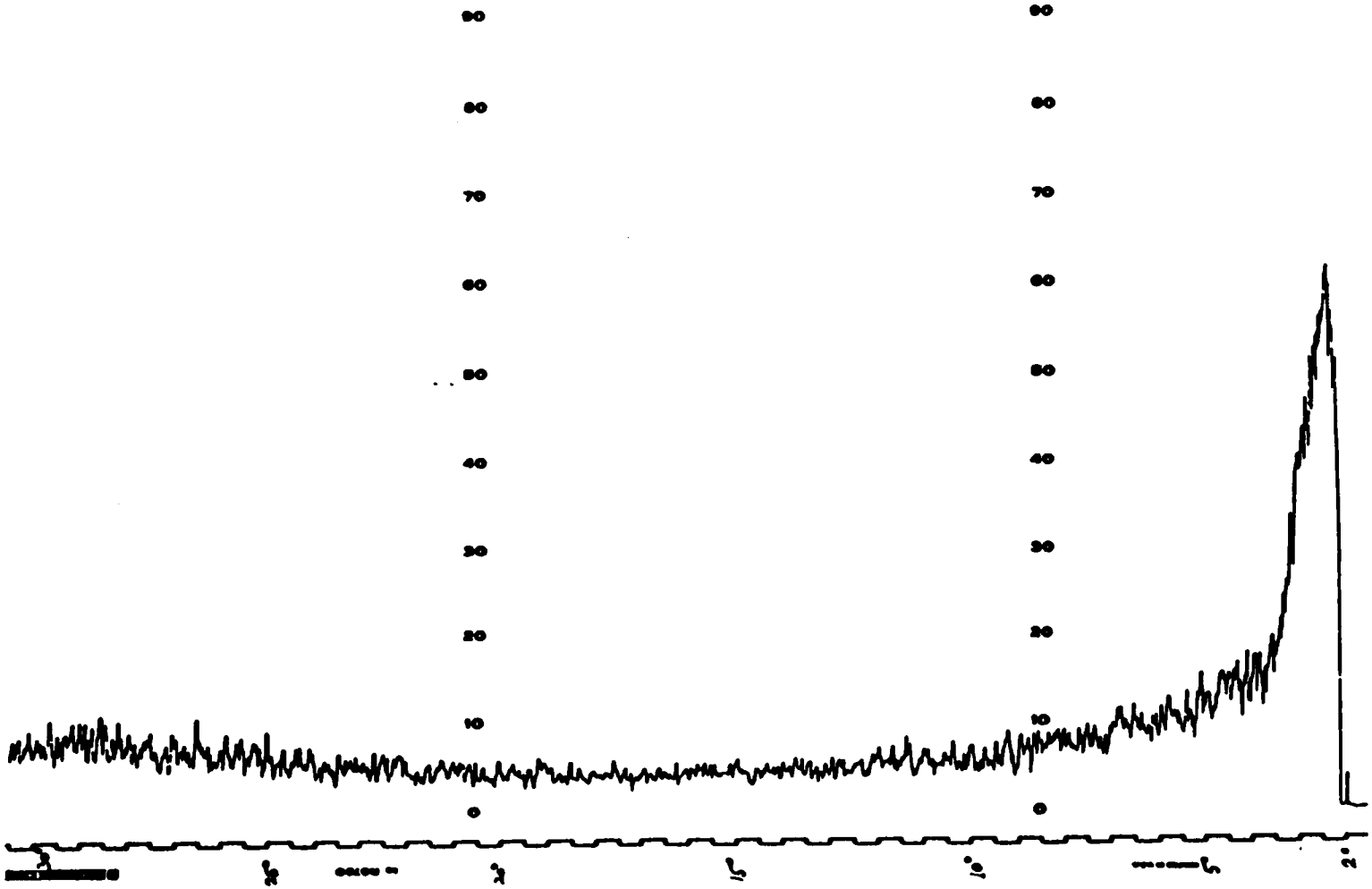


Figure 64. Manganese treatment by polyphosphate and chlorine dioxide in the presence of calcium: x-ray diffraction

However, no crystalline compounds could be identified as the samples were x-ray amorphous.

A similar analysis was performed in the absence of calcium and phosphate. 10 mg/L of manganese (Mn^{2+}) was oxidized by chlorine dioxide and the precipitate was analyzed by x-ray diffraction as before (Figure 65). The precipitate was again found to be x-ray amorphous. These results are consistent with Stumm and Morgan's findings (63) that the oxidized forms of manganese in most natural waters are present in an x-ray amorphous form. Snoeyink and Jenkins (83) also stated that the precipitate which is initially formed may be amorphous and transform slowly to the stable crystalline form. However, this process could involve a relatively longer time period (several months) compared to the usual time period (3 days) within which the treated water would pass out of the distribution system. Chemical analysis was done on the precipitates formed in manganese treatment by polyphosphate D and hypochlorite to determine the percentages of manganese, phosphate and calcium. Samples were filtered through a 0.1 micron filter 13 days after manganese treatment by polyphosphate D and hypochlorite. The samples used for chemical analysis were obtained from the experiment testing polyphosphate dosage effects in the presence of calcium (Section 4.3.3). Sodium bicarbonate was also present to provide an alkalinity of 155 mg/L as calcium carbonate. After filtration, the filter was dried for 72 hours at room temperature. The

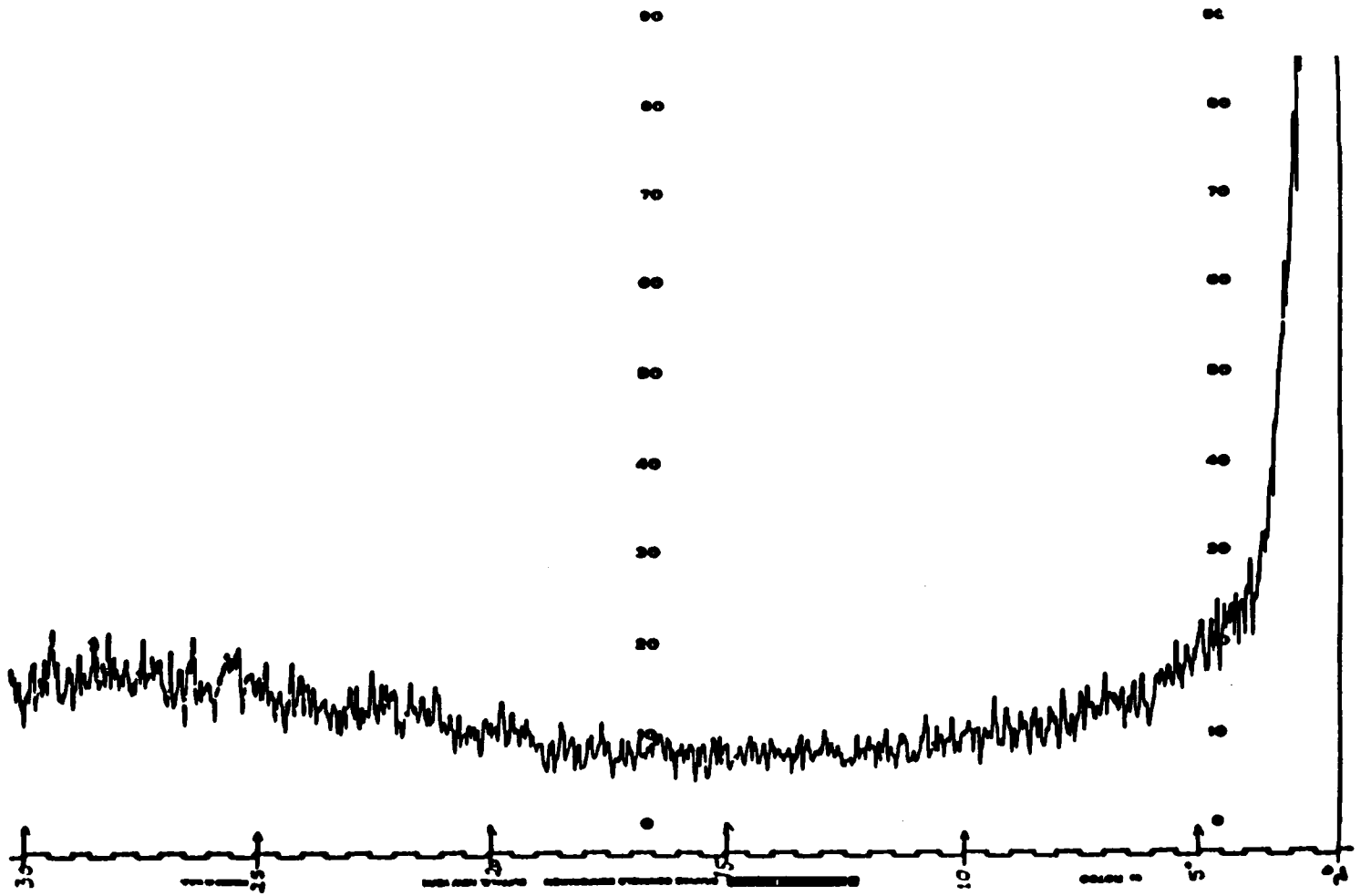


Figure 65. Manganese treatment by polyphosphate and chlorine dioxide in the absence of calcium: x-ray diffraction

residue on the filter (5 mg) was dissolved in nitric acid and diluted to 500 ml. This solution was analyzed for total PO_4, manganese, and calcium. The amount of total PO_4, manganese, and calcium were 0.625, 0.639, and 1.315 mg (6.58×10^{-3}, 1.16×10^{-2}, and 3.29×10^{-2} moles) respectively. The total weight of the precipitate was 5 mg. The weight percentages of phosphate, manganese and calcium in the precipitate were as follows:

PO_4 = 12.5 %;

Mn = 12.8%; and

Ca = 26.3 % (65.75% calcium as calcium carbonate). The molar ratio of calcium : phosphate was 5:1. This ratio was compared with the molar ratio of calcium : phosphate in several phosphate forms such as calcium hydrogen phosphate, $CaHPO_4(s)$, calcium dihydrogen phosphate ($Ca(H_2PO_4)_{2(s)}$), hydroxyapatite ($Ca_5(PO_4)_3OH_{(s)}$), and calcium pyrophosphate ($Ca_2P_2O_{7(s)}$). The ratios of calcium:phosphate for these calcium-phosphate solids were not identical to the 5:1 ratio (of calcium:phosphate) determined for the precipitate by chemical analysis.

It is evident that manganese was present as particulates on day 13 (the day of sampling) in this experiment, as manganese was retained on the filters. In experiments on manganese treatment by polyphosphate and hypochlorite, polyphosphate inhibited manganese oxidation for a period of 10 days. However, since this precipitation was observed on the thirteenth day after treatment, it is possible

that manganese was oxidized by hypochlorite between day 10 and day 13 and present as colloidal particulates. Also, the manganese particulates may have been destabilized by the calcium which was present in this experiment, resulting in coalescence and particle growth to a size above the nominal membrane pore size of 0.1 micron.

4.10 STREAMING CURRENT

4.10.1 Polyphosphate and Chlorine Dioxide Dosage Effects on Streaming Current

In the previous section, the manganese precipitates which were present as colloids in the polyphosphate/chlorine dioxide method were evaluated by x-ray diffraction methods and were found to be amorphous. As these precipitates could not be identified, the cause for the failure of the silicate/chlorine dioxide technique (due to the high discoloration produced) could not be explained in terms of the type of precipitate that was formed during oxidation of manganese by chlorine dioxide. Further studies were done using streaming current detectors to determine whether streaming current can predict good treatment or can be used as an indication of poor manganese treatability. To achieve this objective, the correlation between color, filterability, and turbidity (parameters by which treatment effectiveness was determined) and streaming current was studied. Results of this study are shown in Figures 66-71 and Table 15.

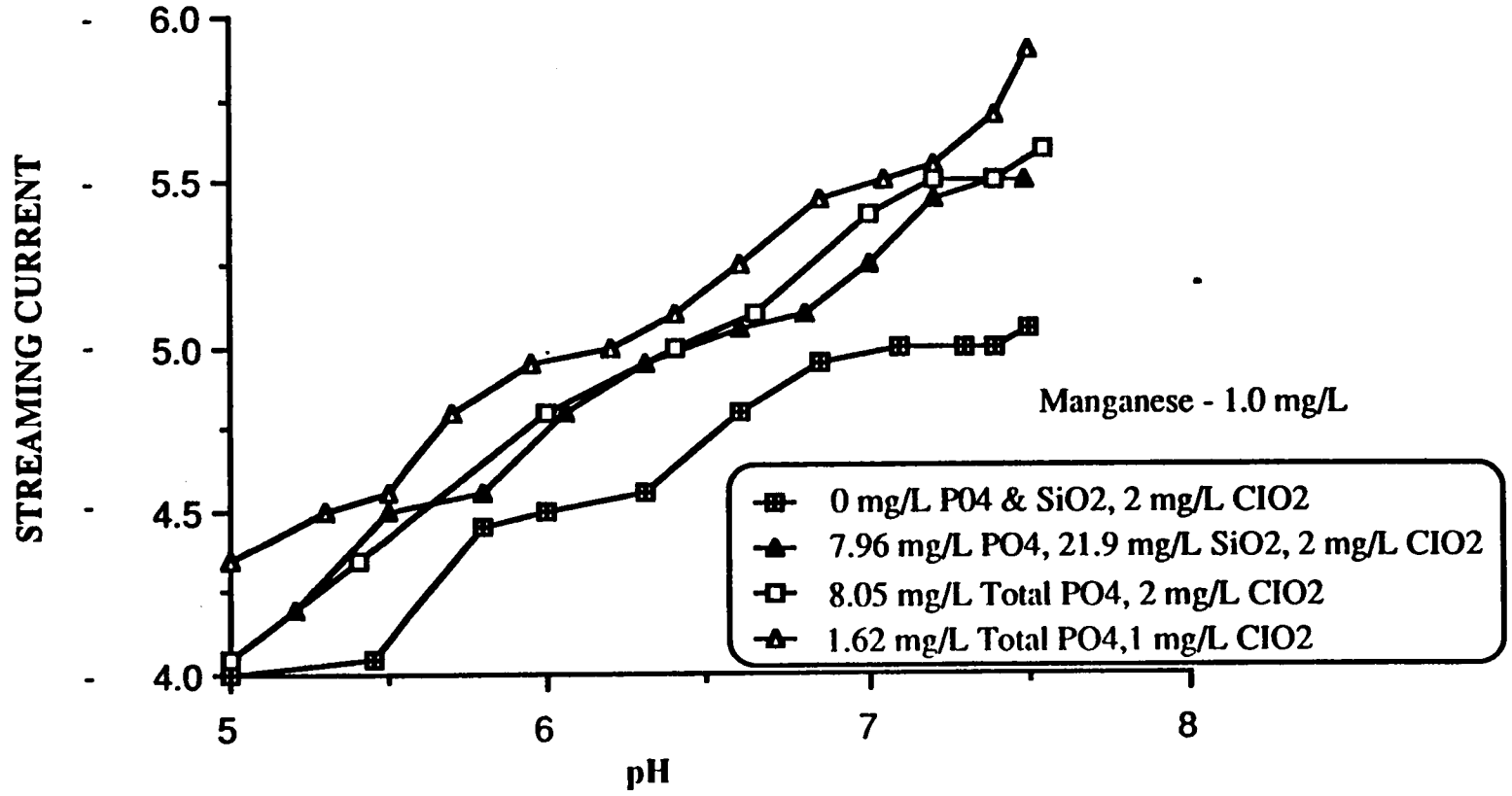


Figure 66. Manganese treatment by polyphosphate A and chlorine dioxide in the absence of calcium: streaming current, day 1

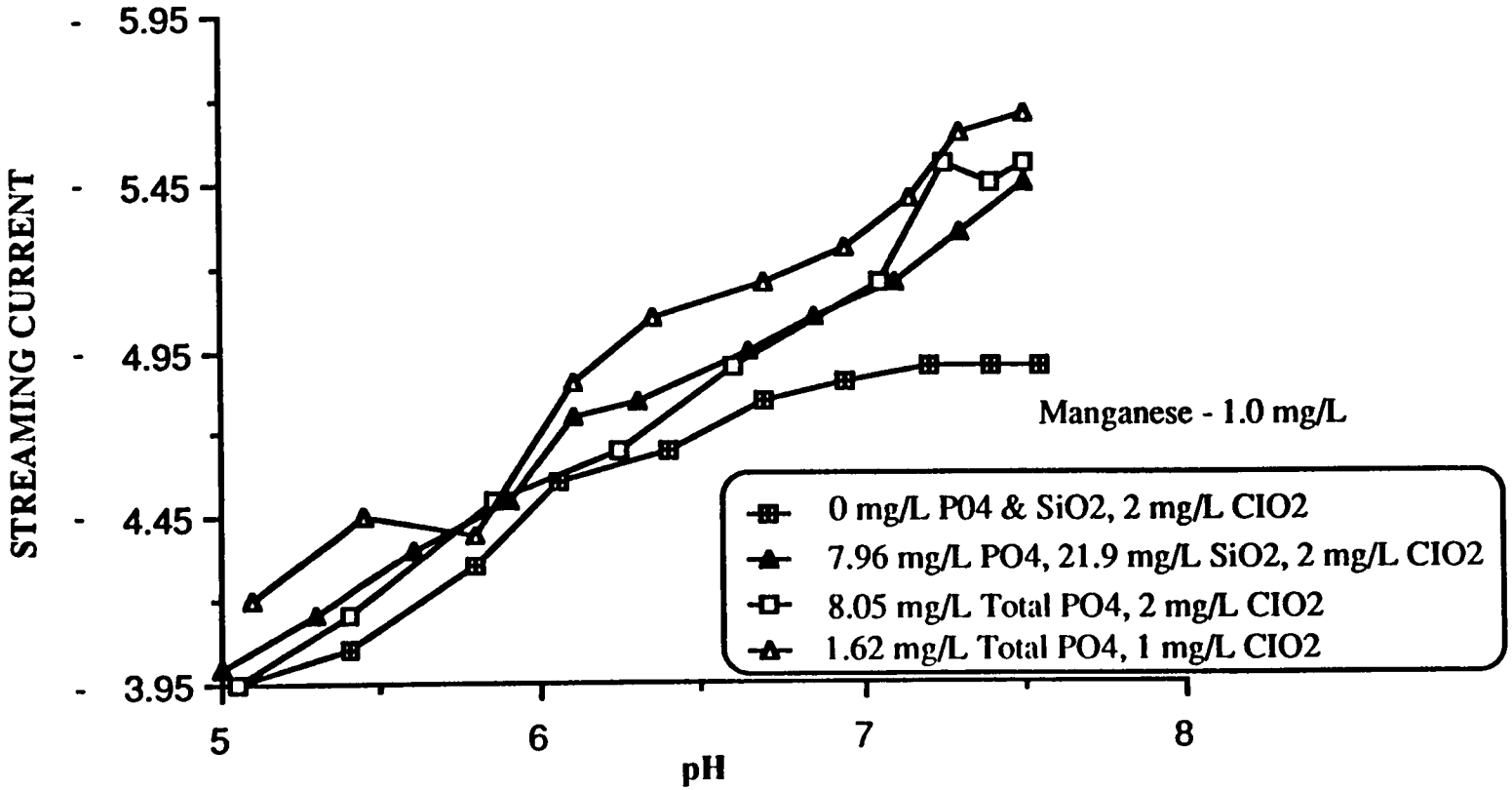


Figure 67. Manganese treatment by polyphosphate A and chlorine dioxide in the absence of calcium: streaming current, day 3

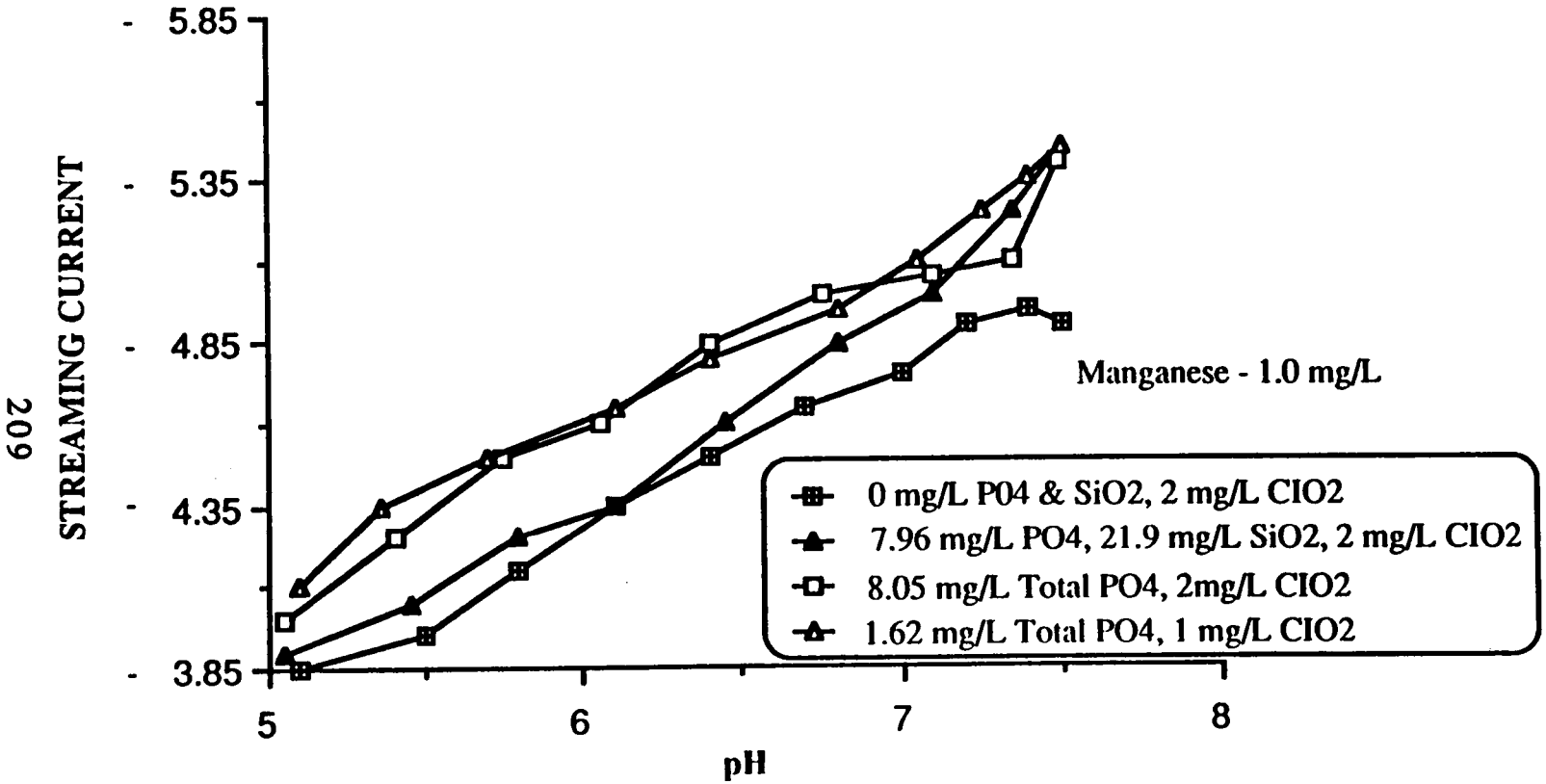


Figure 68. Manganese treatment by polyphosphate A and chlorine dioxide in the absence of calcium: streaming current, day 5

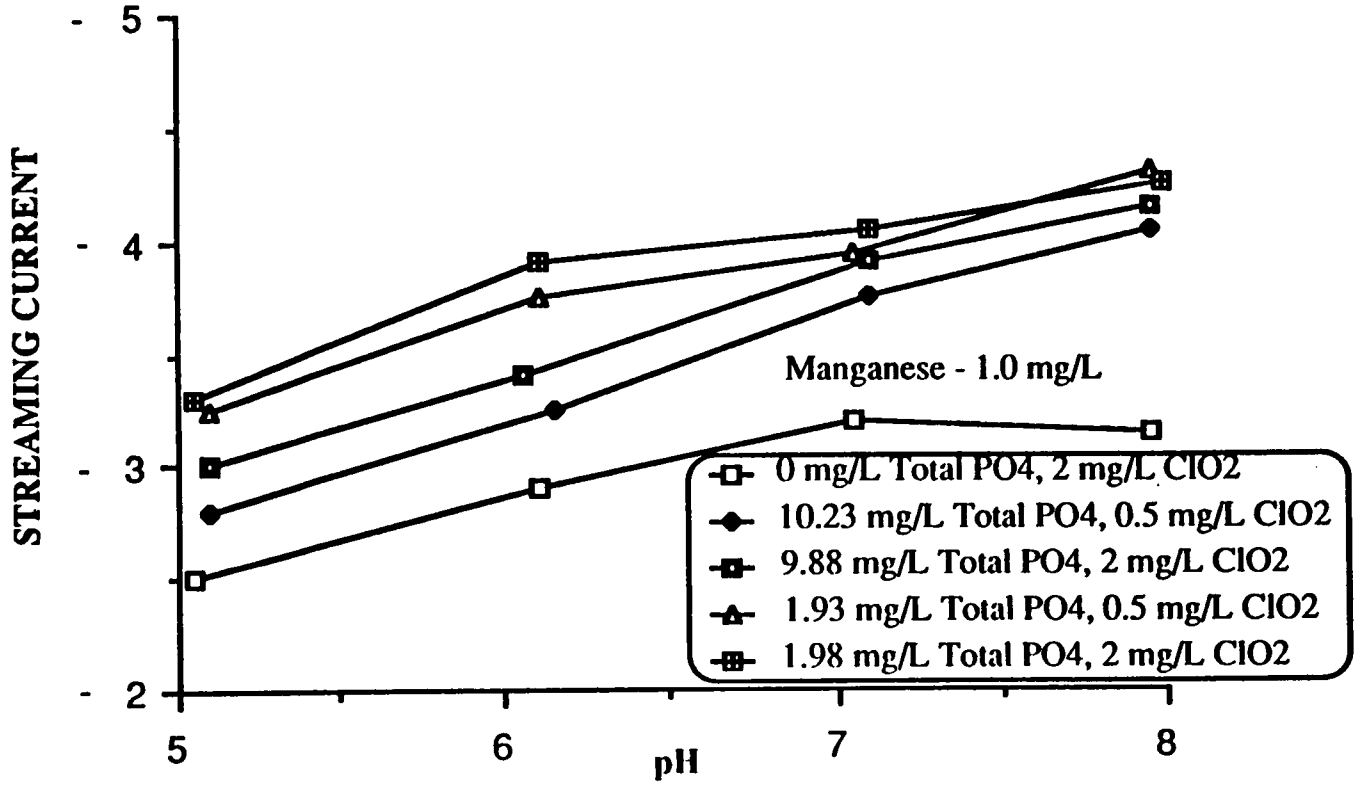


Figure 69. Manganese treatment by polyphosphate D and chlorine dioxide in the absence of calcium: streaming current, day 1

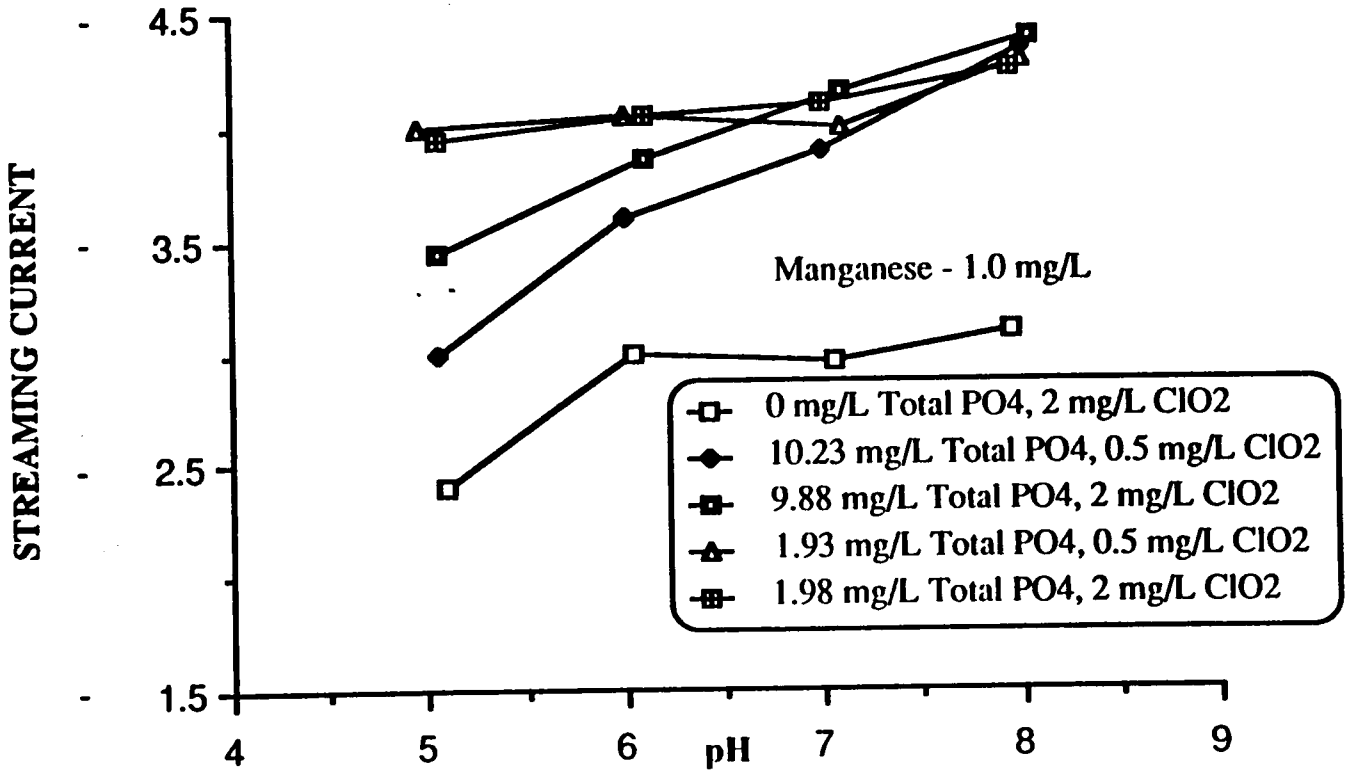


Figure 70. Manganese treatment by polyphosphate D and chlorine dioxide in the absence of calcium: streaming current, day 3

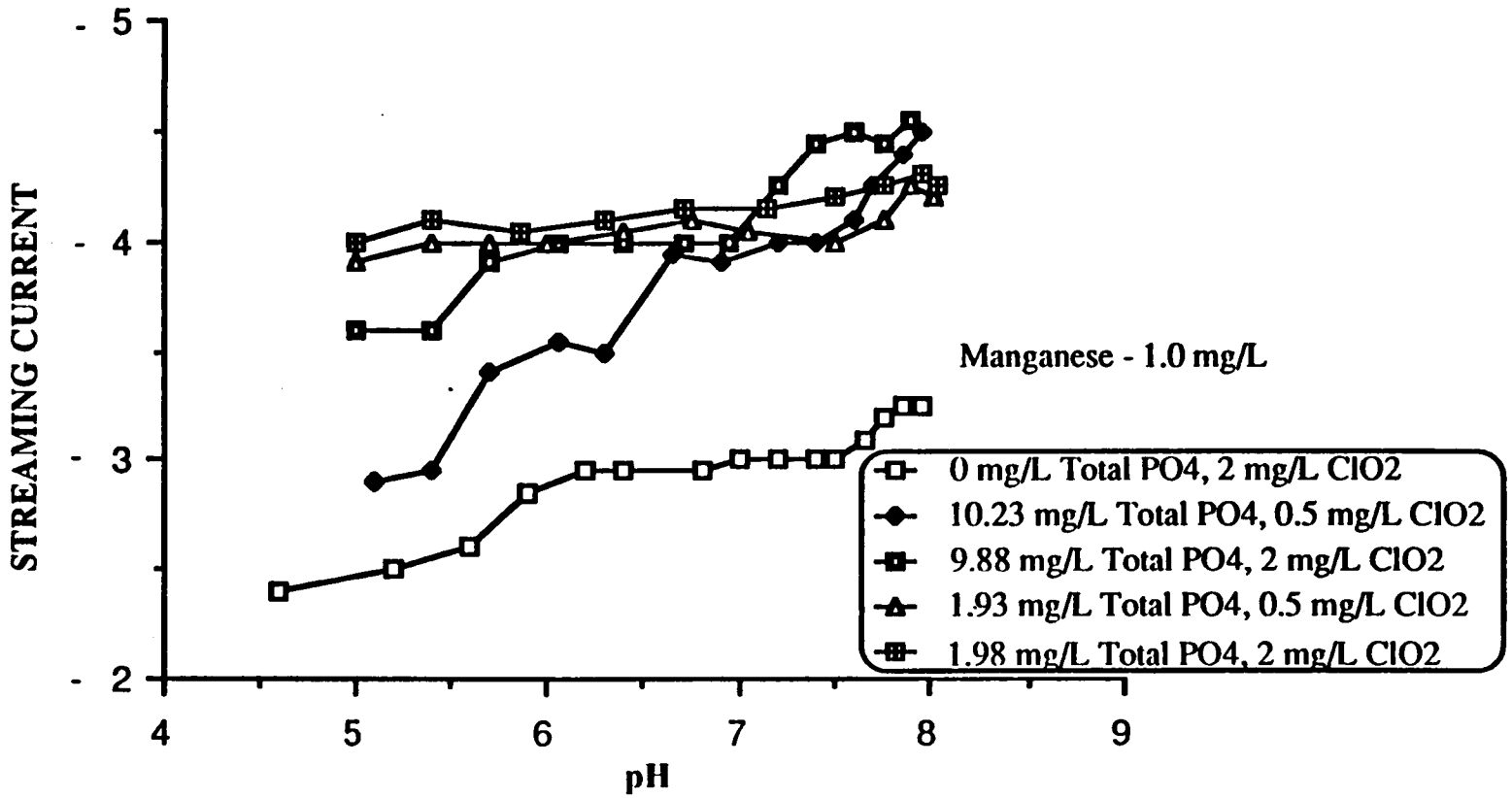


Figure 71. Manganese treatment by polyphosphate D and chlorine dioxide in the absence of calcium: streaming current, day 5

Table 15. Effect of polyphosphate and chlorine dioxide dosage on streaming current on day 3

Filterability %	Turbidity NTU	Color units	Streaming Current units	PO_4 mg/L	ClO_2 dosage
93	0.60	305	-4.90	0	2.0
100	0.23	130	-5.10	7.96	2.0
98	0.20	175	-5.10	8.05	2.0
99	0.25	210	-5.30	1.62	1.0

From the tables and figures it is evident that streaming current was not affected to any significant extent by treatment. The difference in streaming current noticed between treated bottles was almost within the normal deviation in streaming current readings for the standard colloid ($\pm$ 0.25 streaming current units) for the period of this experiment. As the present study found that successful manganese treatment does not involve a colloidal mechanism, the fact that the streaming current detector did not respond to manganese treatability is not surprising.

4.10.2 Statistical Analysis to Verify the Reliability of the Streaming Current Detector for the Period of Use

Streaming current (SC) readings for standard colloids were taken over a period of several months to determine the reliability of

readings obtained with the streaming current detector. The streaming current readings obtained with the same instrument and results of statistical computations for standard deviation (SD), coefficient of variation (CV) and 90% confidence interval (90% CI) in separate experiments as well as the overall and average values lead to the conclusion that the streaming current detector was reliable for the period of use of several months. The 90% CI for the mean was within 2% of the mean, and the SD was only 2.364% of the mean (CV) in individual experiments. The overall CV was 9.073% for a period of about 5 months, and the overall 90% CI was within 1.83% of the mean. Nevertheless, there were many outliers, i.e. means of individual experiments of -4.307, -6.20 and -6.20 compared to the overall mean of -5.09. Thus, the streaming current is better compared within an experiment than between experiments. This is evident from the overall SD and CV (0.462, 9.073) for all streaming current data compared to the mean for the values obtained in individual experiments (0.116, 2.364). Regrettably, the instrument manufacturer has made no provisions for instrument calibration. Results of statistical computations are presented in Table 16.

Table 16. Reliability of the streaming current detector

Date of expt.	1/15/88	1/22/88 to 1/27/88	2/1/88 to 2/3/88	2/5/88 to 2/7/88	2/23/88 to 2/28/88	3/31/88 to 4/4/88	4/4/88 to 4/20/88	4/16/88 to 4/20/88	5/4/88 to 5/18/88	5/14/88 to 5/18/88	all data	each expt.
Mean	-5.08	-4.307	-5.243	-5.15	-5.331	-4.792	-4.908	-4.881	-6.200	-6.200	-5.092	-5.105
SD	0.130	0.315	0.130	0.045	0.100	0.111	0.092	0.075	0.071	0.071	0.462	0.116
%CV	2.560	7.314	2.480	0.874	1.876	2.316	1.874	1.537	1.145	1.145	9.073	2.364
90% CI for the mean	-5.08± 0.079	-4.307± 0.231	-5.243± 0.107	-5.150± 0.037	-5.331± 0.067	-4.792± 0.091	-4.908± 0.076	-4.881± 0.050	-6.200± 0.058	-6.200± 0.058	-5.092± 0.093	-5.105± 0.087

SD = Standard Deviation

CV = Coefficient of Variation as a percentage of the mean

CI = Confidence Interval

4.11 GENERAL DISCUSSION

Color was found to be the most significant variable in the silicate/chlorine dioxide, polyphosphate/chlorine dioxide, and polyphosphate/hypochlorite methods of manganese treatment. Color was significantly lower when manganese was treated by polyphosphate and hypochlorite, as polyphosphate inhibited the oxidation of manganese by hypochlorite. The results showed a strong relationship between greater phosphate dosages and lower manganese oxidation. Hence, the polyphosphate/hypochlorite method has a distinct advantage over the silicate/chlorine dioxide, silicate/hypochlorite and polyphosphate/chlorine dioxide methods in manganese treatment, as treatment by this method produced high filterability as well as low turbidity and color. As polyphosphate inhibited the oxidation of manganese by hypochlorite causing very little color to be produced, this was determined to be an important mechanism for the success of this technique. Other mechanisms may include polyphosphate complexation with manganese.

Ultrafiltration studies were done to determine if a polyphosphate-manganese complex was present when manganese oxidation was inhibited in the polyphosphate/hypochlorite method. The molecular weight of the polyphosphate used in these studies was 1785 gram/mole (polyphosphate A). Low filterability (< 10%) through the 1000 MW cut-off ultrafilter favors the hypothesis that a polyphosphate-manganese complex (with a molecular weight more than 1000 gram/mole) which was resistant to oxidation was formed.

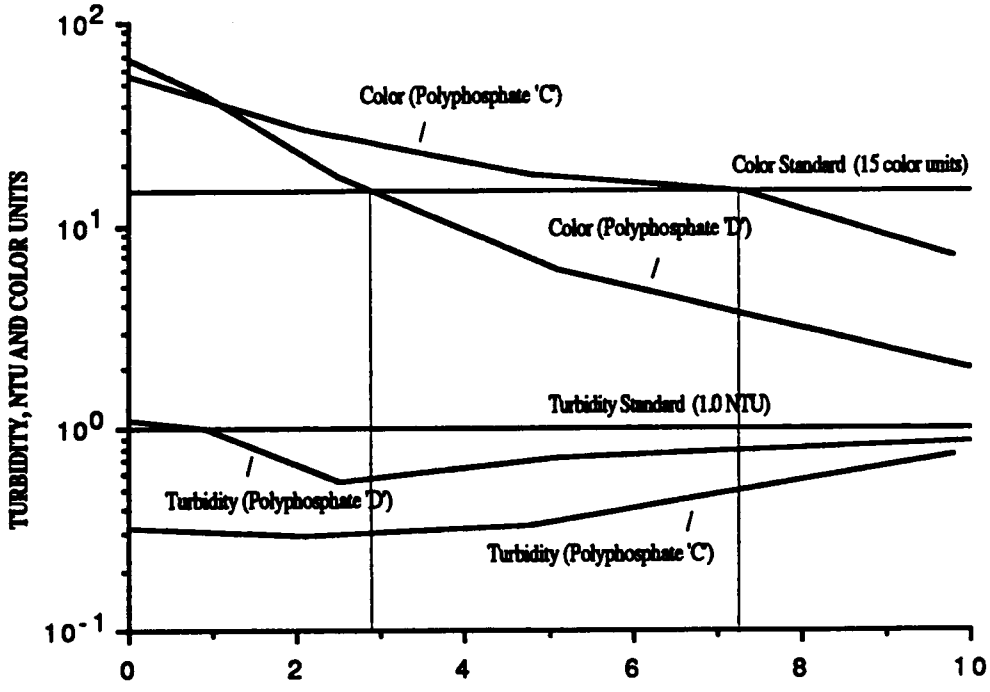
In the polyphosphate/chlorine dioxide method, this oxidation was not inhibited by polyphosphates and high color was produced, suggesting that the polyphosphate/hypochlorite technique is unique compared to the other methods studied in this research.

Prior to this research, it was hypothesized that manganese must be rapidly oxidized and dispersed in the colloidal form for effective treatment. However, this research found manganese oxidation to be detrimental to treatment, as manganese oxidation directly correlated with color. High color was produced and manganese was oxidized and present as colloidal particles in the polyphosphate/chlorine dioxide methods. The presence of manganese as colloidal particulates in the polyphosphate/chlorine dioxide method was verified by ultrafiltration analysis (using 200,000 MW cut off ultrafilters corresponding to an approximate pore size of 0.0075 microns). Even though manganese was present as colloids in the polyphosphate/chlorine dioxide method, this method (polyphosphate/chlorine dioxide) was not successful due to the high discoloration produced. Similarly, the silicate/chlorine dioxide method was also found to be unsuccessful in sequestering manganese, as high discoloration was produced.

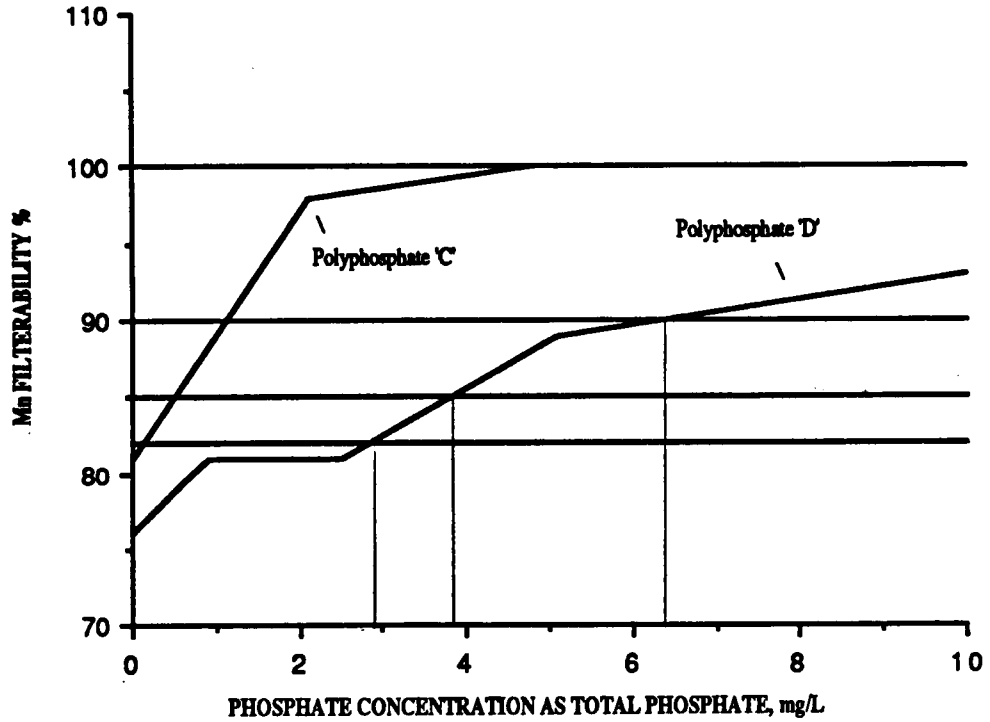
Experiments designed to obtain sufficient data to correlate the characteristics of polyphosphates with treatment effectiveness were unfruitful as no significant differences could be observed between the effectiveness of the various polyphosphates (Section 4.3.5). However, higher color was noticed when an orthophosphate

was used instead of polyphosphates. As Figures 72 and 73 illustrate, a phosphate dosage of 7.3 mg/L (polyphosphate C) is required to obtain a filterability of 100%, turbidity less than 1.0 NTU and color less than 15 color units. Differences noticed in the filterability, turbidity, and color between polyphosphates C and D are believed to be due to experimental error as explained in Section 4.3.5 and not due to the type of polyphosphate used. For polyphosphate D, a dosage of 6.4 mg/L is required to obtain a filterability of 90%, turbidity less than 1.0 NTU and color less than 15 color units. If 85% filterability is the criteria used to assess treatment effectiveness, a phosphate dosage of 3.8 mg/L would be sufficient (turbidity and color will be below 1.0 NTU and 15 color units respectively). However, if the chosen filterability criteria is less than 82% (corresponding to phosphate dosages less than 2.8 mg/L), color would be higher than 15 color units even though the turbidity is less than 1.0 NTU. In this research, no obvious discoloration was noticed on the filters when manganese filterability was greater than 90%. Slight discoloration of the filters was observed at about 85% filterability and increased consistently with decreasing filterability, due to the retention of manganese oxides.

Consistent with MINTEQ predictions, turbidity increased with the polyphosphate dosage in the presence of hardness (100 mg/L calcium as calcium carbonate) due to the formation of a calcium-phosphate precipitate. At pH 6 low turbidity was observed consistent with MINTEQ predictions.



a. Phosphate dosage versus turbidity and color



b. Phosphate dosage versus Mn filterability

Figure 72. Phosphate dosage versus color, turbidity and filterability

5.0 CONCLUSIONS

The following are the conclusions derived from this experimental investigation:

1. Polyphosphate and hypochlorite were determined to be the best sequestrant and oxidant combination in laboratory experiments, for manganese treatment as this method gave lower color, lower turbidity, and higher filterability.

2. Manganese could not be sequestered by sodium silicates or polyphosphates with chlorine dioxide, as high color was produced due to oxidation of manganese by chlorine dioxide

3. Polyphosphates inhibited manganese oxidation by hypochlorite, leading to the conclusion that this is an important mechanism by which polyphosphates sequester manganese.

4. Ultrafiltration results using 1000 MW and 200,000 MW cut-off ultrafiltration membranes indicate that polyphosphates may have complexed with Mn^{2+} making this complex resistant to oxidation by hypochlorite.

5. Results obtained using MINTEQ predict that manganese (Mn^{2+}) oxidation to manganese dioxide by hypochlorite is thermodynamically favorable. However, manganese dioxide may not be formed initially during oxidation even though it is

the thermodynamically most stable phase. Precipitates such as manganite (MnOOH) may form initially and transform to manganese dioxide. Even though in one experiment this oxidation did not take place for a period of 10 days when polyphosphate and hypochlorite were present, manganese was oxidized by hypochlorite and precipitated by day 13 in this case, as it was retained on 0.1 micron filters. Hence, manganese oxidation by hypochlorite is only delayed in the presence of phosphates.

6. Turbidity increased with polyphosphate dosages in the presence of 100 mg/L calcium as calcium carbonate due to the formation of a calcium-phosphate precipitate. MINTEQ predicted that hydroxyapatite is thermodynamically favored at pH 7 (for phosphate dosages greater than 6.4) and pH 8 (all phosphate dosages) at hardness levels of 100 mg/L as calcium carbonate. As indicated earlier, even though hydroxyapatite is thermodynamically the most stable precipitate that may form under conditions in this research, other precipitates may form initially and transform to the more stable form. MINTEQ results predict that hydroxyapatite precipitation will not occur at pH 6 at the phosphate dosages (1 to 10 mg/L) and hardness levels in this research (100 mg/L as calcium carbonate). This is also consistent with results obtained in this research, as treatment at pH 6 gave lower turbidity and color, and higher filterability than at pH 7. MINTEQ predicted that in addition to

hydroxyapatite, calcium carbonate would also precipitate at pH 8 which is also consistent with the results obtained in this research, as higher turbidity was obtained at pH 8 than at pH 7.

7. The identity of manganese- and calcium-phosphate precipitates in this research could not be determined by x-ray diffraction as the precipitates were x-ray amorphous. The weight percentages of manganese, calcium and phosphate in the precipitate was determined by chemical analysis to be 12.8%, 26.3%, and 12.5% respectively, and the molar ratio of calcium : phosphate in the precipitate was found to be 1 : 5.

8. Results of statistical analysis indicate that the effectiveness of the polyphosphates tested in this research with hypochlorite may not be significantly different. This implies that the characteristics of polyphosphates (reversion rate, % PO4, and molecular weight) may not have a significant effect on manganese treatability. However, the data used to arrive at this conclusion was limited. Therefore in future, replicates of several polyphosphates (in addition to the four polyphosphates used in this research) should be tested to perform a better statistical analysis and arrive at a firm conclusion. Higher color was observed when orthophosphates were used. Better manganese treatability with polyphosphates may be due to their ability to form stronger complexes with manganese and retard manganese oxidation by hypochlorite.

9. No obvious correlation was seen between streaming current and manganese treatability in laboratory experiments consistent with the findings of this study that successful manganese sequestration does not involve a colloidal mechanism.

10. The extent to which reproducibility of results was achieved in this research was tested in a single experiment using bottles dosed similarly (triplicates) with polyphosphate and hypochlorite or chlorine dioxide. Reasonably consistent results were noticed for similar bottles. Only in one set of bottles, did one bottle show significantly lower turbidity on day 5 than the other two bottles.

11. Proper digestion procedures will have to be employed in the phosphate digestion procedure. Improper digestion procedures will result in an under-estimation of the polyphosphate dosage. The phosphate digestion procedure used in this research is valid as only 10% increase in total phosphate was observed between digestion time periods of 30 minutes and 10 hours (Section 3.0).

6.0 RECOMMENDATIONS TO UTILITIES

Based on the findings of this research, the following recommendations are made to utilities:

1. Utilities should use polyphosphate and hypochlorite instead of silicates to limit manganese oxidation and the subsequent discoloration it causes, as polyphosphates inhibit manganese oxidation by hypochlorite. By this method, the dual purposes of sequestration and disinfection can be achieved.

2. Although not much difference was found in the effectiveness of the polyphosphates used in this study, utilities should test several polyphosphates before selecting the type of polyphosphate to be used in manganese sequestration, as the shelf-life and other characteristics may vary for different polyphosphates. The present study tested only a few polyphosphates.

3. Polyphosphates should be added prior to hypochlorite to minimize potential manganese oxidation.

4. In this research, higher phosphate dosages sequestered manganese for a longer period of time, but produced higher turbidity in the presence of hardness. Hence, utilities should test different dosages and adopt the dosage that gives the best treatment for the residence time in its distribution system, as

the water quality may be different from those in this experimental investigation.

5. If the pH of the groundwater is high (> pH 7), some deterioration in manganese treatability may be noticed due to an increase in the degree of manganese oxidation by hypochlorite at higher pH levels and calcium-phosphate precipitation. Manganese treatability may be improved by lowering the pH.

6. A calcium-phosphate precipitate was formed when polyphosphates were added in the presence of 100 mg/L calcium as calcium carbonate, causing turbidity. The white precipitate that was observed may not be objectionable to consumers. Low discoloration was maintained even though a calcium-phosphate precipitate was formed.

7. The Standard Methods Analytical procedure (APHA et al. 1985) and the digestion step should be used for total phosphate analysis. Tests should be performed at various digestion times to determine if the polyphosphate measured increases with the digestion time. The digestion time that detects > 90% of the phosphate should be used.

7.0 RECOMMENDATIONS FOR FURTHER STUDIES

Studies recommended to further the understanding of the manganese sequestration process are listed below:

1. This research was performed under controlled conditions using model groundwater prepared in the laboratory. Future studies could apply the findings of the present study to evaluation of the performance of polyphosphates in actual sequestration facilities.

2. Further field tests should be performed to determine if streaming current detectors can be used by utilities to adjust the sequestrant feed rates.

3. Since the oxidation state of manganese could not be identified in the present study, future studies should be performed to distinguish between different manganese oxidation states.

4. In future studies, the effectiveness of the polyphosphate technique should be tested in the presence of both iron and manganese.

5. Separate studies should be performed without controlling the pH as well as by adjusting the pH to the respective levels at 60 minute intervals throughout the experiment.

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APPENDIX

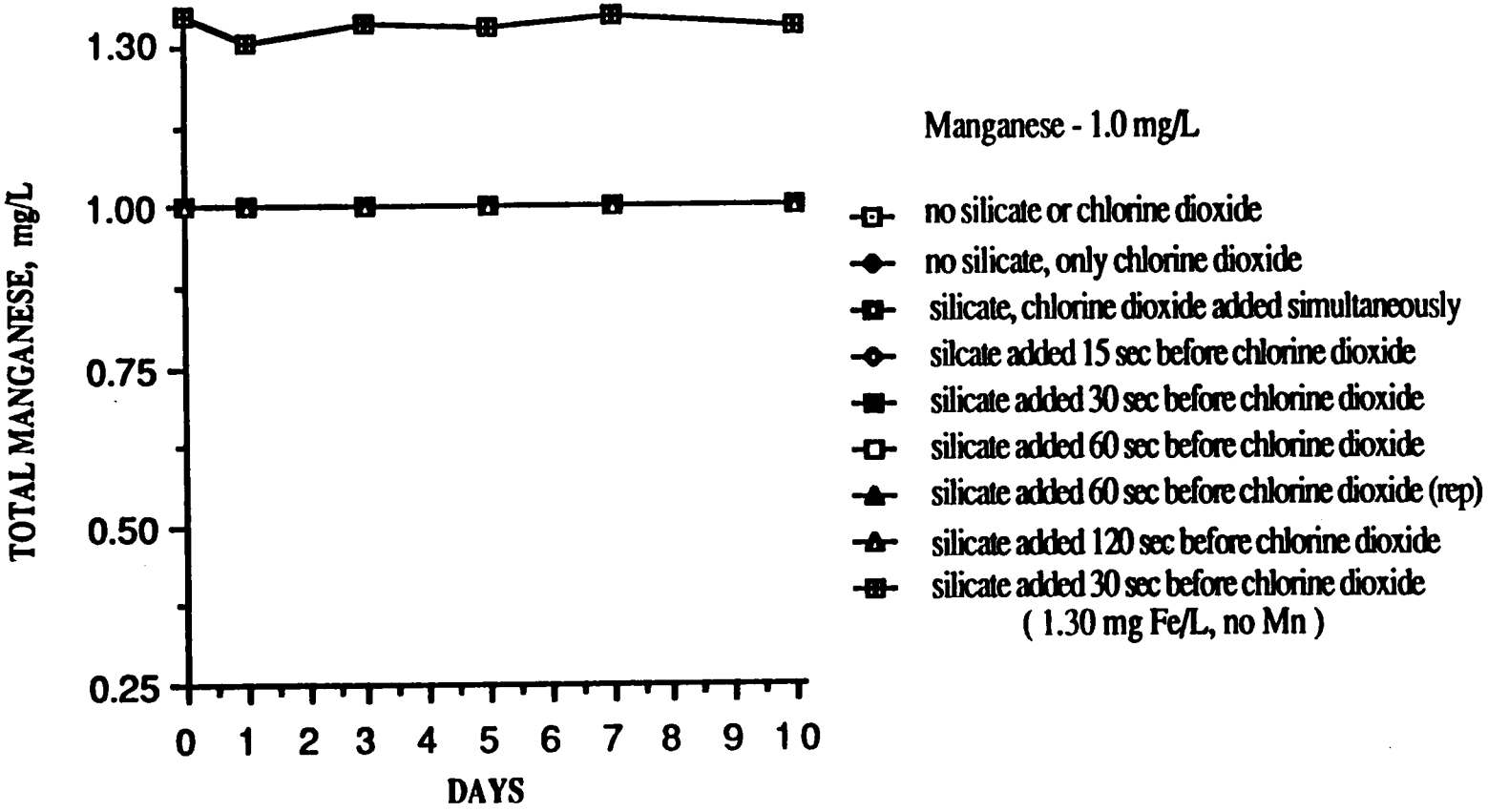

Figure A1. Lag time effects of silicate and chlorine dioxide on manganese treatment: total manganese

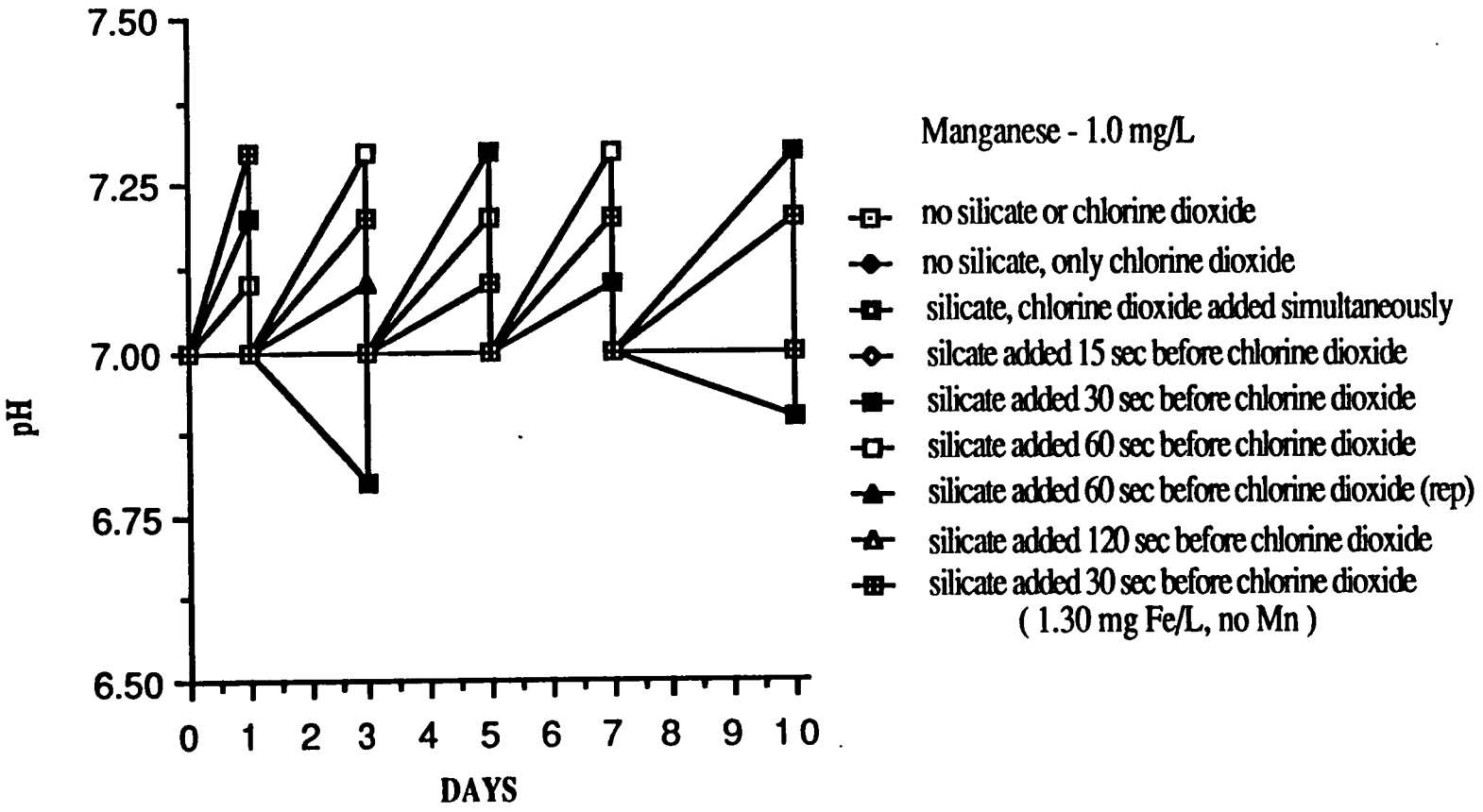

Figure A2. Lag time effects of silicate and chlorine dioxide on manganese treatment: pH

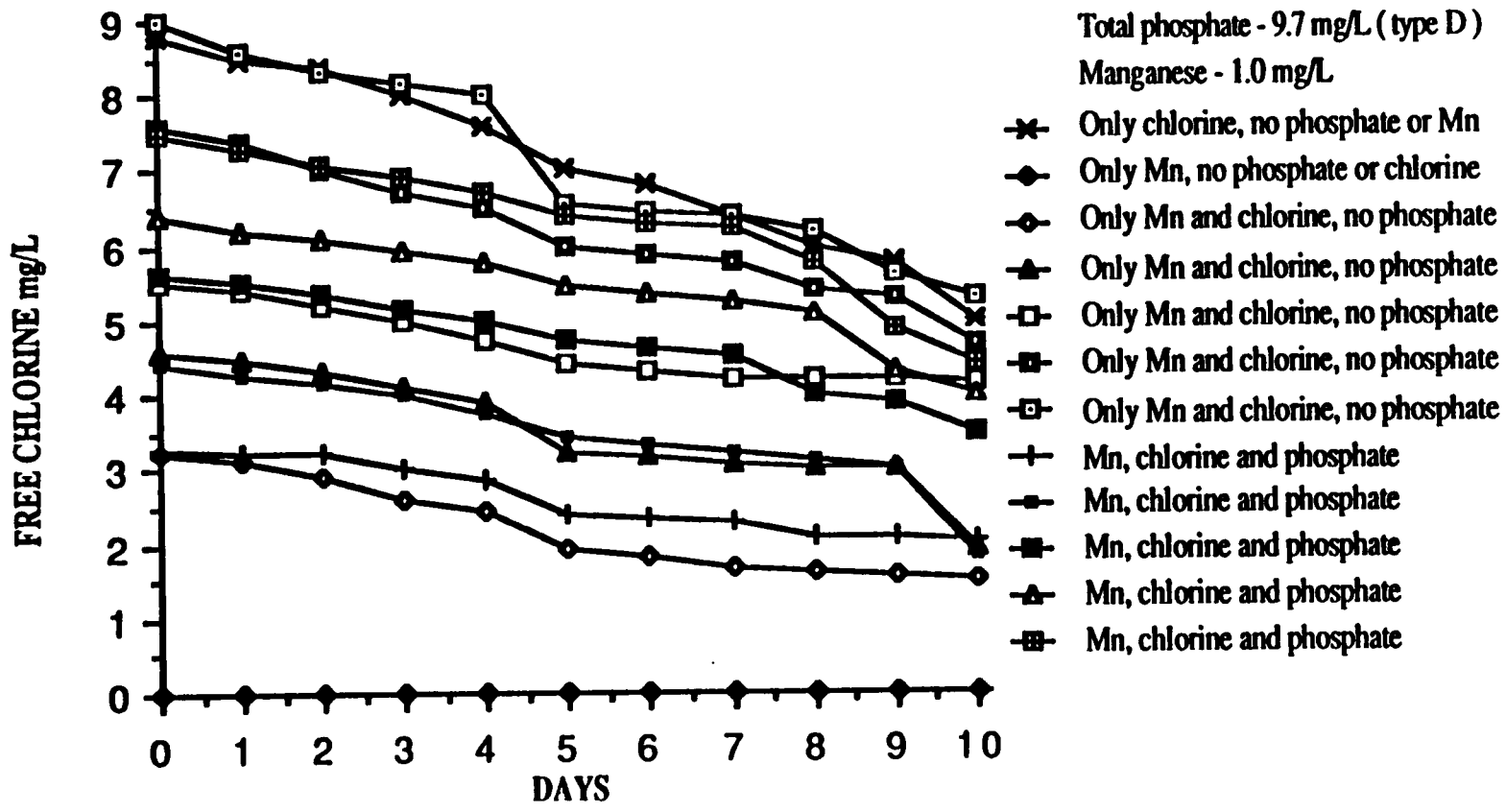

Figure A3. Study of manganese oxidation by hypochlorite in the absence of calcium: free chlorine

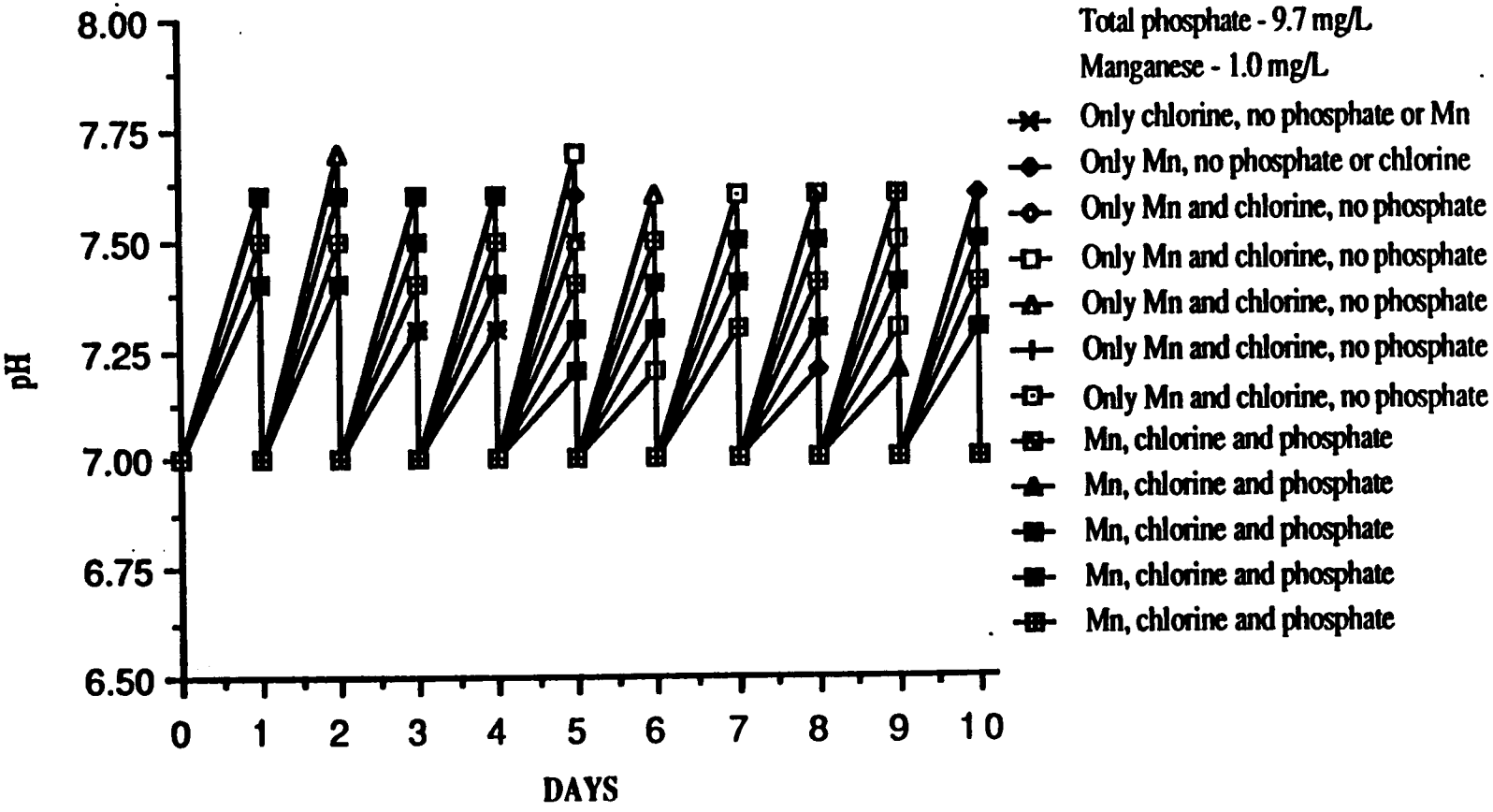

Figure A4. Study of manganese oxidation by hypochlorite in the absence of calcium: pH

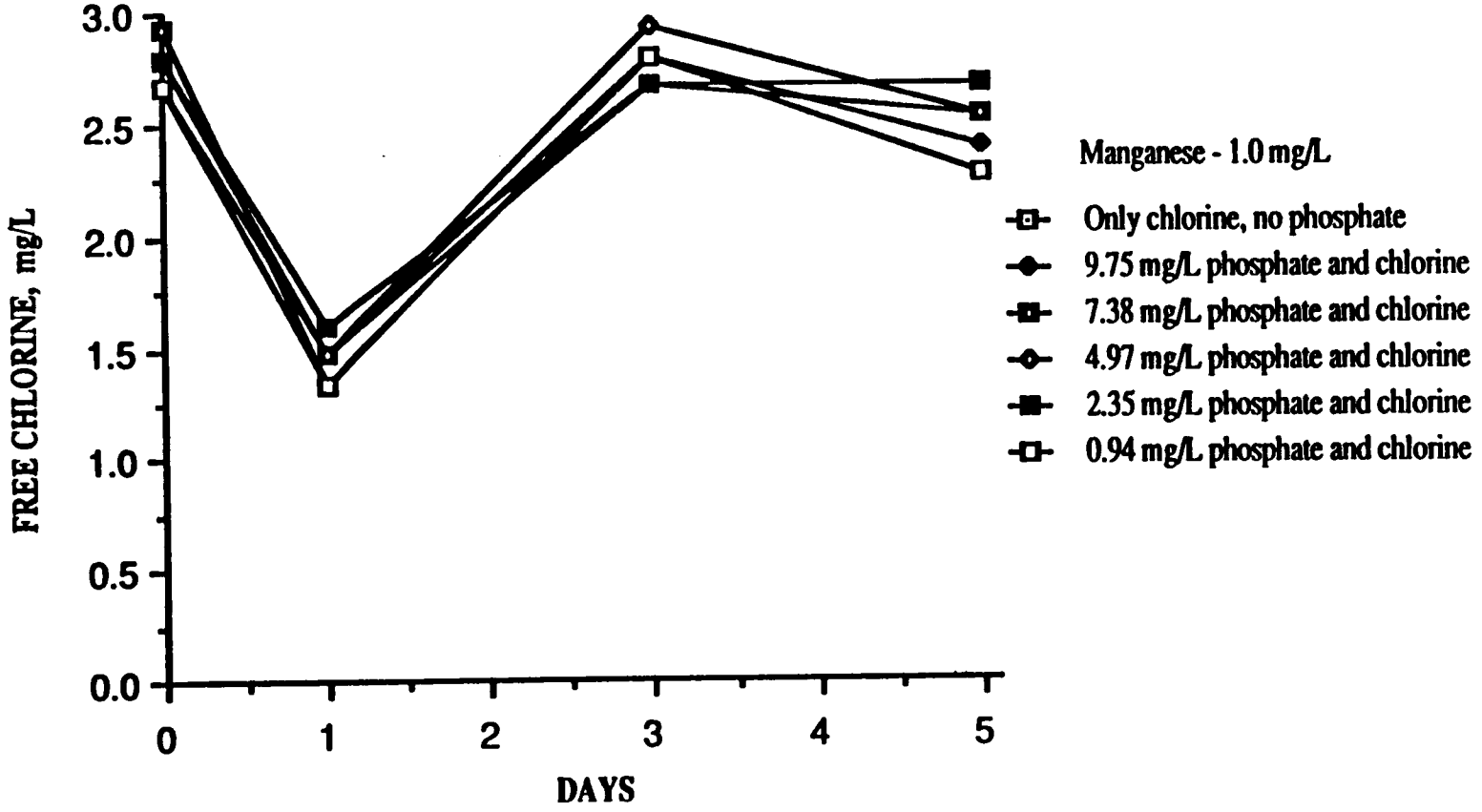

Figure A5. Manganese treatment with polyphosphate D and hypochlorite in the absence of calcium: free chlorine

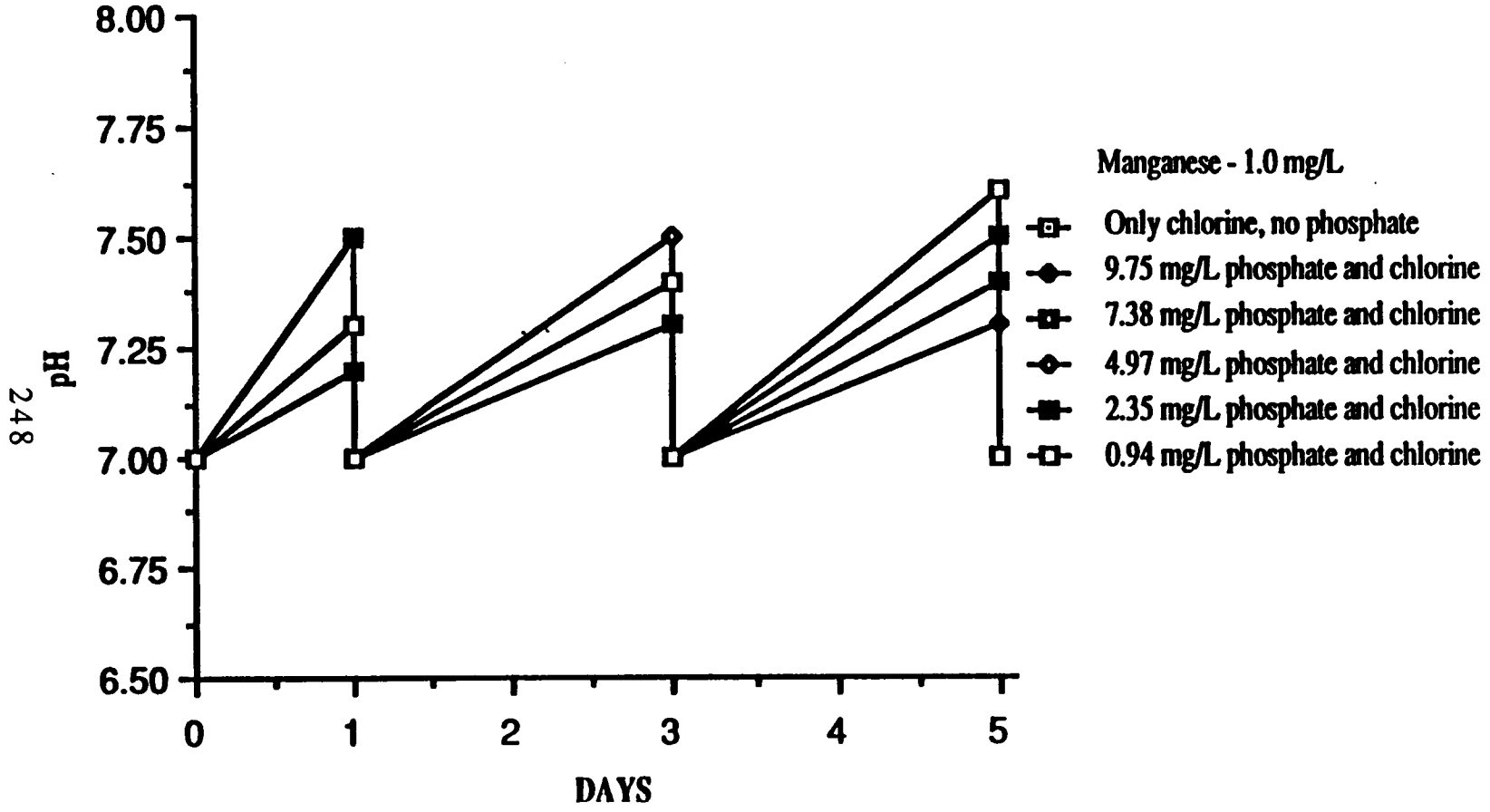

Figure A6. Manganese treatment with polyphosphate D and hypochlorite in the absence of calcium: pH

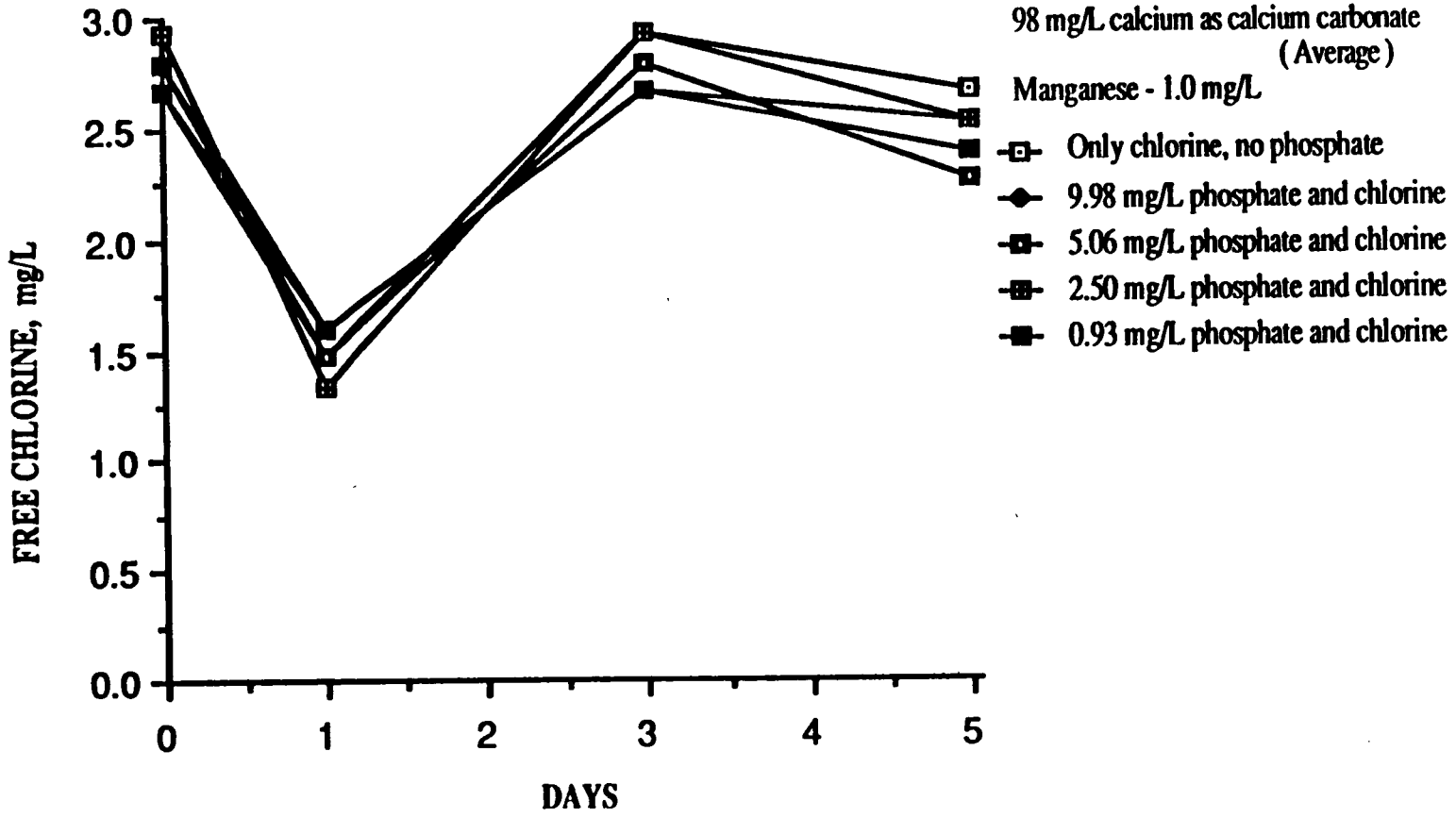

Figure A7. Manganese treatment with polyphosphate D and hypochlorite in the presence of calcium: free chlorine

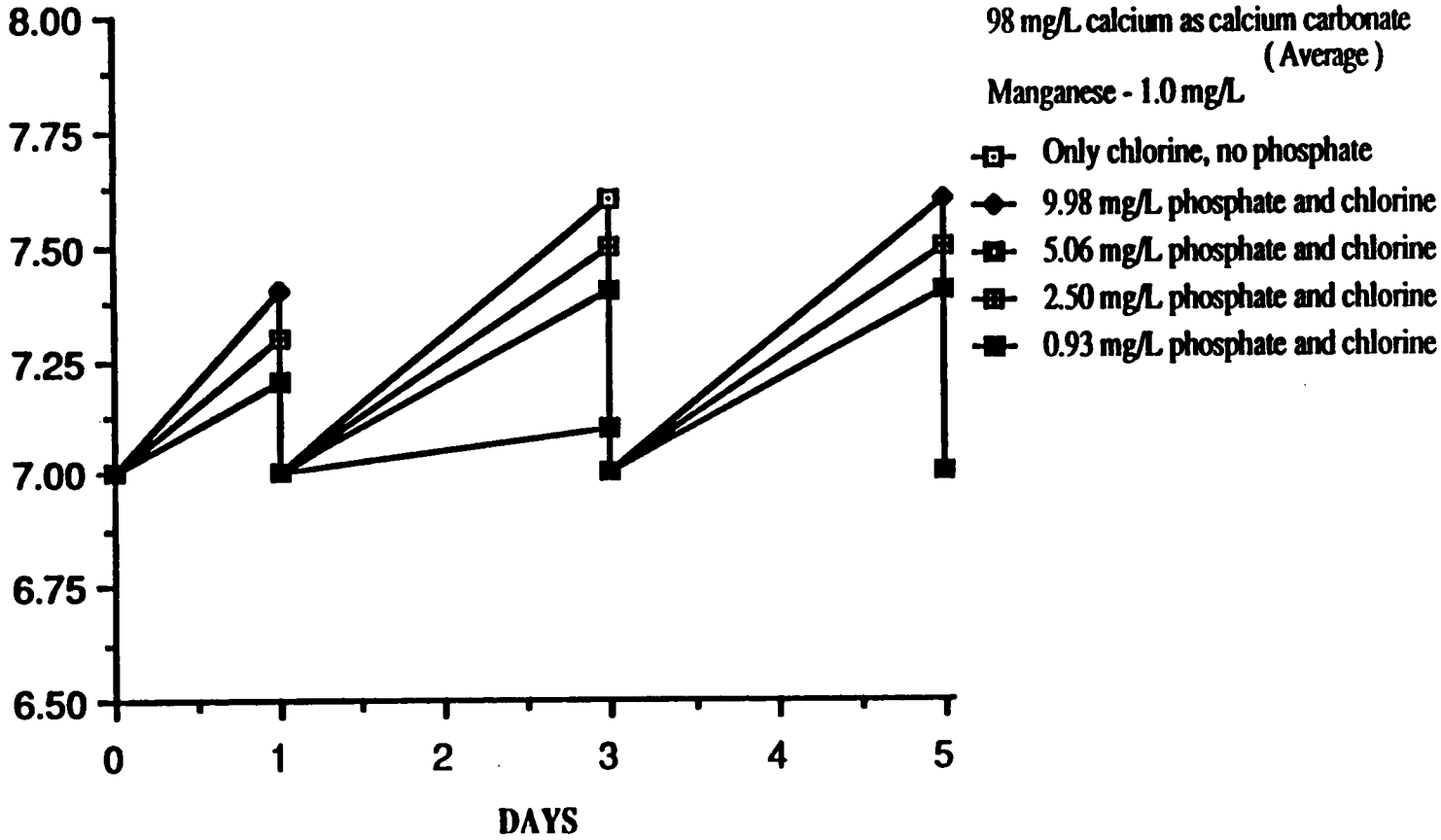

Figure A8. Manganese treatment with polyphosphate D and hypochlorite in the presence of calcium: pH

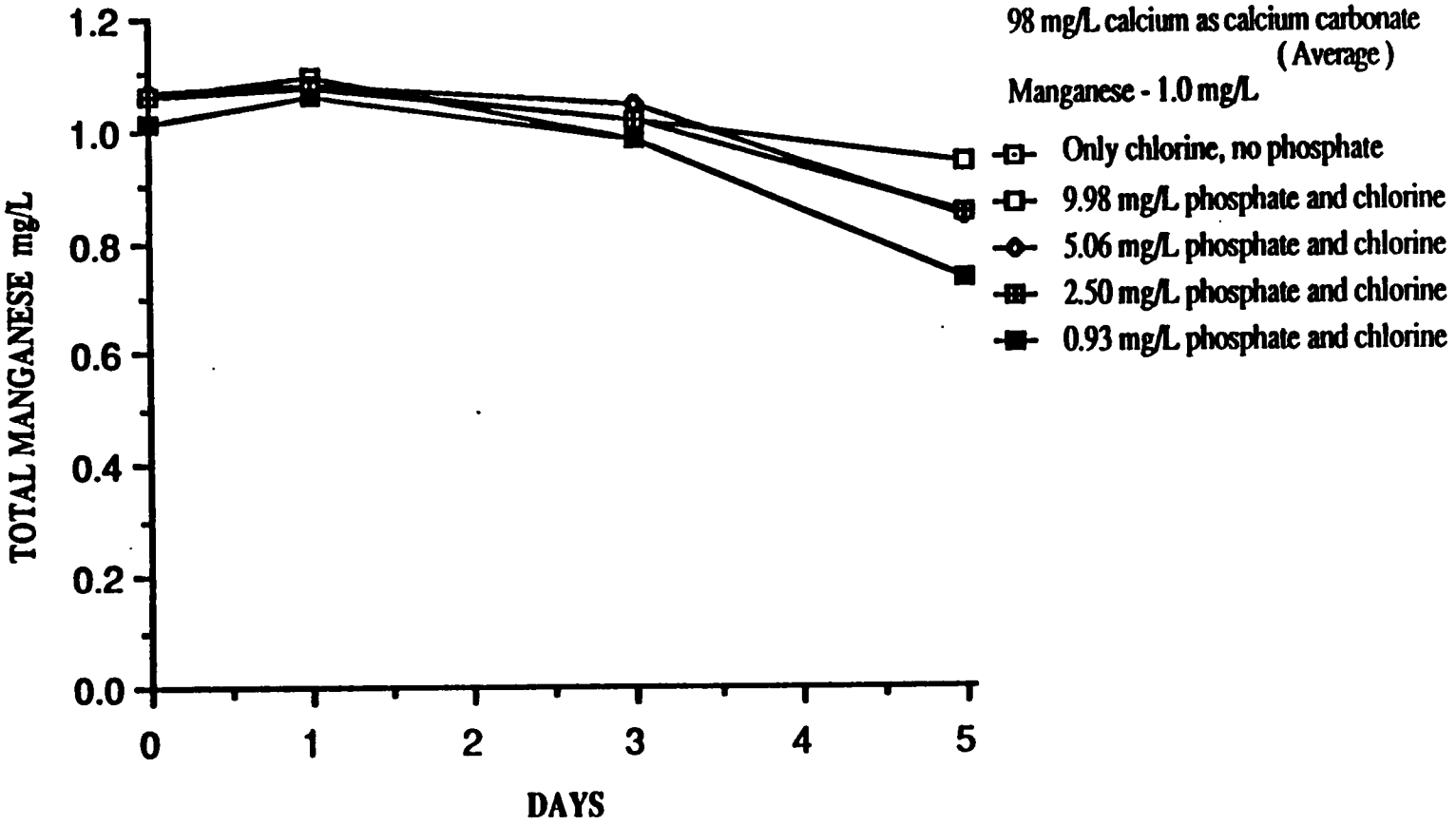

Figure A9. Manganese treatment with polyphosphate D and hypochlorite in the presence of calcium: total manganese

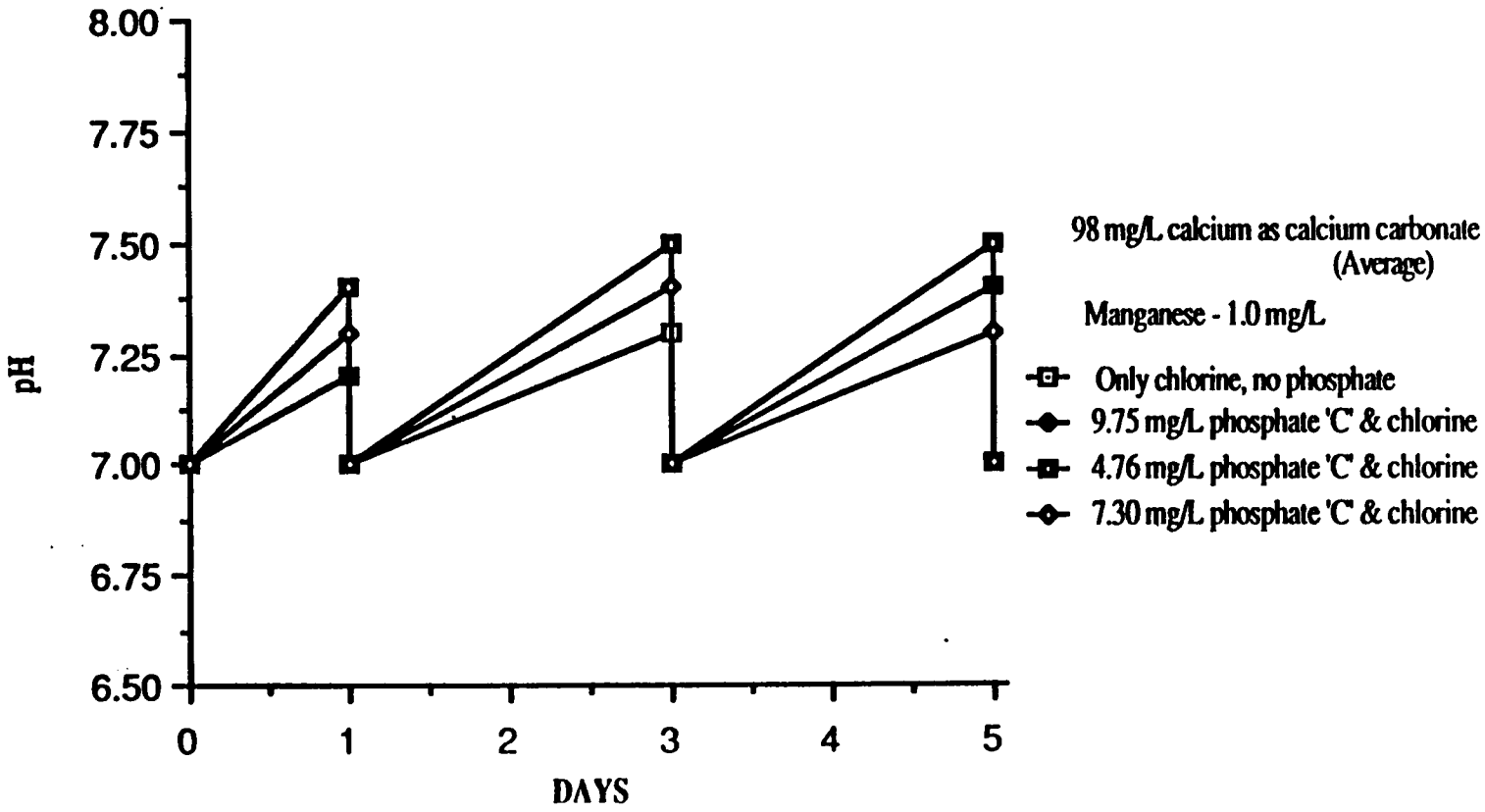

Figure A10. Manganese treatment with polyphosphate C and hypochlorite in the presence of calcium: pH

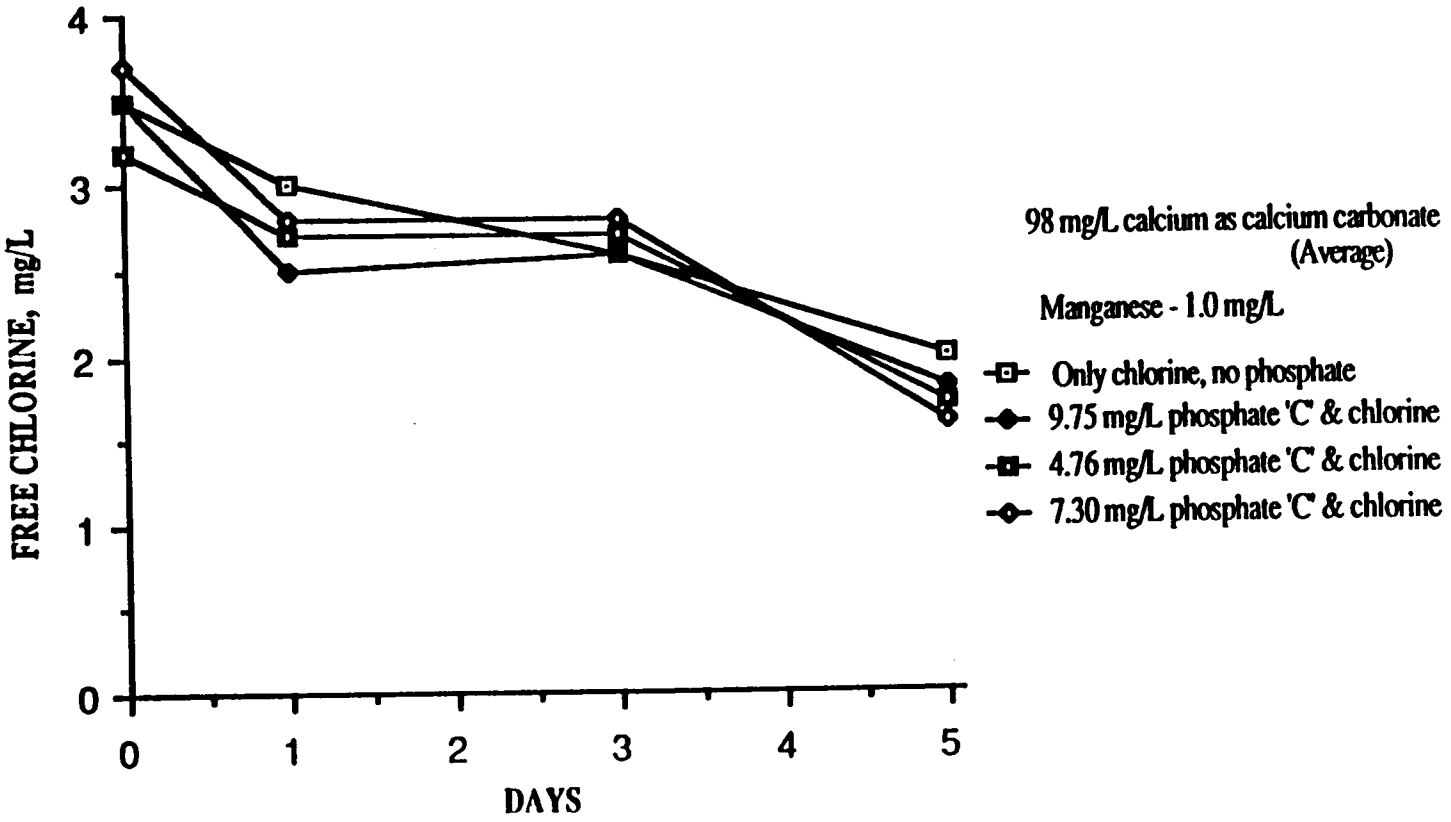

Figure A11. Manganese treatment with polyphosphate C and hypochlorite in the presence of calcium: free chlorine

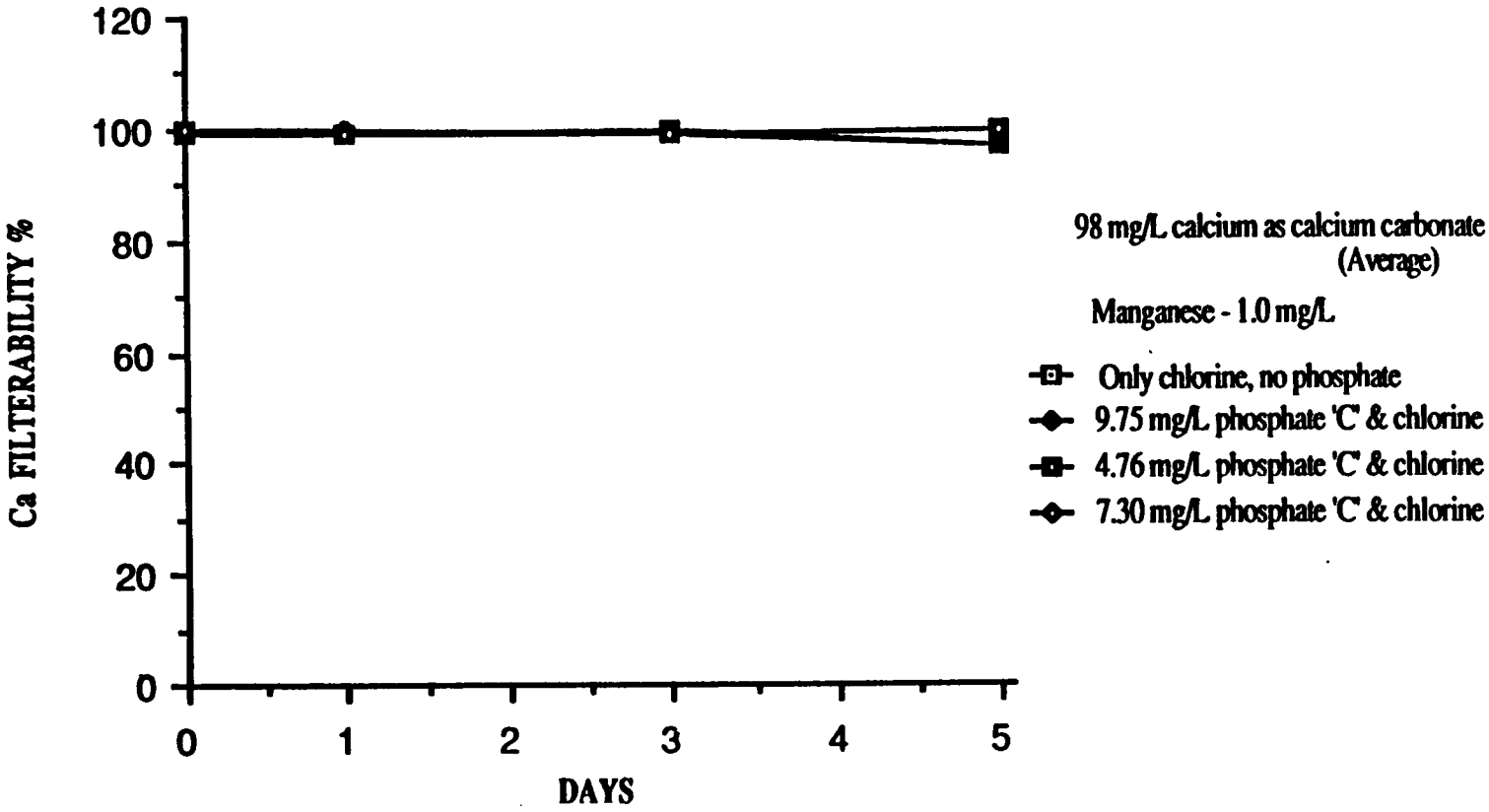

Figure A12. Manganese treatment with polyphosphate C and hypochlorite in the presence of calcium: calcium filterability

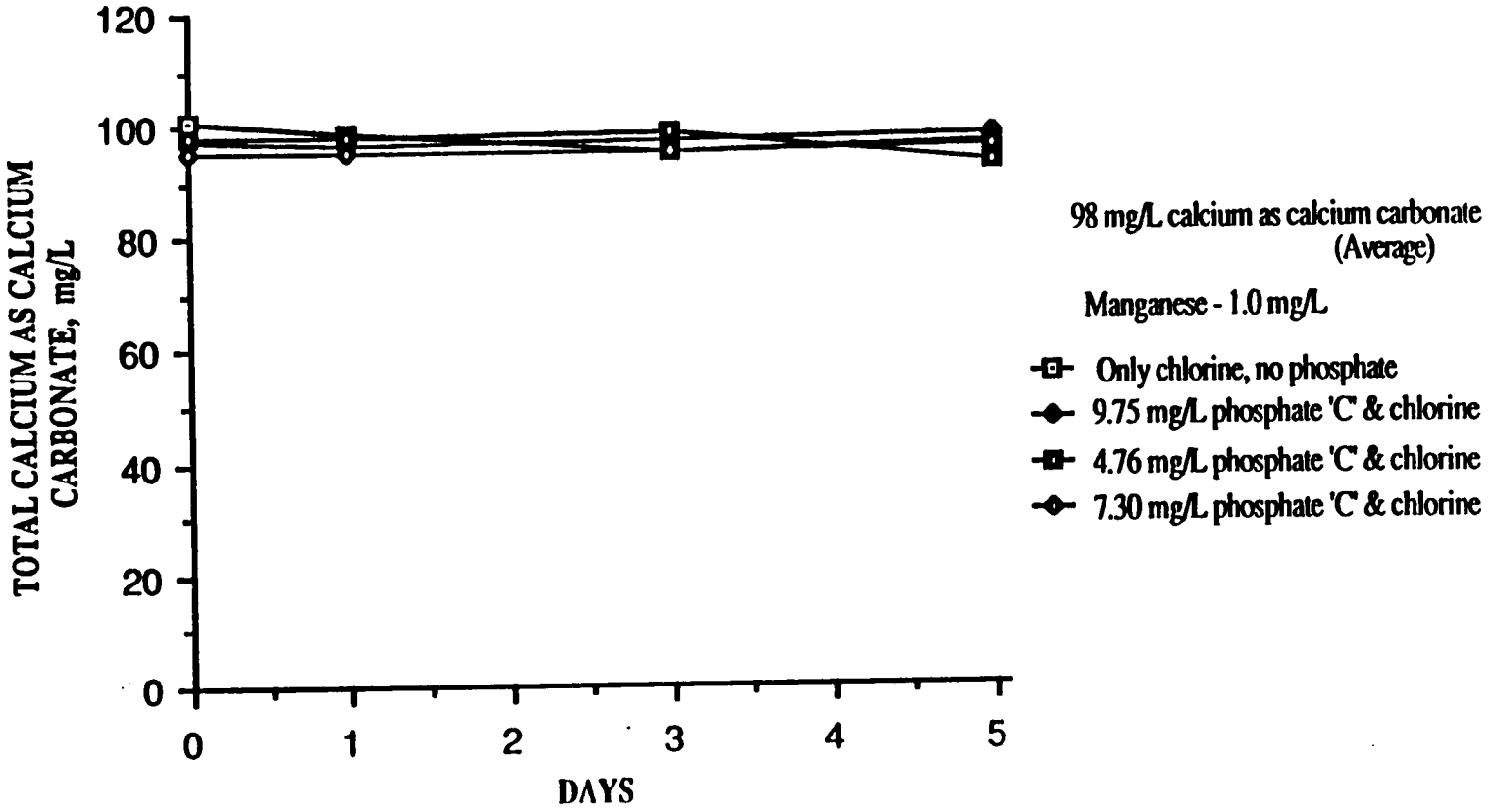

Figure A13. Manganese treatment with polyphosphate C and hypochlorite in the presence of calcium: total calcium

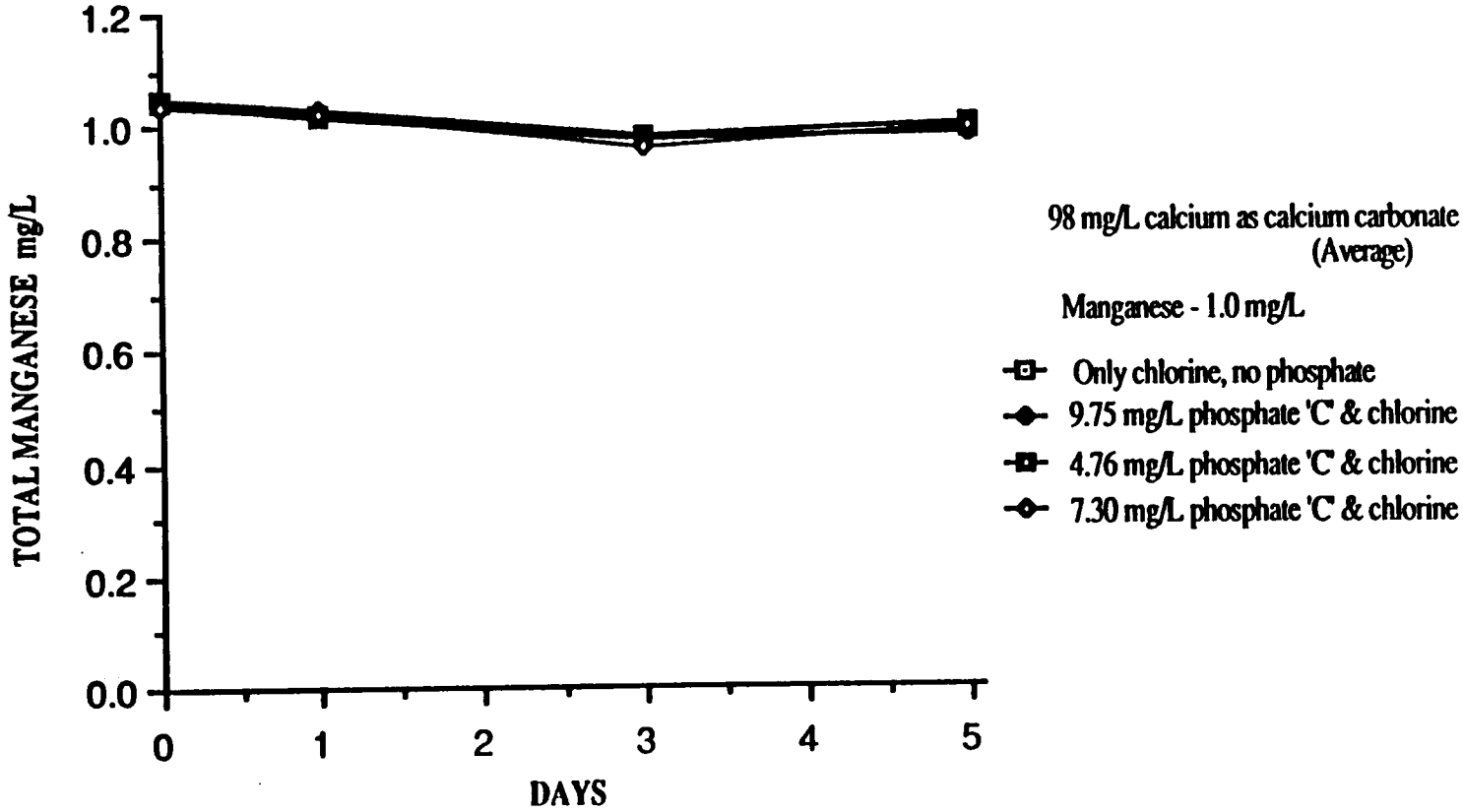

Figure A14. Manganese treatment with polyphosphate C and hypochlorite in the presence of calcium: total manganese

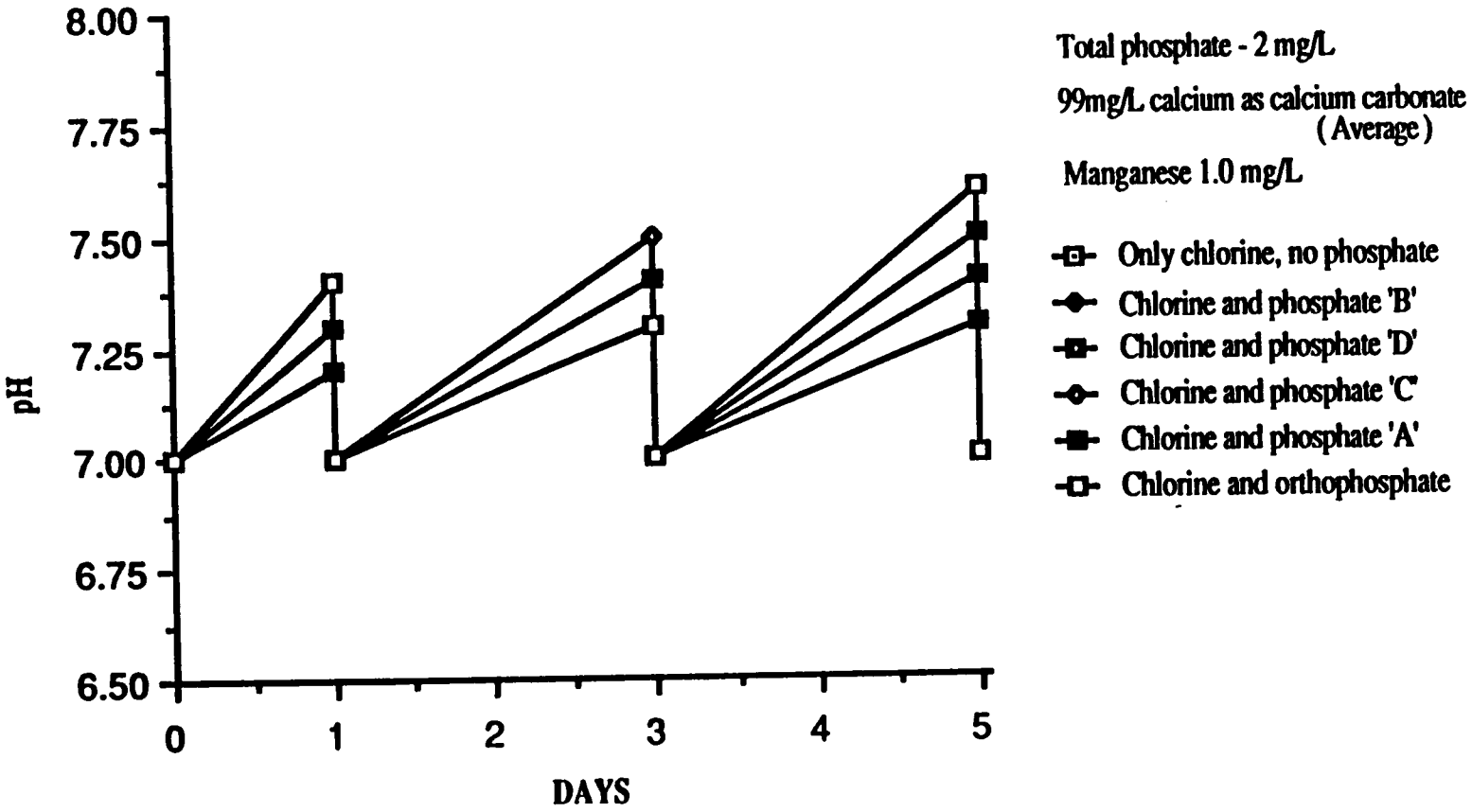

Figure A15. Comparison of the manganese sequestering ability of several polyphosphates and an orthophosphate with hypochlorite in the presence of calcium: pH

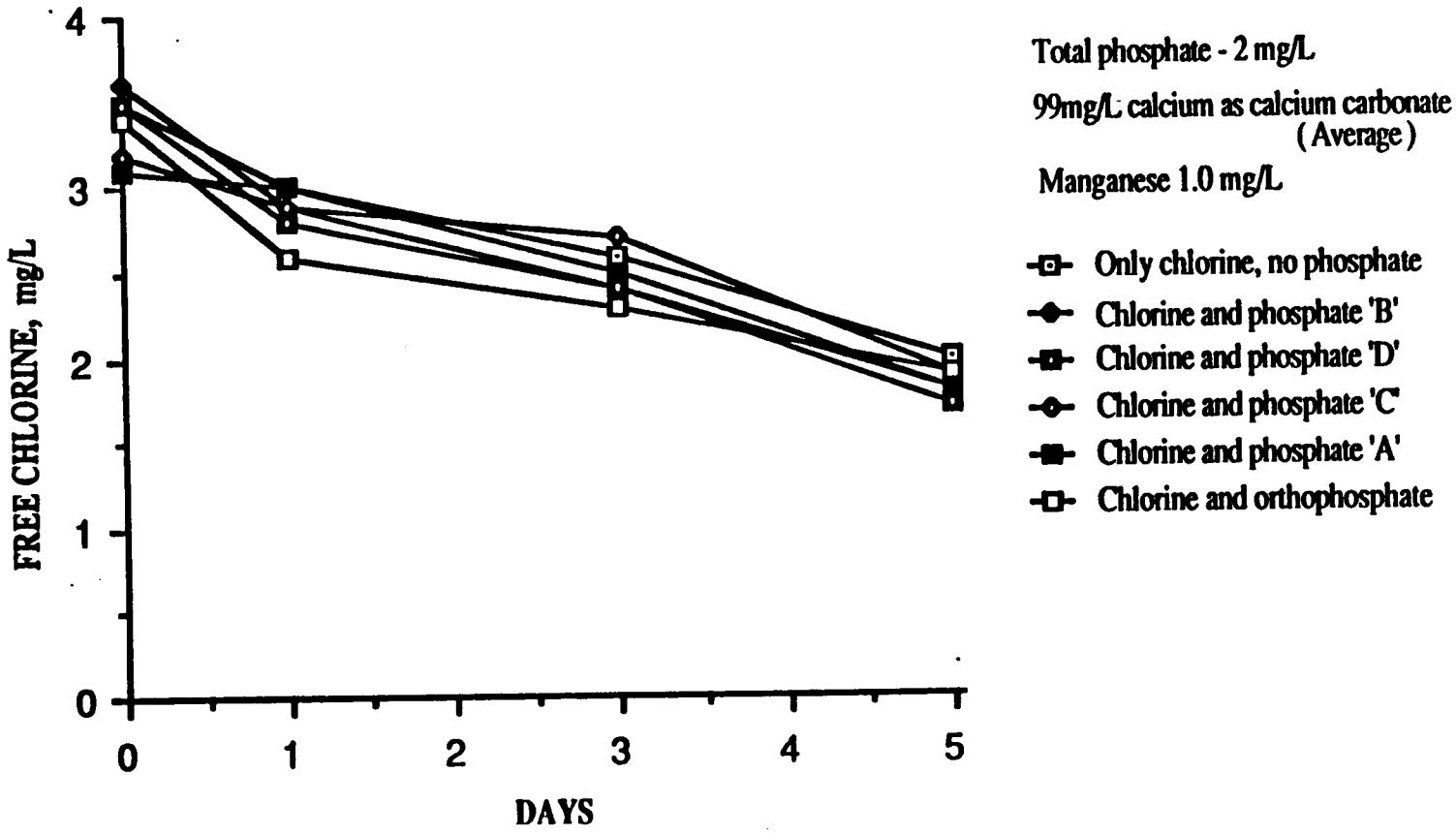

Figure A16. Comparison of the manganese sequestering ability of several polyphosphates and an orthophosphate with hypochlorite in the presence of calcium: free chlorine

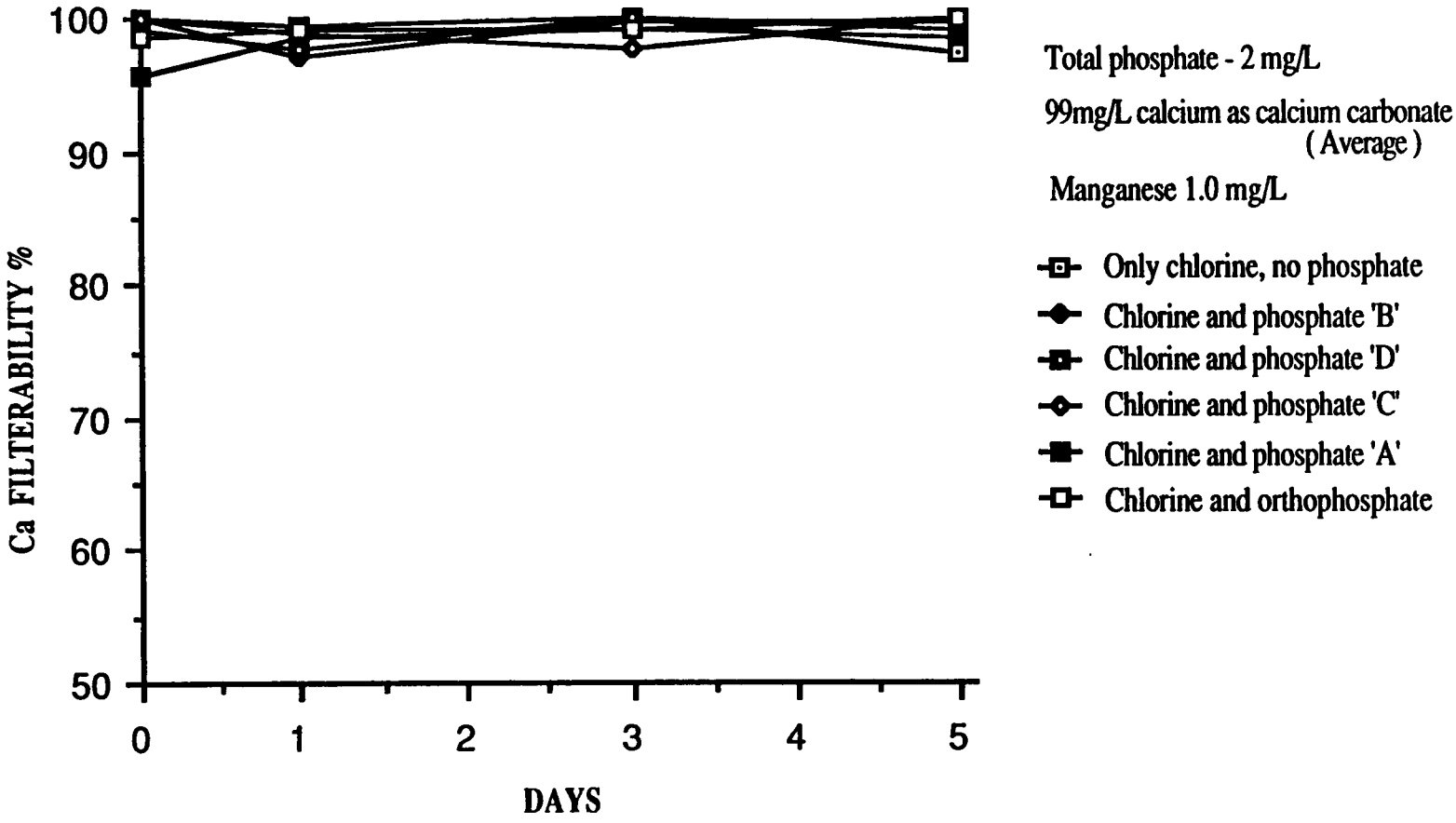

Figure A17. Comparison of the manganese sequestering ability of several polyphosphates and an orthophosphate with hypochlorite: calcium filterability

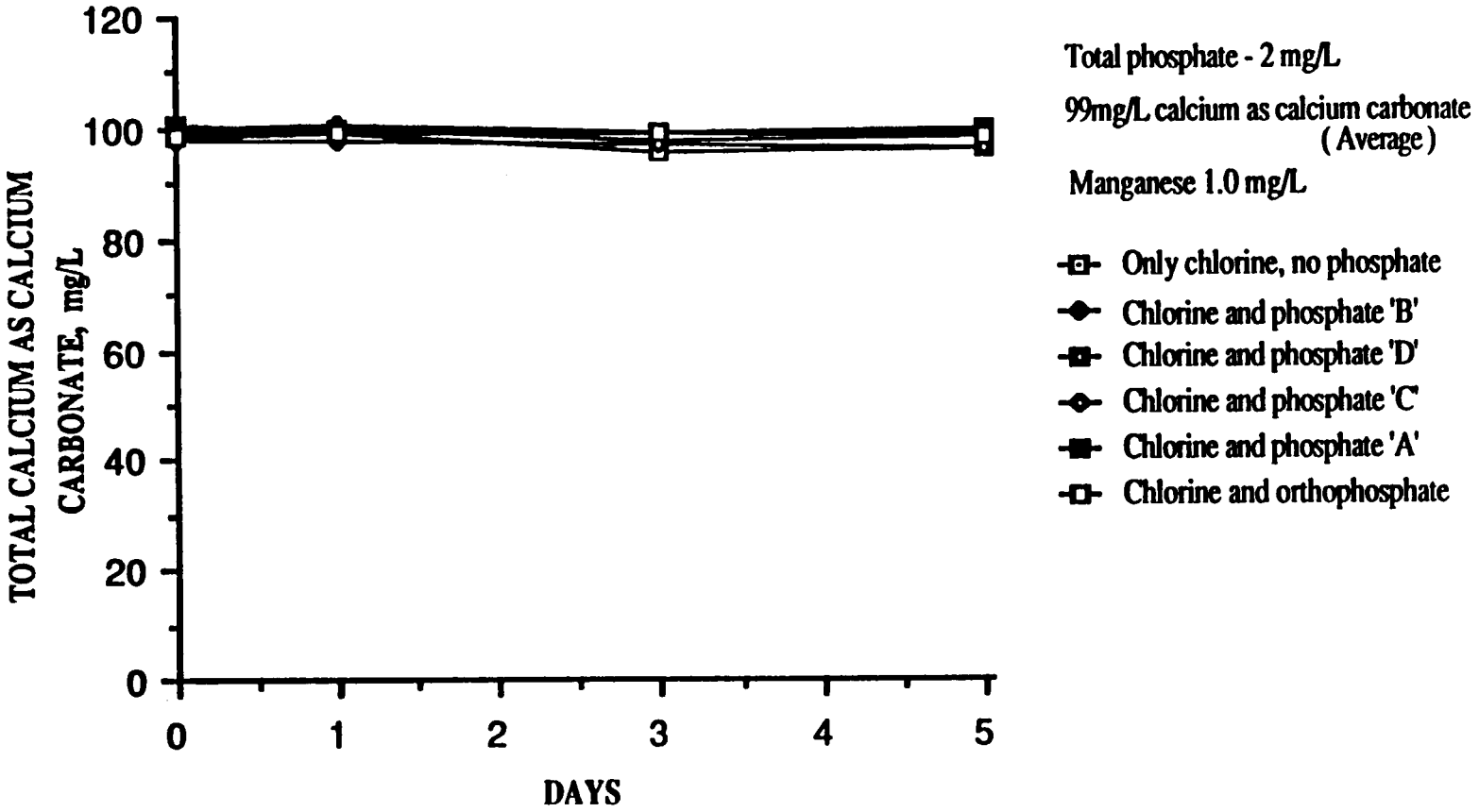

Figure A18. Comparison of the manganese sequestering ability of several polyphosphates and an orthophosphate with hypochlorite: total calcium

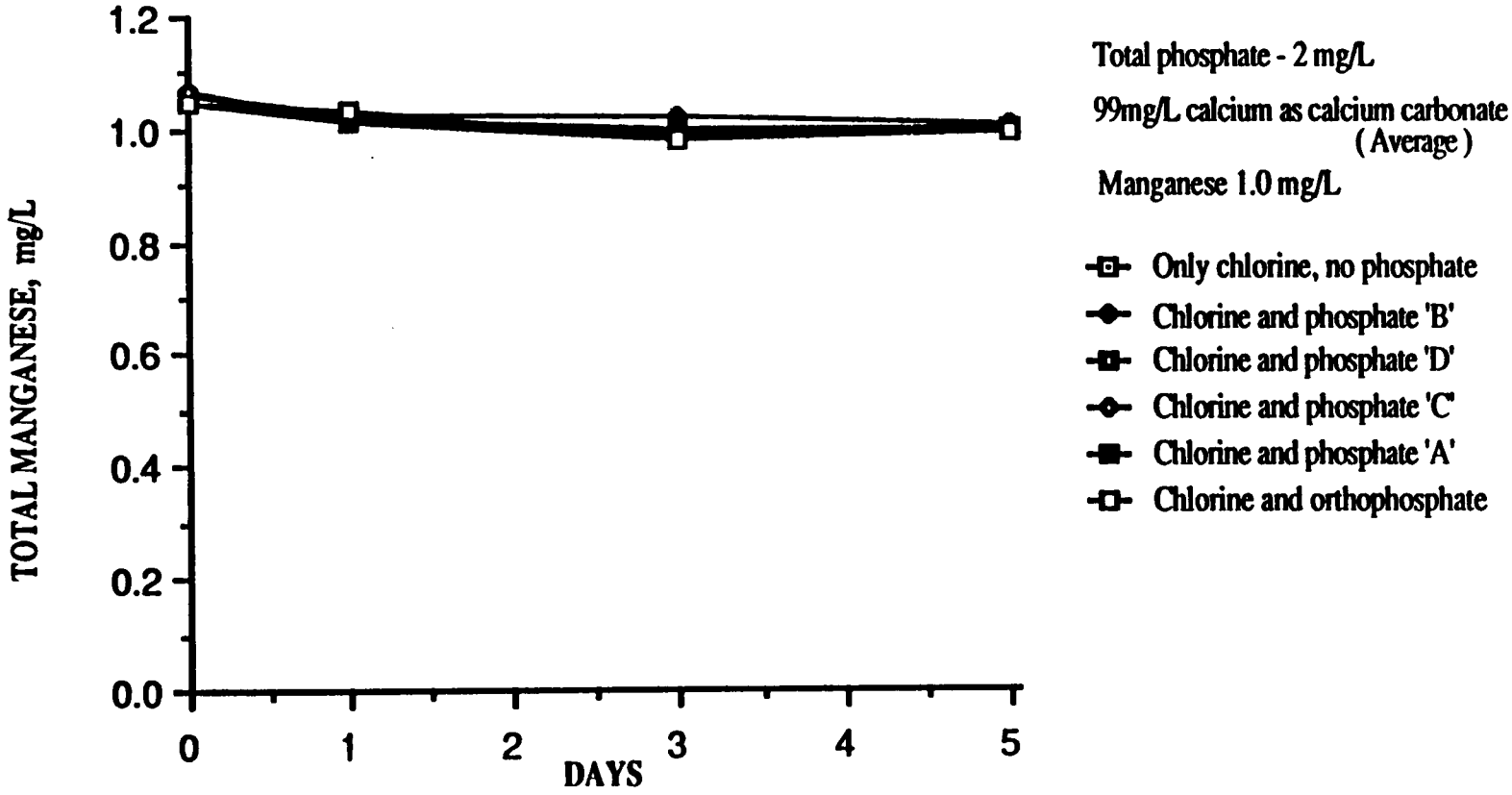

Figure A19. Comparison of the manganese sequestering ability of several polyphosphates and an orthophosphate with hypochlorite: total manganese

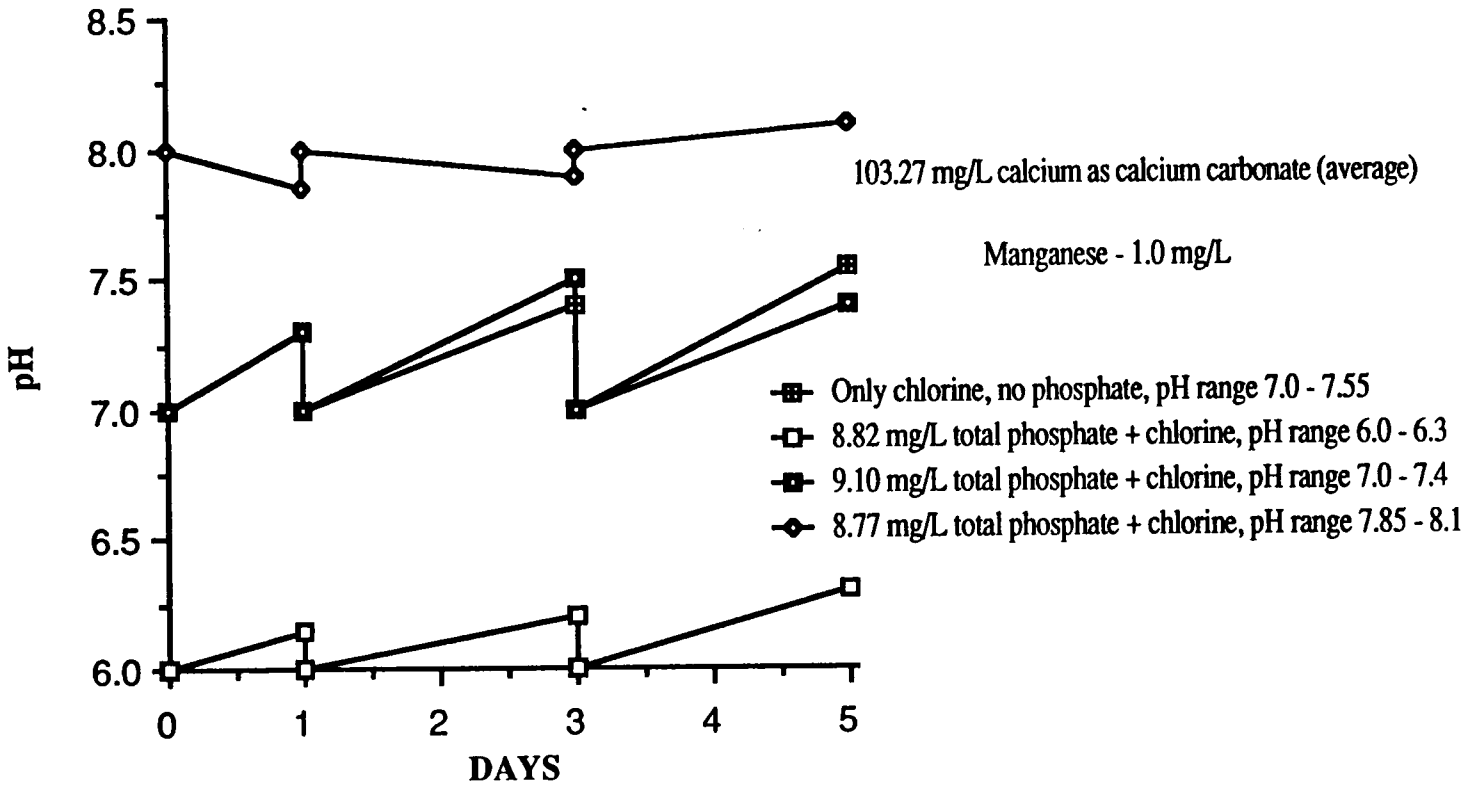

Figure A20. pH effects on manganese treatment by polyphosphate and hypochlorite: pH

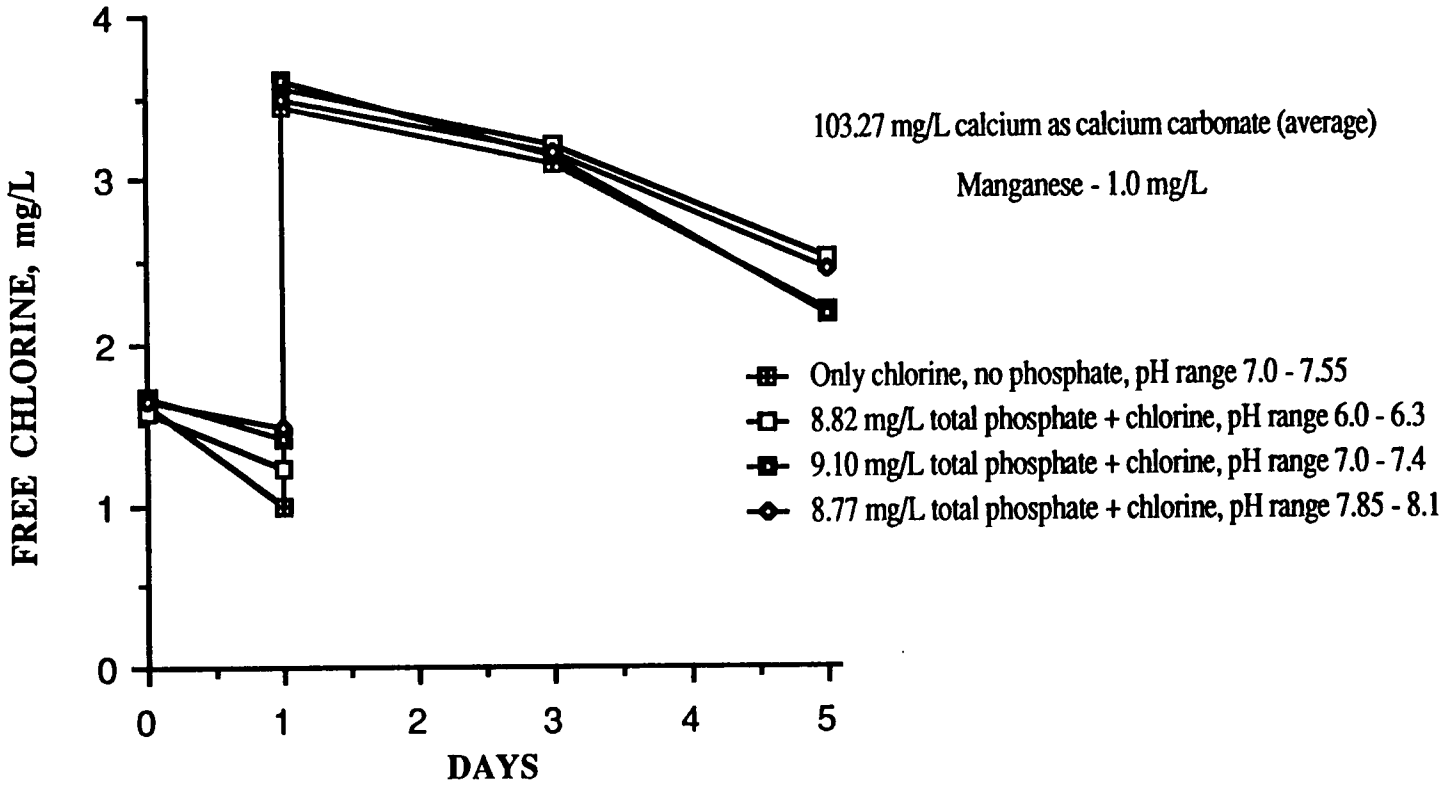

Figure A21. pH effects on manganese treatment by polyphosphate and hypochlorite: free chlorine

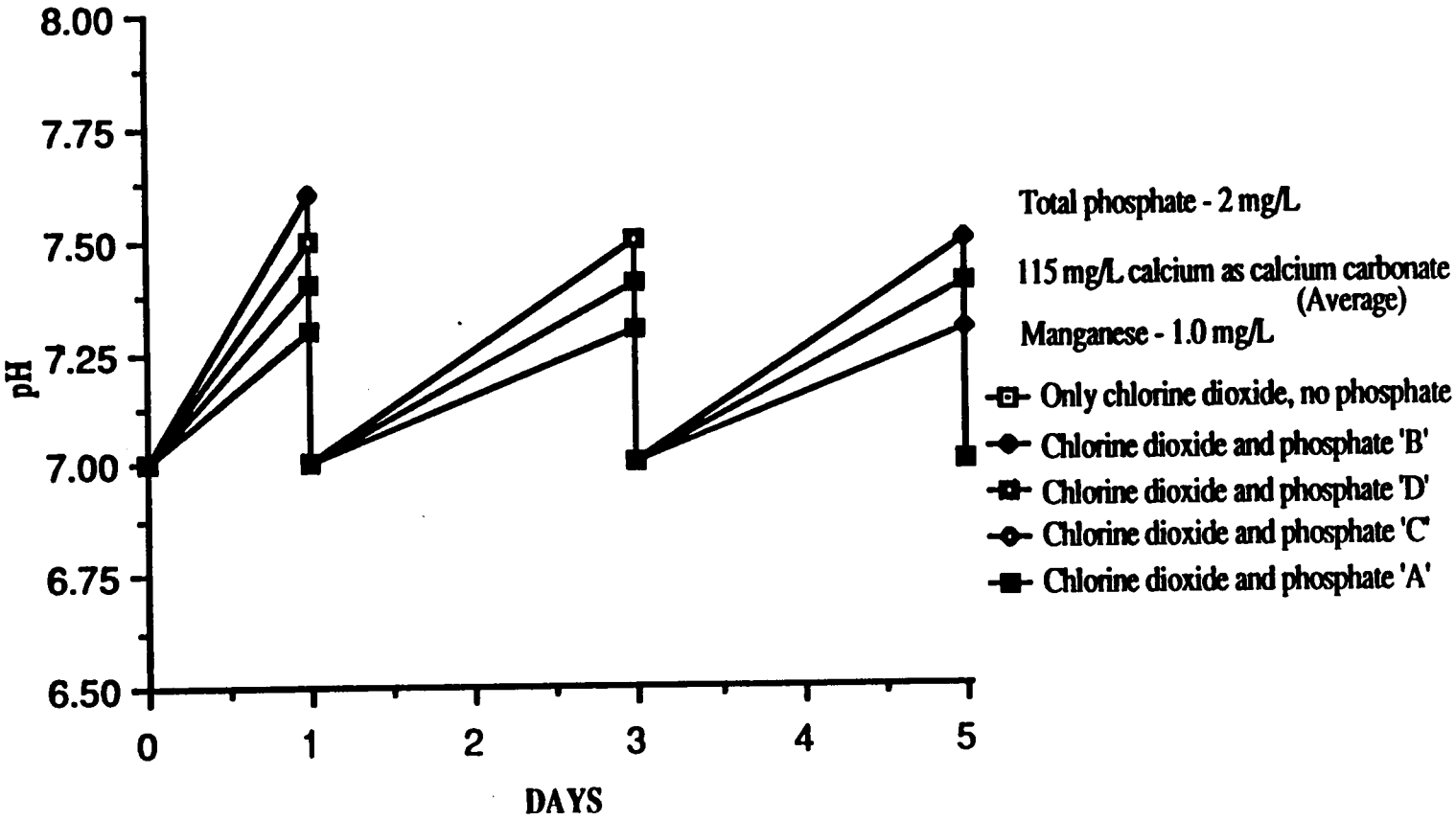

Figure A22. Comparison of the manganese sequestering ability of several polyphosphates and chlorine dioxide in the presence of calcium: pH

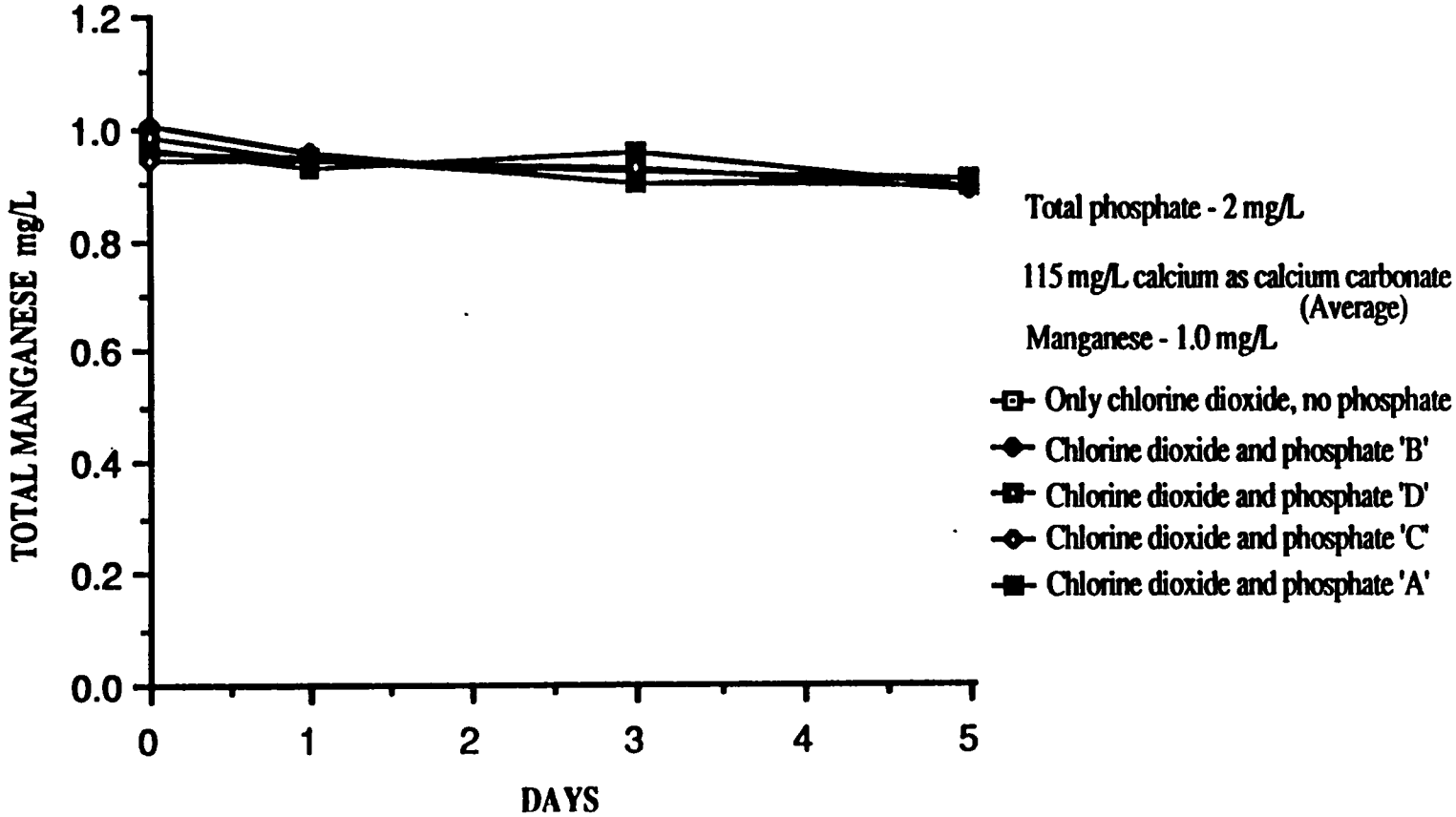

Figure A23. Comparison of the manganese sequestering ability of several polyphosphates and chlorine dioxide in the presence of calcium: total manganese

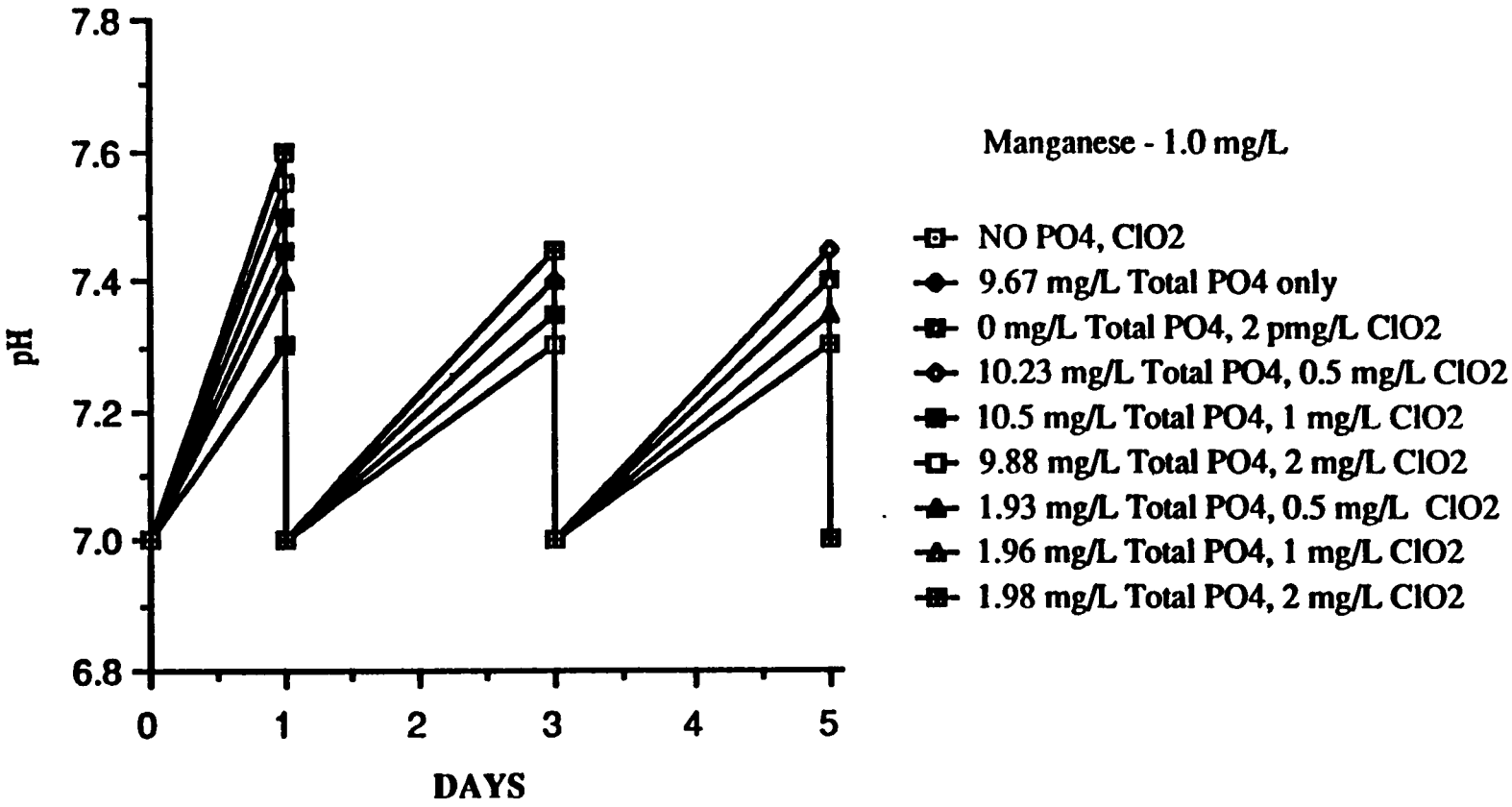

Figure A24. Manganese treatment with polyphosphate D and chlorine dioxide in the absence of calcium: pH

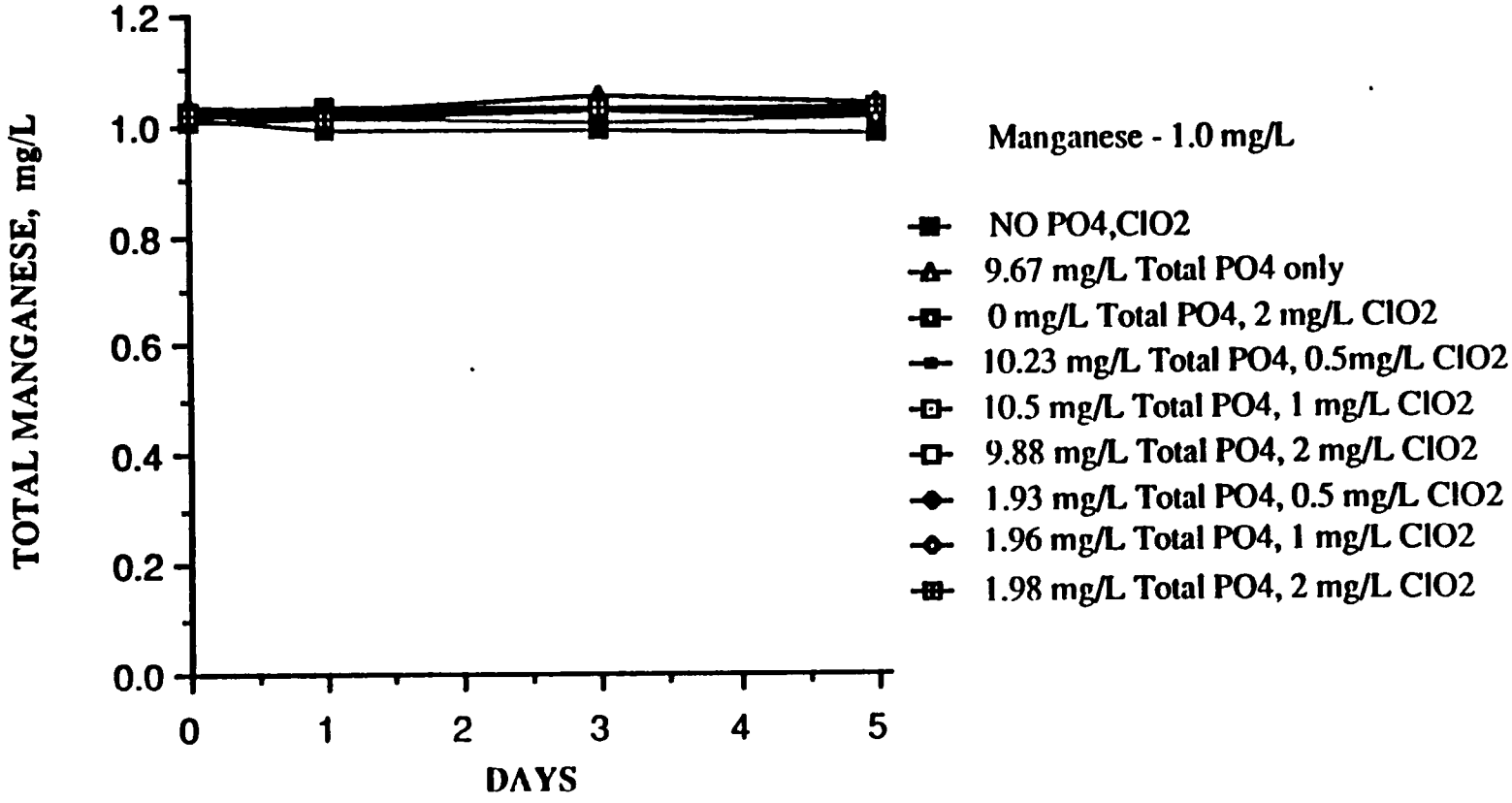

Figure A25. Manganese treatment with polyphosphate D and chlorine dioxide in the absence of calcium: total manganese

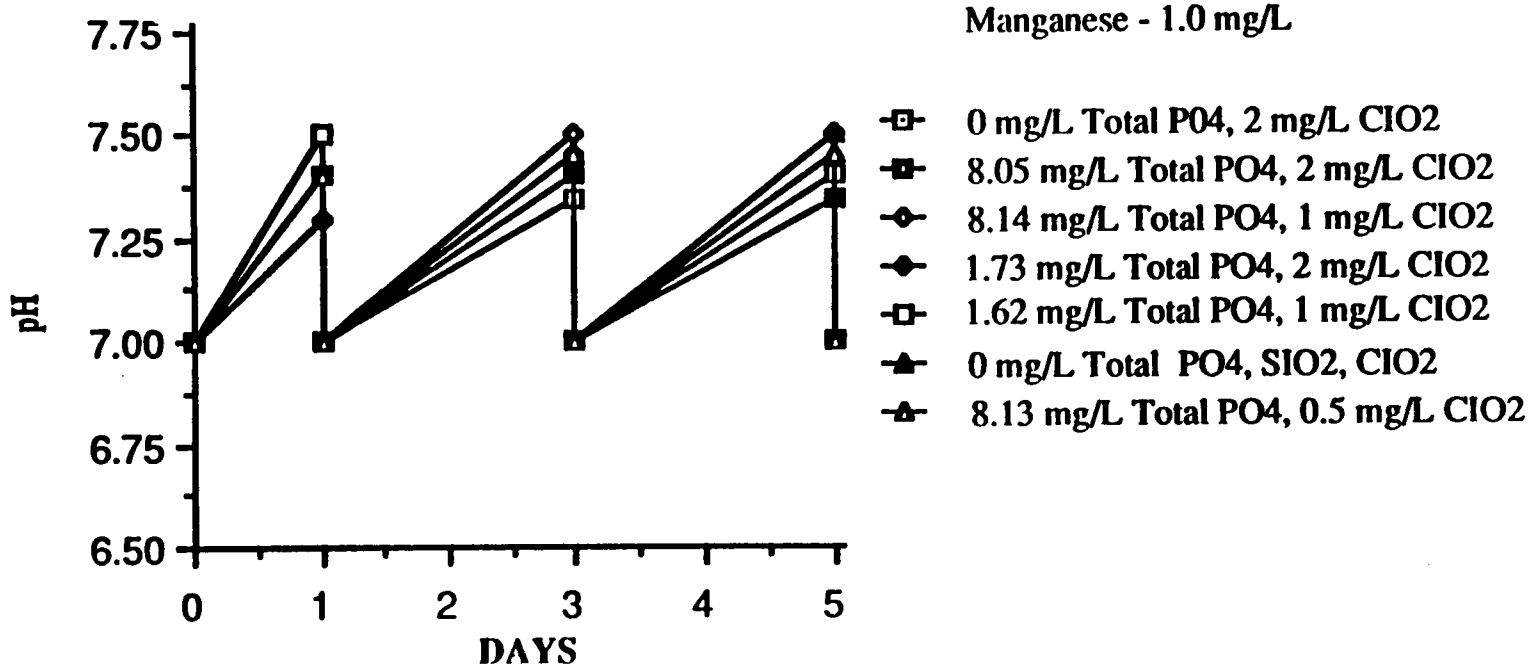

Figure A26. Manganese treatment with polyphosphate A and chlorine dioxide in the absence of calcium: pH

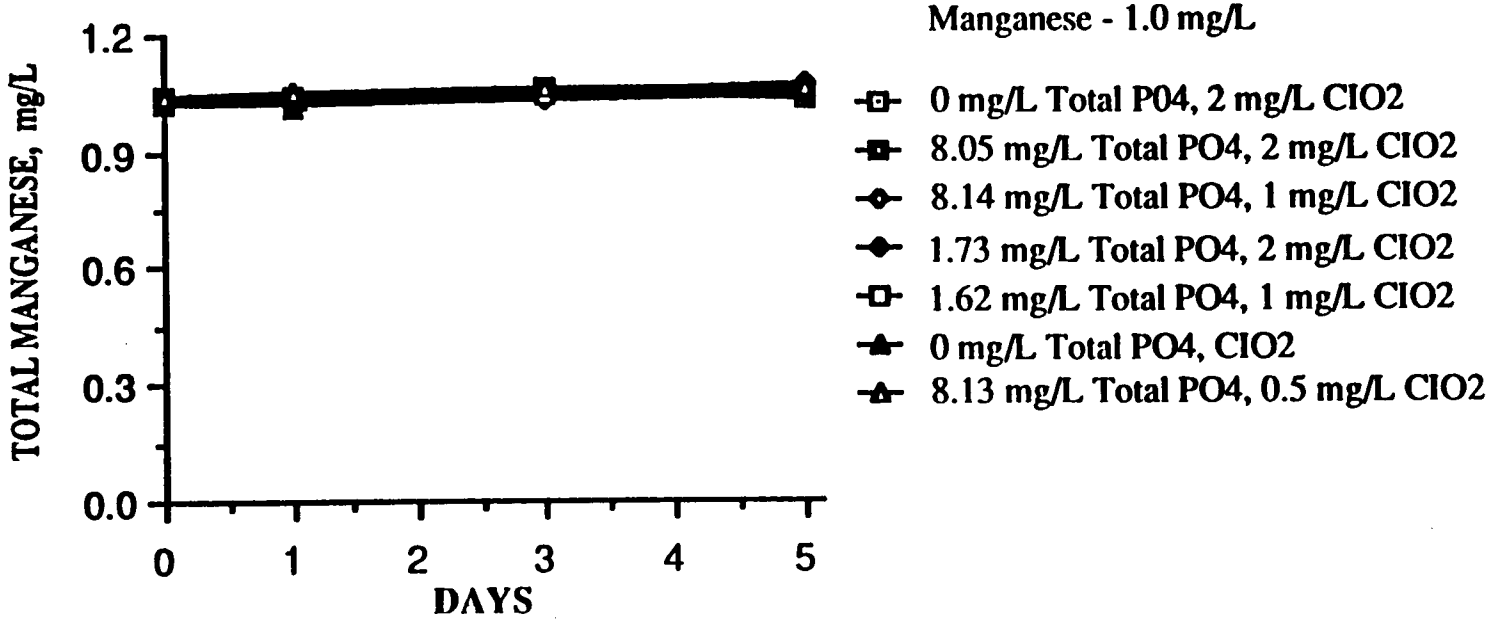

Figure A27. Manganese treatment with polyphosphate A and chlorine dioxide in the absence of calcium: total manganese

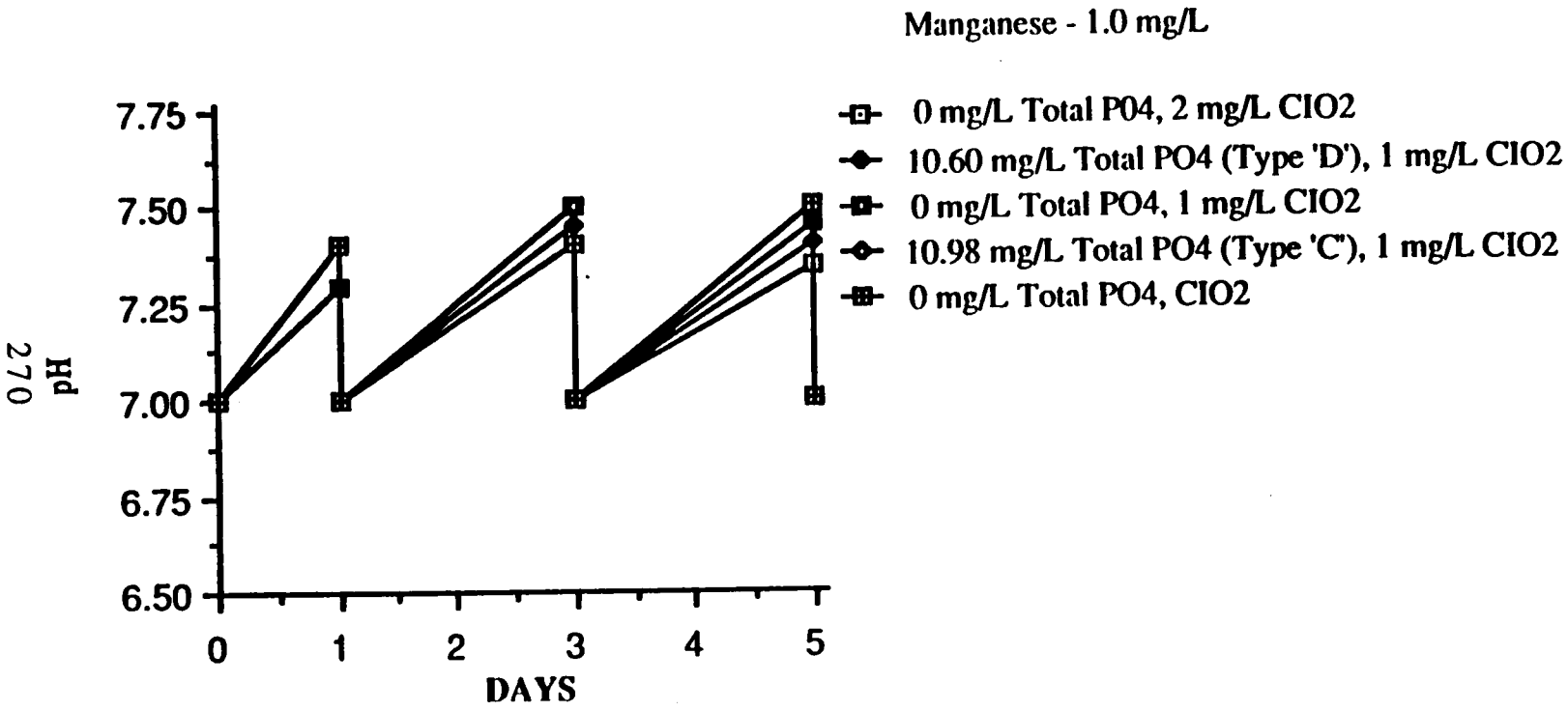

Figure A28. Manganese treatment with polyphosphate C and chlorine dioxide in the absence of calcium: pH

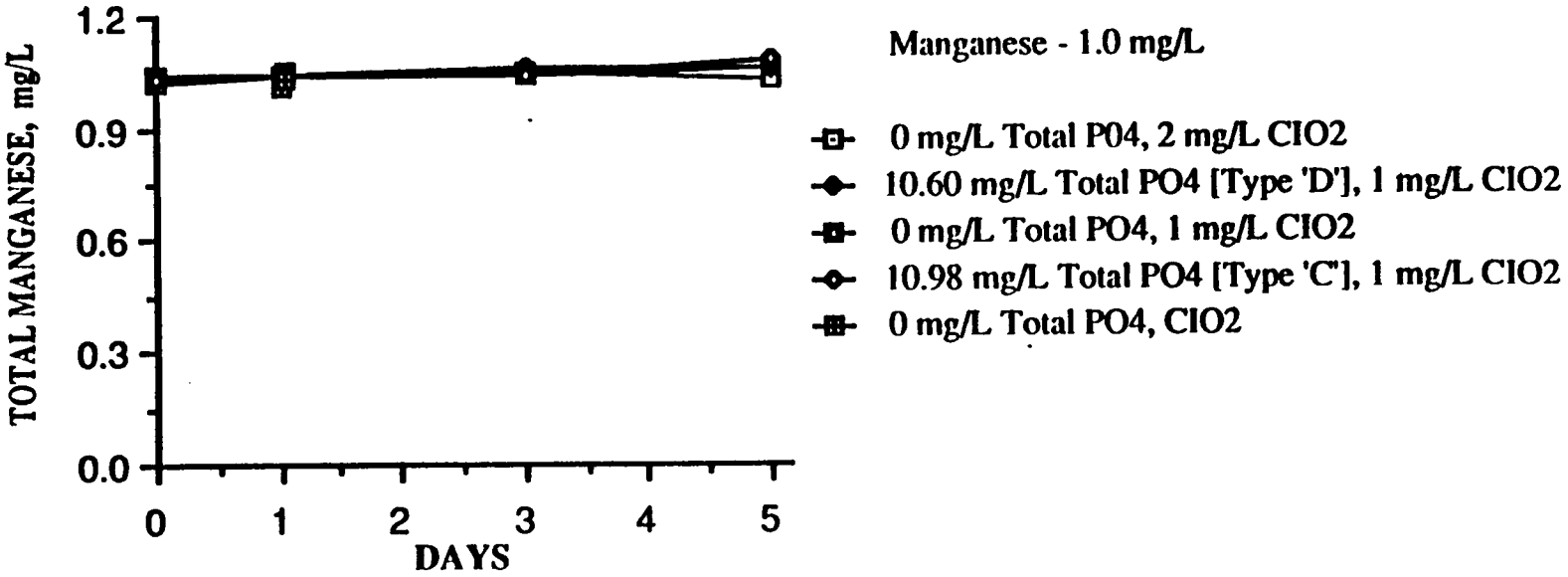

Figure A29. Manganese treatment with polyphosphate C and chlorine dioxide in the absence of calcium: total manganese

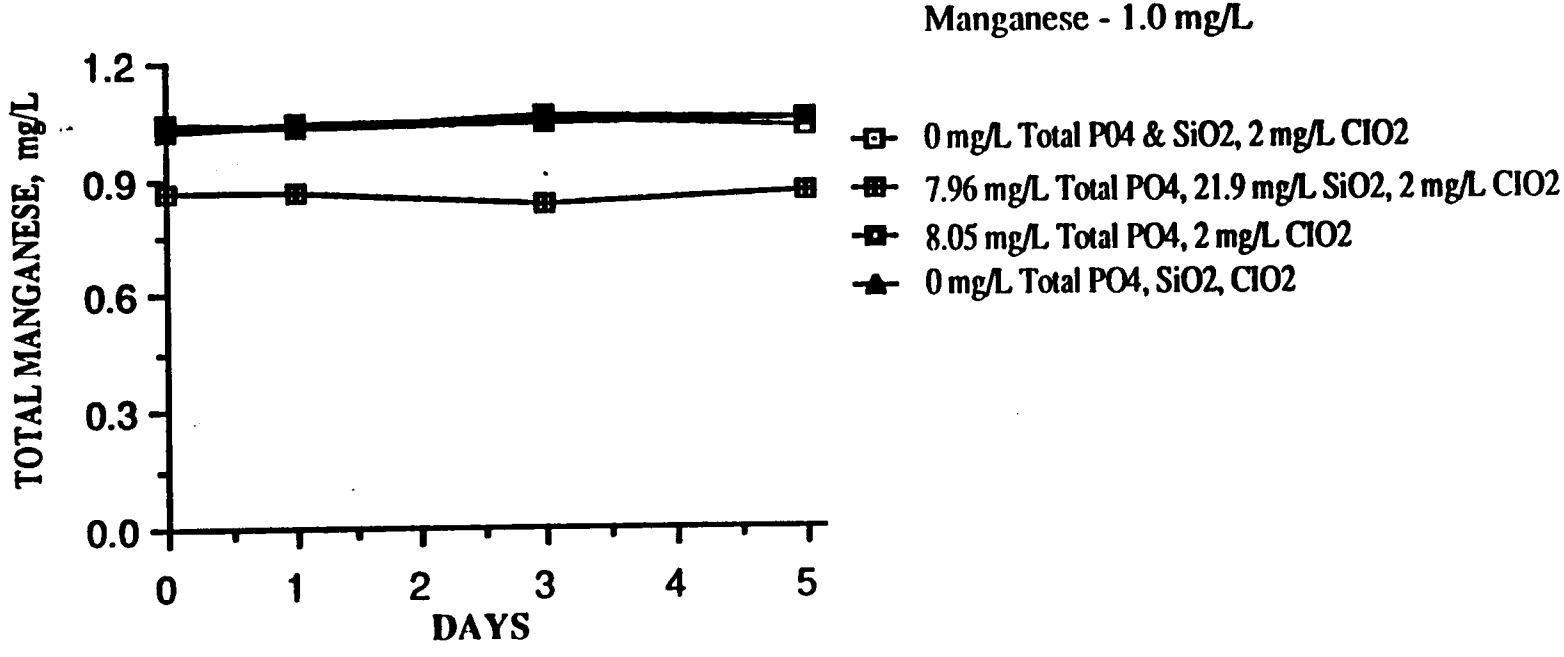

Figure A30. Manganese treatment by polyphosphate A and silicate in conjunction with chlorine dioxide in the absence of calcium: total manganese

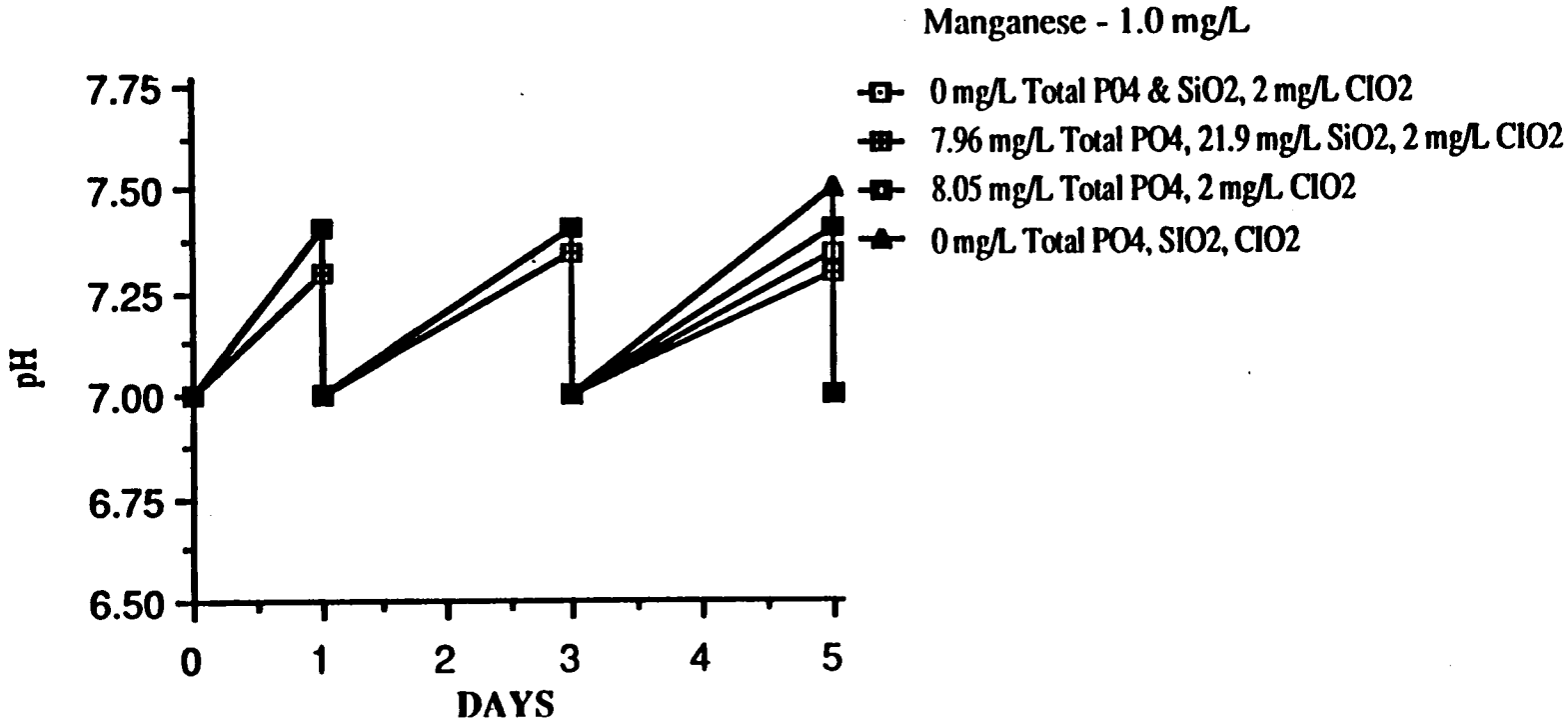

Figure A31. Manganese treatment by polyphosphate A and silicate in conjunction with chlorine dioxide in the absence of calcium: pH

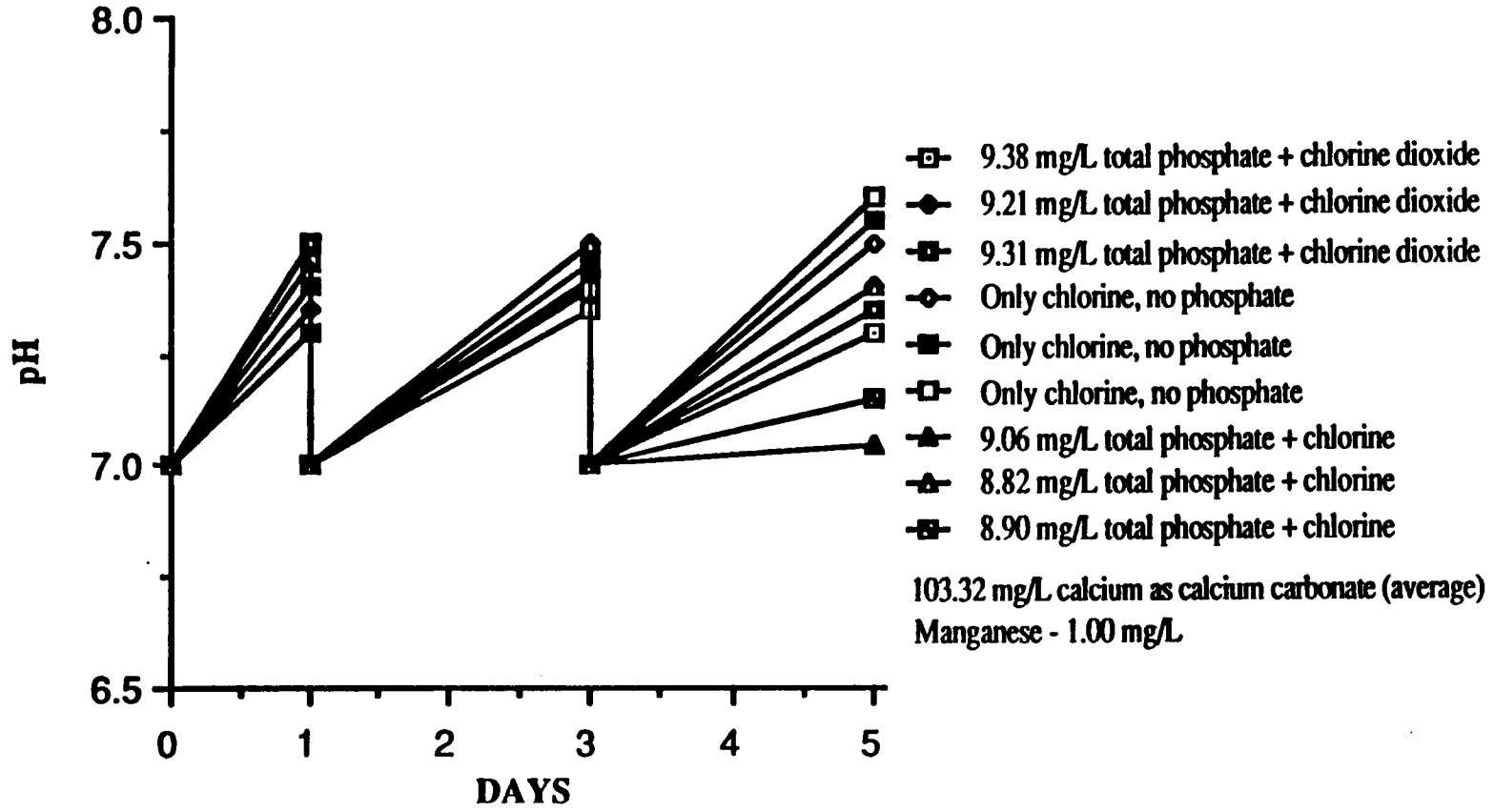

Figure A32. Quality control verification of polyphosphate/chlorine dioxide and polyphosphate/hypochlorite methods: pH

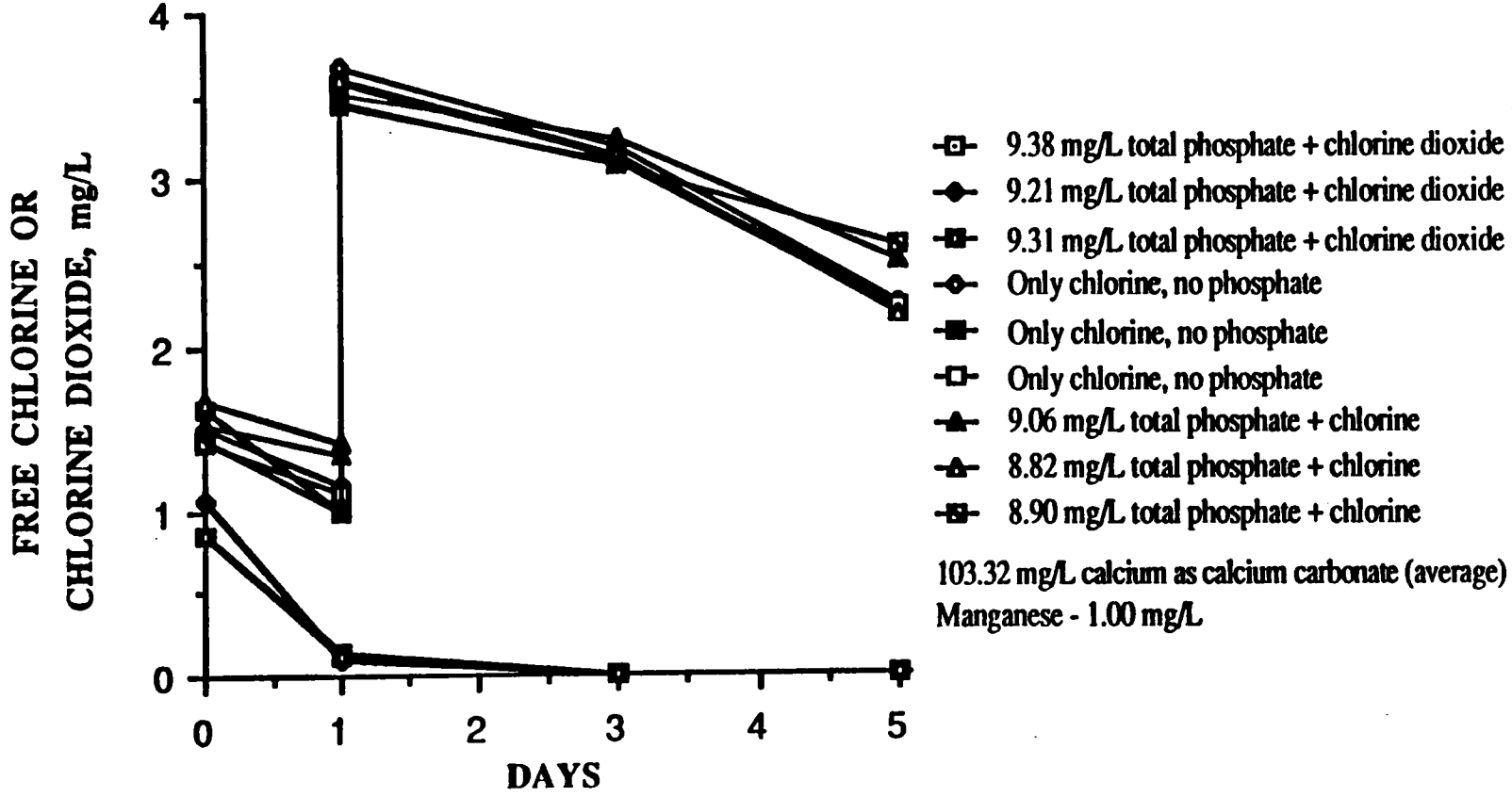

Figure A33. Quality control verification of polyphosphate/chlorine dioxide and polyphosphate/hypochlorite methods: free chlorine

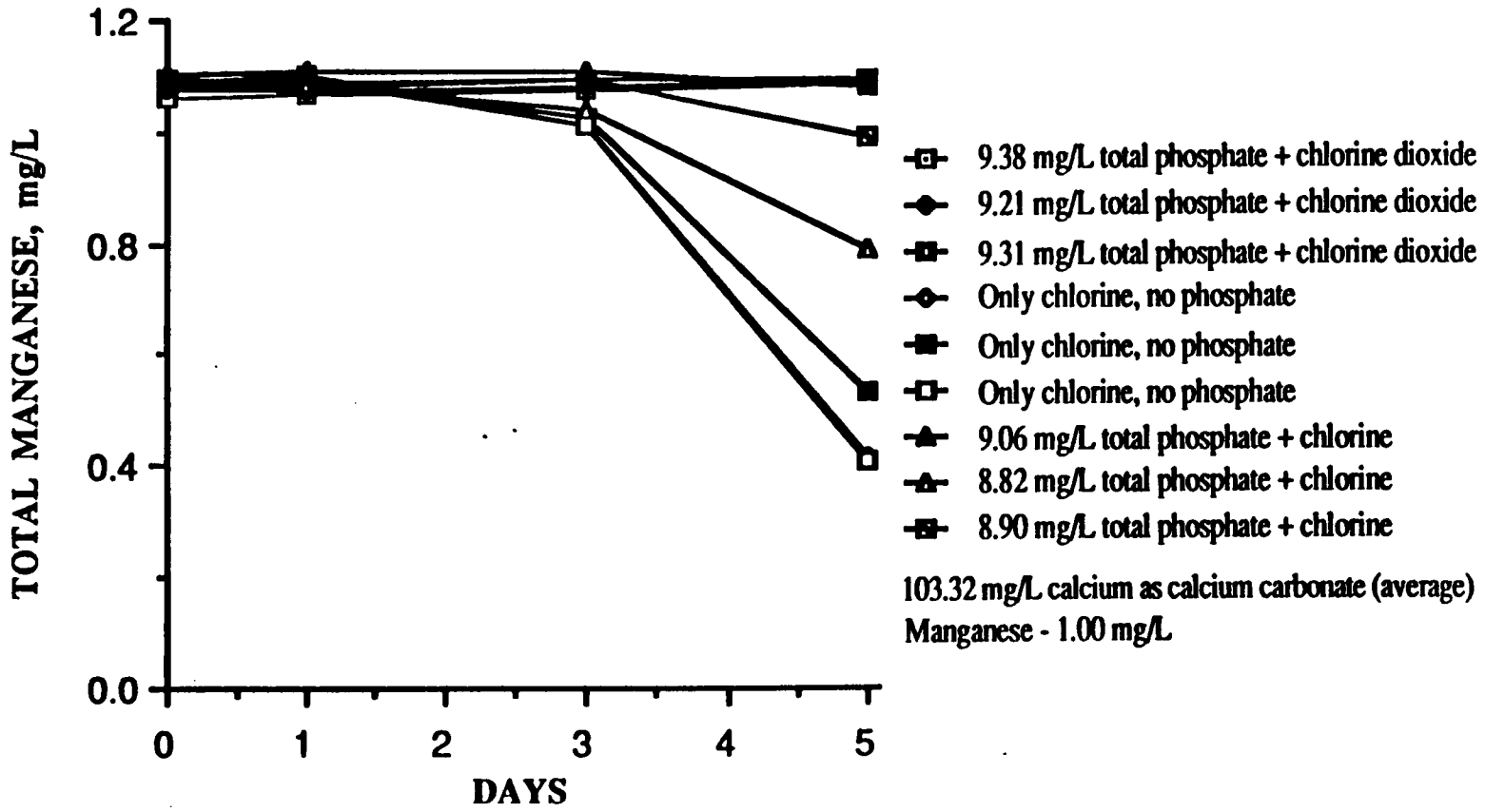

Figure A34. Quality control verification of polyphosphate/chlorine dioxide and polyphosphate/hypochlorite methods: total manganese

TABLE A 1. Lag time effects of silicate and chlorine dioxide on manganese treatment

Jar #	Pre-dosage				Post-dosage				Dosage		Day 0			
	pH	Turb[a]	D.O.[b]	%Fe^{2+}	pH	Turb	D.O.	%Fe^{2+}	SiO_2[c]	ClO_2[d]	Totm	%Film	Totf	%Filf
0/0	7.0	0.33	<0.1	n	7.0	0.33	<0.1	n	0	0	1.0	100	n	n
0c/0s	7.0	0.30	<0.1	n	7.1	1.00	<0.1	n	0	1.0	1.0	97	n	n
7/0	7.0	0.38	<0.1	n	7.3	0.50	<0.1	n	20.6	1.1	1.0	100	n	n
7/5[k]	7.0	0.29	<0.1	n	7.2	0.64	<0.1	n	21.2	1.1	1.0	100	n	n
7/10[l]	7.0	0.35	<0.1	n	7.2	0.75	<0.1	n	21.3	1.1	1.0	90	n	n
7/20[m]	7.0	0.31	<0.1	n	7.3	0.45	<0.1	n	21.0	1.0	1.0	95	n	n
7/20[i]	7.0	0.33	<0.1	n	7.2	0.47	<0.1	n	20.6	1.1	1.0	97	n	n
7/30[n]	7.0	0.30	<0.1	n	7.2	0.67	<0.1	n	21.3	1.0	1.0	90	n	n
7/30[j]	7.0	0.34	<0.1	n	7.2	0.65	<0.1	n	20.6	1.1	1.0	90	n	n
7/13	7.0	0.33	<0.1	92	7.3	0.36	<0.1	0	15.1	1.0	n	n	1.3	100

a Turbidity units in NTU
b Dissolved oxygen in mg/L
c Silicate dosage in mg/L as SiO2
d ClO2 concentration in mg/L
i, j Duplicates of 7/20 and 7/30
k Lag time 15 secs; l Lag time 30 secs
m Lag time 60 secs; n Lag time 120 secs
n Not present
Totf Total iron in mg/L
%Filf Percent iron filterability
Totm Total manganese in mg/L
%Film Percent manganese filterability

TABLE A 1. Continued

Jar #	Day 1						Day 3						Day 5					
	pH	Turb[a]	Totm	%Film	Totf	%Filf	pH	Turb[a]	Totm	%Film	Totf	%Filf	pH	Turb[a]	Totm	%Film	Totf	%Filf
0/0	7.1	0.45	1.0	90	n	n	7.0	0.52	1.0	100	n	n	7.2	0.45	1.0	90	n	n
0c/0s	7.2	0.95	1.0	97	n	n	6.8	1.0	1.0	90	n	n	7.0	1.0	1.0	90	n	n
7/0	7.0	0.55	1.0	80	n	n	7.3	0.95	1.0	10	n	n	7.3	0.98	1.0	0	n	n
7/5[k]	7.3	0.5	1.0	90	n	n	7.2	0.6	1.0	90	n	n	7.1	0.73	1.0	90	n	n
7/10[l]	7.2	0.65	1.0	90	n	n	6.8	0.81	1.0	90	n	n	7.3	0.82	1.0	90	n	n
7/20[m]	7.1	0.4	1.0	97	n	n	7.3	0.53	1.0	98	n	n	7.2	0.52	1.0	96	n	n
7/20[i]	7.0	0.35	1.0	95	n	n	7.1	0.55	1.0	100	n	n	7.3	0.54	1.0	94	n	n
7/30[n]	7.2	0.7	1.0	90	n	n	7.1	0.8	1.0	90	n	n	7.1	0.87	1.0	90	n	n
7/30[j]	7.3	0.85	1.0	90	n	n	na	na	na	na	n	n	7.2	0.86	1.0	90	n	n
7/13	7.3	0.46	n	n	1.26	100	7.2	0.58	n	n	1.29	100	7.1	0.45	n	n	1.28	100

k Color units
na - not available

TABLE A 1. Continued

Jar #	Day 7						Day 10						Day 19						
	pH	Turb[a]	Totm	%Film	Totf	%Filf	pH	Turb[a]	Totm	%Film	Totf	%Filf	pH	Turb[a]	Totm	%Film	Totf	%Filf	Color[k]
0/0	7.1	0.50	1.0	85	n	n	7.0	0.67	1.0	85	n	n	na	na	na	na	n	n	30
0c/0s	7.2	1.0	1.0	83	n	n	7.3	1.2	1.0	85	n	n	na	na	na	na	n	n	285
7/0	7.3	1.0	1.0	0	n	n	7.2	1.1	1.0	0	n	n	na	na	na	na	n	n	na
7/5[k]	7.2	0.87	1.0	85	n	n	6.9	1.0	1.0	90	n	n	na	na	na	na	n	n	245
7/10[l]	7.2	0.79	1.0	90	n	n	7.3	0.98	1.0	90	n	n	na	na	na	na	n	n	270
7/20[m]	7.3	0.6	1.0	90	n	n	6.9	0.78	1.0	95	n	n	na	na	na	na	n	n	255
7/20[i]	7.2	0.58	1.0	90	n	n	6.9	0.88	1.0	95	n	n	na	na	na	na	n	n	285
7/30[n]	7.1	0.9	1.0	85	n	n	7.0	0.9	1.0	90	n	n	na	na	na	na	n	n	30
7/30[j]	7.3	0.95	1.0	83	n	n	7.1	0.9	1.0	90	n	n	na	na	na	na	n	n	na
7/13	7.2	0.53	n	n	1.30	95	7.2	0.83	n	n	1.28	97	na	na	na	na	na	na	na

k Color units
na - not available

TABLE A 2. Study of manganese oxidation by hypochlorite in the presence and absence of polyphosphates

Jar #	Pre-dosage		Post-dosage		Dosage		Day 0		Day 1				Day 2				Day 3			
	pH	D.O.[a]	pH	D.O.[a]	Cl_2[b]	PO_4[c]	Ox.Mn[d]	Tot[e]	pH	Cl_2	Ox.Mn	Tot	pH	Cl_2	Ox.Mn	Tot	pH	Cl_2	Ox.Mn	Tot
0/0	7.0	<0.1	7.2	<0.1	8.8	0	0	0	7.5	8.5	0	0	7.6	8.4	0	0	7.3	8.0	0	0
0	7.0	<0.1	7.0	<0.1	0	0	0	1.07	7.6	0	0	1.06	7.5	0	0	1.04	7.4	0	0	1.04
6	7.0	<0.1	7.2	<0.1	3.2	0	0	1.03	7.4	3.1	0	1.03	7.6	2.9	0.05	1.02	7.5	2.6	0.16	1.01
8	7.0	<0.1	7.2	<0.1	4.6	0	0	1.04	7.6	4.5	0	1.05	7.4	4.3	0.1	1.02	7.4	4.1	0.19	1.01
10	7.0	<0.1	7.3	<0.1	5.5	0	0	1.02	7.6	5.4	0.01	1.03	7.7	5.2	0.1	1.02	7.5	5.0	0.27	1.01
12	7.0	<0.1	7.2	<0.1	7.6	0	0	1.01	7.4	7.4	0.03	1.01	7.5	7.0	0.14	1.01	7.3	6.7	0.29	1.00
14	7.2	<0.1	7.3	<0.1	9	0	0	1.02	7.6	8.6	0.58	1.03	7.4	8.3	0.89	1.02	7.6	8.2	0.94	1.01
6P	7.2	<0.1	7.3	<0.1	3.3	9.7	0	1.04	7.5	3.3	0	1.03	7.5	3.2	0	1.03	7.5	3.0	0	1.02
8P	7.1	<0.1	7.2	<0.1	4.4	9.8	0	1.02	7.6	4.3	0	1.02	7.6	4.2	0	1.02	7.3	4.0	0	1.02
10P	7.2	<0.1	7.3	<0.1	5.6	9.5	0	1.03	7.6	5.5	0	1.03	7.6	5.4	0	1.01	7.6	5.2	0	1.00
12P	7.3	<0.1	7.3	<0.1	6.4	9.8	0	1.03	7.4	6.2	0	1.02	7.4	7.1	0	1.01	7.5	6.0	0	1.00
14P	7.2	<0.1	7.3	<0.1	7.5	9.8	0	1.02	7.5	7.3	0	1.01	7.5	7.1	0	1.01	7.4	6.9	0	1.01

a Dissolved oxygen in mg/L
b Free chlorine in mg/L
c Polyphosphate dosage in mg/L as total PO_4
d Oxidized manganese concentration as free chlorine equivalent in mg/L
e Total manganese in mg/L

TABLE A2. Continued

Jar #	Day 4				Day 5				Day 6				Day 7				Day 8			
	pH	Cl_2[b]	Ox.Mn[d]	Tot[e]	pH	Cl_2	Ox.Mn	Tot	pH	Cl_2	Ox.Mn	Tot	pH	Cl_2	Ox.Mn	Tot	pH	Cl_2	Ox.Mn	Tot
0/0	7.3	7.6	0	0	7.5	7.0	0	0	7.4	6.8	0	0	7.3	6.4	0	0	7.3	6.0	0	0
0	7.4	0	0	1.03	7.4	0	0	1.02	7.3	0	0	1.03	7.4	0	0	1.02	7.2	0	0	1.01
6	7.5	2.5	0.18	1.00	7.6	1.9	0.26	0.99	7.5	1.8	0.25	0.99	7.4	1.7	0.25	0.98	7.5	1.6	0.28	0.96
8	7.4	3.9	0.21	1.00	7.7	3.2	0.30	0.99	7.5	3.2	0.35	0.99	7.5	3.1	0.45	0.94	7.4	3.0	0.49	0.90
10	7.6	4.8	0.39	1.01	7.5	4.4	0.52	0.98	7.6	4.3	0.60	0.99	7.3	4.2	0.70	0.94	7.3	4.2	0.74	0.84
12	7.5	6.5	0.40	1.00	7.3	6.0	0.55	0.98	7.3	5.9	0.60	0.90	7.5	5.8	0.73	0.85	7.4	5.4	0.72	0.80
14	7.5	8.0	0.95	0.94	7.4	6.6	0.95	0.91	7.2	6.5	0.95	0.88	7.6	6.4	0.96	0.84	7.4	6.2	0.98	0.79
6P	7.4	2.9	0	1.01	7.3	2.4	0	1.00	7.4	2.4	0	0.98	7.4	2.3	0	0.98	2.1	0	0	0.97
8P	7.5	3.8	0	1.01	7.4	3.5	0	1.00	7.3	3.4	0	0.99	7.3	3.3	0	0.99	7.5	3.1	0	0.98
10P	7.6	5.0	0	1.01	7.2	4.8	0	0.99	7.4	4.7	0	0.99	7.4	4.6	0	0.99	7.4	4.0	0	0.98
12P	7.4	5.8	0	1.00	7.3	5.5	0	1.00	7.3	5.4	0	0.99	7.5	5.3	0	0.98	7.5	5.1	0	0.97
14P	7.5	6.7	0	1.01	7.4	6.4	0.03	0.98	7.5	6.3	0	0.98	7.3	6.3	0	0.97	7.4	5.8	0	0.96

TABLE A2. Continued

Jar #	Day 9				Day 10				Day 12			
	pH	Cl_2[b]	Ox.Mn[d]	Tot[e]	pH	Cl_2	Ox.Mn	Tot	Tot	%Fil[f]	%Fil[g]	%Fil[h]
0/0	7.3	5.8	0	0	7.4	5.0	0	0	na	na	na	na
0	7.4	0	0	1.01	7.3	0	0	1.02	1.01	100	99	97
6	7.3	1.6	0.30	0.90	7.6	1.5	0.35	0.85	na	na	na	na
8	7.5	3.0	0.55	0.85	7.5	2.0	0.65	0.79	na	na	na	na
10	7.2	4.2	0.80	0.79	7.4	4.2	0.89	0.72	0.71	5	4	0.1
12	7.4	5.3	0.78	0.81	7.6	4.7	0.90	0.81	na	na	na	na
14	7.3	5.6	1.00	0.88	7.5	5.3	1.00	0.78	na	na	na	na
6P	7.4	2.1	0	0.97	7.4	2.1	0	0.97	na	na	na	na
8P	7.4	3.0	0	0.99	7.5	1.8	0	0.98	na	na	na	na
10P	7.5	3.9	0	0.97	7.4	3.5	0	0.97	0.98	100	98	99
12P	7.4	4.3	0	0.98	7.4	4.0	0	0.99	na	na	na	na
14P	7.6	4.9	0	0.97	7.6	4.4	0	0.96	na	na	na	na

f Percent filterability (0.45 micron filter)
g Percent filterability (0.1 micron filter)
h Percent filterability (200K ultrafilter)
na - Not available

TABLE A 3. Manganese treatment with polyphosphate D and hypochlorite in the presence and absence of calcium

Jar #	Pre-dosage			Post-dosage			Dosage		Day 0				
	pH	Turb[a]	D.O.[b]	pH	Turb	D.O.	PO_4[c]	Cl_2[d]	Tot[e]	%Fil[f]	Ca[g]	%Fil[h]	Color[i]
0/0	7.0	0.19	<0.1	7.1	0.22	<0.1	0	2.8	1.02	87	n	n	0
7/0	7.0	0.18	<0.1	7.1	0.18	<0.1	9.8	2.7	1.04	100	n	n	0
7/5	7.0	0.20	<0.1	7.1	0.22	<0.1	7.4	2.3	1.03	97	n	n	0
7/10	7.0	0.18	<0.1	7.0	0.19	<0.1	5.0	2.7	1.03	92	n	n	0
7/20	7.0	0.20	<0.1	7.1	0.21	<0.1	2.4	2.8	1.02	91	n	n	0
7/30	7.0	0.17	<0.1	7.2	0.20	<0.1	0.9	2.7	1.03	92	n	n	0
7/40	7.0	0.20	<0.1	7.2	0.29	<0.1	0	2.8	1.06	99	103.5	99	0
7/50	7.0	0.17	<0.1	7.0	0.19	<0.1	10.0	2.8	1.06	98	88.7	100	0
7/60	7.0	0.20	<0.1	7.2	0.25	<0.1	5.1	2.7	1.07	99	95.6	100	0
7/70	7.0	0.22	<0.1	7.0	0.28	<0.1	2.5	2.9	1.06	99	100.9	97	0
7/80	7.0	0.19	<0.1	7.0	0.24	<0.1	0.9	2.7	1.01	87	100.5	100	0

[a] Turbidity units in NTU
[b] Dissolved oxygen in mg/L
[c] Polyphosphate dosage in mg/L as total PO_4
[d] Cl_2 concentration in mg/L
[e] Total manganese in mg/L
[f] Percent manganese filterability
[g] Total calcium in mg/L as $CaCO_3$
[h] Percent calcium filterability
[i] Color units
n-not present

TABLE A 3. Continued

Jar #	Day 1								Day 3								Day 5							
	pH	Turb[a]	Cl_2[d]	Tot[e]	%Fil[f]	Ca[g]	%Fil[h]	Color[i]	pH	Turb	Cl_2	Tot	%Fil	Ca	%Fil	Color[i]	pH	Turb	Cl_2	Tot	%Fil	Ca	%Fil	Color
0/0	7.3	1.40	1.5	0.88	50	n	n	170	7.4	2.40	2.7	0.70	0.8	n	n	260	7.4	3.1	2.5	0.68	0.03	n	n	320
7/0	7.2	0.23	1.5	1.09	98	n	n	5	7.5	0.50	2.8	1.07	91	n	n	4	7.3	0.78	2.4	0.96	96	n	n	12
7/5	7.3	0.23	1.3	1.08	97	n	n	4	7.4	0.49	2.8	1.06	90	n	n	9	7.5	0.97	2.3	1.05	81	n	n	25
7/10	7.2	0.26	1.5	1.06	94	n	n	7	7.5	0.65	2.9	1.02	82	n	n	18	7.3	1.40	2.5	1.07	44	n	n	49
7/20	7.5	0.40	1.6	1.05	85	n	n	9	7.3	0.86	2.7	1.01	72	n	n	25	7.4	2.00	2.7	0.87	22	n	n	95
7/30	7.3	0.45	1.3	1.05	82	n	n	12	7.4	0.99	2.8	0.90	92	n	n	72	7.6	2.60	2.3	0.75	0.01	n	n	200
7/40	7.2	0.40	1.5	1.09	89	101.3	94	25	7.6	1.10	2.9	0.99	76	104	98	68	7.4	1.30	2.7	0.74	0.01	95.4	100	65
7/50	7.4	0.50	1.6	1.08	93	86.6	100	8	7.5	0.86	2.7	1.02	93	90.2	99	2	7.6	0.98	2.5	0.94	91	85.9	97	10
7/60	7.3	0.48	1.5	1.08	96	97.7	100	12	7.4	0.73	2.8	1.05	89	93.5	100	6	7.4	0.69	2.3	0.85	61	90.2	98	21
7/70	7.3	0.42	1.3	1.07	96	100.0	100	17	7.5	0.54	2.9	1.02	81	98.3	100	17	7.5	0.65	2.5	0.85	60	94.8	99	51
7/80	7.2	0.60	1.6	1.06	91	101.4	100	26	7.1	1.00	2.7	0.99	81	100.6	100	45	7.4	1.10	2.4	1.10	25	97.1	96.1	60

Table A 4. Comparison of the manganese sequestering ability of several polyphosphates and an orthophosphate with hypochlorite in the presence of calcium

Jar #	Pre-dosage			Post-dosage			Dosage		Day 0				
	pH	Turb[a]	D.O.[b]	pH	Turb	D.O.	PO_4[c]	Cl_2[d]	Tot[e]	%Fil[f]	Ca[g]	%Fil[h]	Color[i]
0/0	7.0	0.15	<0.1	7.2	0.18	<0.1	0	3.5	1.05	97	100.6	100	0
7/0[B]	7.0	0.18	<0.1	7.2	0.19	<0.1	2.0	3.6	1.06	99	99.7	100	0
7/5[D]	7.0	0.20	<0.1	7.1	0.22	<0.1	1.9	3.5	1.05	98	99	99	0
7/10[C]	7.0	0.16	<0.1	7.3	0.20	<0.1	2.1	3.2	1.07	98	97.9	100	0
7/20[A]	7.0	0.19	<0.1	7.2	0.21	<0.1	2.1	3.1	1.05	100	100.2	96	0
7/30[O]	7.0	0.18	<0.1	7.1	0.22	<0.1	2.2	3.4	1.05	99	98.6	99	0
7/40[C]	7.0	0.21	<0.1	7.2	0.23	<0.1	9.8	3.5	1.05	99	97.5	100	0
7/50[C]	7.0	0.23	<0.1	7.3	0.23	<0.1	4.8	3.2	1.04	99	98.0	100	0
7/60[C]	7.0	0.20	<0.1	7.1	0.21	<0.1	7.3	3.7	1.03	99	95.0	100	0
7/70[A]	7.0	0.19	<0.1	7.2	0.20	<0.1	0.9	3.3	1.05	98	97.4	100	0

a Turbidity units in NTU
b Dissolved oxygen in mg/L
c Polyphosphate dosage in mg/L as total PO_4
d Cl_2 concentration in mg/L
e Total manganese in mg/L
f Percent manganese filterability
g Total calcium in mg/L as $CaCO_3$
h Percent calcium filterability
i Color units
A, B, C, D Polyphosphate types
O Orthophosphate

TABLE A 4. Continued

Jar #	Day 1								Day 3								Day 5							
	pH	Turb[a]	Cl_2[d]	Tot[e]	%Fil[f]	Ca[g]	%Fil[h]	Color[i]	pH	Turb	Cl_2	Tot	%Fil	Ca	%Fil	Color[i]	pH	Turb	Cl_2	Tot	%Fil	Ca	%Fil	Color
0/0	7.2	0.32	3.0	1.01	89	98.9	100	25	7.3	0.32	2.6	0.98	81	95.6	100	56	7.4	0.35	2.0	1.00	60	96.4	97	80
7/0[B]	7.3	0.31	2.9	1.03	99	100.4	97	10	7.4	0.31	2.4	1.02	93	99.0	100	20	7.5	0.45	1.8	1.01	81	99.0	100	45
7/5[D]	7.2	0.33	2.8	1.02	100	99.9	98	12	7.3	0.33	2.4	0.99	96	97.5	100	25	7.3	0.34	1.7	1.00	77	98.3	99	50
7/10[C]	7.2	0.29	2.9	1.02	100	98.0	99	9	7.5	0.29	2.7	0.98	98	97.2	98	30	7.4	0.30	1.9	0.99	82	96.4	100	55
7/20[A]	7.3	0.30	3.0	1.03	100	100.0	99	14	7.4	0.30	2.5	1.00	85	99.5	99	32	7.5	0.55	1.8	1.00	78	100.0	99	42
7/30[O]	7.4	0.32	2.6	1.03	100	99.1	99	10	7.3	0.32	2.3	0.98	96	98.9	99	48	7.6	0.44	1.9	0.99	79	98.4	100	65
7/40[C]	7.2	0.75	2.5	1.03	100	97.0	100	3	7.4	0.75	2.6	0.98	100	97.7	99	7	7.4	1.20	1.8	0.98	96	98.3	97	4
7/50[C]	7.4	0.30	2.7	1.02	100	98.2	99	6	7.5	0.33	2.7	0.97	100	98.7	99	18	7.5	0.45	1.7	0.98	94	93.5	100	38
7/60[C]	7.3	0.50	2.8	1.02	100	99.3	100	4	7.4	0.50	2.8	0.96	100	95.3	99	15	7.3	0.78	1.6	0.99	93	96.2	100	29
7/70[A]	7.2	0.24	2.5	1.03	94	98.6	100	11	7.3	0.24	2.7	1.01	82	95.4	98	35	7.5	0.30	1.8	0.95	65	94.0	100	60

Table A 5. pH effects on manganese treatment by polyphosphate and hypochlorite

Jar #	Pre-dosage			Post-dosage			Dosage		Day 0				
	pH	Turb[a]	D.O.[b]	pH	Turb	D.O.	PO_4[c]	Cl_2[d]	Tot[e]	%Fil[f]	Ca[g]	Ox.Mn[h]	Color[i]
50	7.0	0.17	< 0.1	7.2	0.15	< 0.1	0	1.62	1.09	100	104.0	0.01	0
80	7.0	0.20	< 0.1	7.2	0.13	< 0.1	8.82	1.66	1.09	100	101.8	0	0
100	7.0	0.25	< 0.1	7.2	0.19	< 0.1	9.10	1.57	1.09	99	104.2	0.01	0
110	7.0	0.21	< 0.1	7.1	0.21	< 0.1	8.77	1.65	1.08	100	103.1	0.02	0

[a] Turbidity units in NTU
[b] Dissolved oxygen in mg/L
[c] Polyphosphate dosage in mg/L as total PO_4
[d] Cl_2 concentration in mg/L
[e] Total manganese in mg/L
[f] Percent manganese filterability
[g] Total calcium in mg/L as $CaCO_3$
[h] Oxidized manganese as free Cl_2 equivalent in mg/L
[i] Color units

Table A 5. Continued

Jar #	Day 1							Day 3							Day 5						
	pH	Turb[a]	Cl_2[d]	Tot[e]	%Fil[f]	Ox.Mn[h]	Color[i]	pH	Turb	Cl_2[d]	Tot	%Fil	Ox.Mn	Color	pH	Turb	Cl_2[d]	Tot	%Fil	Ox.Mn	Color
50	7.30	0.34	1.0	1.10	96	0.06	15	7.40	0.55	3.10	1.03	78	0.05	40	7.55	3.10	2.2	0.53	9.2	0.61	80
80	7.30	0.42	1.4	1.09	99	0.04	0	7.50	0.70	3.15	1.04	88	0	10	7.40	0.70	2.2	0.79	83	0.23	40
100	6.15	0.34	1.23	1.10	99	0	0	6.20	0.45	3.22	1.09	99	0	0	6.30	0.50	2.52	1.09	98	0	5
110	7.85	0.56	1.48	1.09	34	0.02	5	7.90	0.83	3.16	1.07	67	0	5	8.10	1.00	2.44	0.52	70	0.32	50

Table A 6. Side-by-side comparison of the manganese sequestering ability of several polyphosphates with chlorine dioxide in the presence of calcium

Jar #	Pre-dosage			Post-dosage			Dosage		Day 0				
	pH	Turb[a]	D.O.[b]	pH	Turb	D.O.	PO_4[c]	ClO_2[d]	Tot[e]	%Fil[f]	Ca[g]	%Fil[h]	Color[i]
0/0	7.0	0.40	<0.1	7.2	0.45	<0.1	0	0.8	0.96	94	113	98	34
7/0[B]	7.0	0.35	<0.1	7.3	0.41	<0.1	1.87	0.8	1.01	94	105	96	3
7/5[D]	7.0	0.42	<0.1	7.2	0.44	<0.1	1.91	0.8	0.98	98	118	99	5
7/10[C]	7.0	0.36	<0.1	7.3	0.40	<0.1	1.95	0.8	0.94	100	120	98	2
7/20[A]	7.0	0.40	<0.1	7.2	0.44	<0.1	0.52	0.8	0.96	99	119	99	0
7/40[C]	7.0	0.35	<0.1	7.3	0.40	<0.1	9.66	0.8	0.96	95	122	97	2
7/50[C]	7.0	0.40	<0.1	7.2	0.42	<0.1	4.74	0.8	0.98	93	122	95	3

a Turbidity units in NTU
b Dissolved oxygen in mg/L
c Polyphosphate dosage in mg/L as total PO_4
d ClO_2 concentration in mg/L
e Total manganese in mg/L
f Percent manganese filterability
g Total calcium in mg/L as $CaCO_3$
h Percent calcium filterability
i Color units
A, B, C, D Polyphosphate types

Table A 6. Continued

Jar #	Day 1					Day 3					Day 5				
	pH	Turb[a]	Tot[e]	%Fil[f]	Color[i]	pH	Turb	Tot	%Fil	Color	pH	Turb	Tot	%Fil	Color
0/0	7.5	0.60	0.95	77	45	7.5	0.75	0.90	63	59	7.4	0.80	0.90	63	95
7/0[B]	7.6	0.65	0.95	82	26	7.4	0.79	0.90	83	45	7.5	0.83	0.91	75	74
7/5[D]	7.4	0.53	0.94	95	18	7.4	0.63	0.92	94	30	7.4	0.70	0.91	79	53
7/10[C]	7.5	0.47	0.94	95	16	7.5	0.57	0.93	93	25	7.3	0.67	0.89	88	41
7/20[A]	7.3	0.49	0.93	88	18	7.3	0.61	0.96	93	28	7.4	0.72	0.89	88	48
7/40[C]	7.4	0.70	0.97	96	8	7.4	0.83	0.94	99	16	7.5	1.10	0.94	93	20
7/50[C]	7.5	0.61	0.92	97	6	7.5	0.67	0.93	94	20	7.4	0.92	0.93	95	31

TABLE A 7. Manganese treatment with polyphosphate D and chlorine dioxide in the absence of calcium

Jar #	Pre-dosage			Post-dosage			Dosage		Day 0				
	pH	Turb[a]	D.O.[b]	pH	Turb	D.O.	PO_4[c]	ClO_2[d]	Tot[e]	%Fil[f]	%Fil[g]	Ox.Mn[h]	Color[i]
10	7.0	0.26	<0.1	7.0	0.26	<0.1	0	0	1.01	100	100	0	0
20	7.0	0.25	<0.1	7.1	0.27	<0.1	9.67	0	1.03	100	97	0	0
30	7.0	0.22	<0.1	7.1	0.73	<0.1	0	2.0	1.00	93	0.50	1.15	315
40	7.0	0.27	<0.1	7.2	0.25	<0.1	10.23	0.5	1.02	92	72	0.175	3
50	7.0	0.27	<0.1	7.1	0.33	<0.1	10.50	1.0	1.02	97	-	0.35	30
60	7.0	0.26	<0.1	7.2	0.20	<0.1	9.88	2.0	1.02	100	15	0.90	210
70	7.0	0.21	<0.1	7.1	0.23	<0.1	1.93	0.5	1.02	93	-	0.35	70
80	7.0	0.29	<0.1	7.2	0.31	<0.1	1.96	1.0	1.03	95	53	0.58	130
90	7.0	0.21	<0.1	7.2	0.19	<0.1	1.98	2.0	1.02	98	-	1.05	200

[a] Turbidity units in NTU
[b] Dissolved oxygen in mg/L
[c] Polyphosphate dosage in mg/L as total PO_4
[d] ClO_2 concentration in mg/L
[e] Total manganese in mg/L
[f] Percent manganese filterability (0.1 micron filter)
[g] Percent manganese filterability (200k ultrafilter)
[h] Oxidized manganese concentration as free chlorine equivalent in mg/L
[i] Color units

TABLE A 7. Continued

Jar #	Day 1							Day 3							Day 5						
	pH	Turb[a]	Tot[e]	%Fil[f]	%Fil[g]	Ox.Mn[h]	Color[i]	pH	Turb	Tot	%Fil	%Fil	Ox.Mn	Color	pH	Turb	Tot	%Fil	%Fil	Ox.Mn	Color
10	7.5	0.23	0.99	100	88	0	0	7.3	0.35	0.99	99	82	0	0	7.4	0.45	0.98	100	80	0	0
20	7.5	0.22	1.03	100	88	0	0	7.3	0.32	1.05	99	76	0	0	7.3	0.42	1.04	100	74	0	0
30	7.45	0.75	1.01	90	7	1.29	330	7.35	0.82	1.03	83	0.49	1.35	310	7.3	0.76	1.02	90	0.59	1.11	305
40	7.5	0.7	1.02	92	34	0.28	70	7.4	0.99	1.03	93	36	0.31	65	7.45	0.90	1.02	93	69	0.275	70
50	7.3	0.26	1.03	96	-	0.53	120	7.3	0.32	1.03	99	-	0.54	110	7.4	0.35	1.03	99	-	0.44	110
60	7.55	0.20	1.03	99	50	1.13	230	7.3	0.30	1.03	100	3.3	1.17	245	7.4	0.31	1.03	99	5.5	1.00	270
70	7.4	0.21	1.01	94	-	0.55	70	7.4	0.29	1.01	97	-	0.57	70	7.35	0.37	1.01	94	-	0.50	80
80	7.4	0.20	1.02	98	31	0.81	120	7.4	0.27	1.03	97	1.4	0.82	120	7.4	0.33	1.01	98	2.8	0.70	125
90	7.6	0.21	1.01	98	-	1.24	215	7.45	0.3	1.03	97	-	1.28	220	7.3	0.30	1.04	98	-	1.10	235

Table A 8. Manganese treatment with polyphosphate A, C, and D and polyphosphate A and silicate in conjunction with chlorine dioxide in the absence of calcium

Jar #	Pre-dosage			Post-dosage			Dosage		Day 0				
	pH	Turb[a]	D.O.[b]	pH	Turb	D.O.	PO_4[c]	ClO_2[d]	Tot[e]	%Fil[g]	%Fil[h]	Ox.Mn[i]	Color[j]
10	7.0	0.13	<0.1	7.1	0.50	<0.1	0	2.0	1.02	95	43	1.31	295
20[A]	7.0	0.17	<0.1	7.2	0.12	<0.1	7.96[f]	2.0	0.87	96	45	1.28	115
30[A]	7.0	0.14	<0.1	7.2	0.10	<0.1	8.05	2.0	1.04	97	53	0.98	120
40[A]	7.0	0.18	<0.1	7.1	0.09	<0.1	8.14	1.0	1.04	98	-	1.0	125
50[D]	7.0	0.10	<0.1	7.2	0.12	<0.1	10.60	1.0	1.04	96	-	0.57	83
60	7.0	0.14	<0.1	7.1	0.16	<0.1	0	1.0	1.04	97	-	1.28	235
70[C]	7.0	0.12	<0.1	7.1	0.24	<0.1	10.98	1.0	1.03	98	-	0.50	53
80[A]	7.0	0.14	<0.1	7.1	0.13	<0.1	1.73	2.0	1.02	100	-	1.39	185
90[A]	7.0	0.17	<0.1	7.2	0.12	<0.1	1.62	1.0	1.03	97	-	1.07	170
100	7.0	0.14	<0.1	7.0	0.14	<0.1	0	0	1.01	95	59	0	0
110[A]	7.0	0.18	<0.1	7.1	0.13	<0.1	8.13	0.5	1.04	99	-	0.97	120

[a] Turbidity units in NTU
[b] Dissolved oxygen in mg/L
[c] Polyphosphate dosage in mg/L as total PO_4
[d] ClO_2 concentration in mg/L
[e] Total manganese in mg/L
[f] 21.9 mg/L SiO_2 added in addition to polyphosphate
[g] Percent manganese filterability (0.1 micron filter)
[h] Percent manganese filterability (200k ultrafilter)
[i] Oxidized manganese concentration as free chlorine equivalent in mg/L
[j] Color units
A, C, D Polyphosphate types

Table A 8. Continued

Jar #	Day 1							Day 3							Day 5						
	pH	Turb[a]	Tot[e]	%Fil[g]	%Fil[h]	Ox.Mn[i]	Color[j]	pH	Turb	Tot	%Fil	%Fil	Ox.Mn	Color	pH	Turb	Tot	%Fil	%Fil	Ox.Mn	Color
10	7.4	0.55	1.04	94	7	1.41	305	7.4	0.6	1.05	93	5.6	1.42	305	7.35	0.65	1.03	98	12	1.43	310
20[A]	7.3	0.10	0.87	69	65	1.40	130	7.35	0.23	0.84	100	48	1.40	130	7.3	0.30	0.87	100	58	1.36	130
30[A]	7.4	0.13	1.03	100	61	1.16	160	7.4	0.20	1.06	98	16	1.16	175	7.4	0.28	1.05	98	23	1.15	170
40[A]	7.5	0.10	1.04	98	-	1.17	150	7.5	0.18	1.05	100	-	1.10	175	7.5	0.20	1.06	96	-	1.09	140
50[D]	7.4	0.15	1.04	100	-	1.06	125	7.45	0.15	1.06	98	-	1.03	135	7.5	0.20	1.06	96	-	1.09	140
60	7.3	0.20	1.04	97	-	1.34	235	7.5	0.20	1.04	99	-	1.37	255	7.45	0.32	1.06	93	-	1.40	250
70[C]	7.4	0.15	1.04	100	-	1.24	130	7.4	0.16	1.04	100	-	1.26	120	7.4	0.23	1.08	94	-	1.23	125
80[A]	7.3	0.14	1.02	99	-	1.50	200	7.45	0.20	1.03	99	-	1.42	215	7.5	0.32	1.04	95	-	1.38	220
90[A]	7.5	0.10	1.03	100	-	1.21	190	7.35	0.15	1.04	99	-	1.19	210	7.4	0.20	1.05	95	-	1.23	205
100	7.4	0.13	1.04	89	70	0	0	7.4	0.25	1.03	99	81	0	0	7.5	0.35	1.05	81	85	0	0
110[A]	7.4	0.13	1.05	99	-	1.19	170	7.45	0.2	1.06	97	-	1.13	175	7.45	0.33	1.06	73	-	1.16	180

Table A 9. Quality control verification of polyphosphate/chlorine dioxide and polyphosphate/hypochlorite methods

Jar #	Pre-dosage			Post-dosage			Dosage			Day 0				
	pH	Turb[a]	D.O.[b]	pH	Turb	D.O.	PO_4[c]	ClO_2[d]	Cl_2[e]	Tot[f]	%Fil[g]	Ca[h]	Ox.Mn[i]	Color[j]
10	7.0	0.20	<0.1	7.1	1.25	<0.1	9.38	0.86	-	1.064	1.5	103.3	1.12	75
20	7.0	0.21	<0.1	7.2	1.15	<0.1	9.21	1.07	-	1.072	2.3	103.4	1.09	80
30	7.0	0.18	<0.1	7.2	1.20	<0.1	9.31	0.86	-	1.085	2.1	102.3	1.15	80
40	7.0	0.18	<0.1	7.1	0.25	<0.1	0.13	-	1.51	1.083	100	102.3	0.01	0
50	7.0	0.17	<0.1	7.2	0.15	<0.1	0.11	-	1.62	1.091	100	104	0.01	0
60	7.0	0.20	<0.1	7.1	0.15	<0.1	0.08	-	1.42	1.089	100	106	0.03	0
70	7.0	0.22	<0.1	7.1	0.12	<0.1	9.06	-	1.52	1.103	99	103	0.05	0
80	7.0	0.20	<0.1	7.2	0.13	<0.1	8.82	-	1.66	1.090	100	102	0	0
90	7.0	0.19	<0.1	7.1	0.15	<0.1	8.90	-	1.44	1.093	100	103	0.04	0

a Turbidity units in NTU
b Dissolved oxygen in mg/L
c Polyphosphate dosage in mg/L as total PO_4
d ClO_2 concentration in mg/L
e Cl_2 concentration in mg/L
f Total manganese in mg/L
g Percent manganese filterability
h Total calcium in mg/L as $CaCO_3$
i Oxidized manganese concentration as free chlorine equivalent in mg/L
j color units

Table A 9. Continued

Jar #	Day 1								Day 3								Day 5							
	pH	Turb[a]	Cl_2[d]	ClO_2[e]	Tot[f]	%Fil[g]	Ox.Mn[i]	Color[j]	pH	Turb	Cl_2	ClO_2	Tot	%Fil	Ox.Mn	Color	pH	Turb	Cl_2	ClO_2	Tot	%Fil	Ox.Mn	Color
10	7.40	1.20	-	0.14	1.07	2.2	1.10	80	7.35	1.25	-	0	1.08	1.5	0.98	70	7.30	1.30	-	0	1.09	3.4	1.11	105
20	7.35	1.25	-	0.10	1.08	2.4	1.05	70	7.40	1.45	-	0	1.08	6.4	0.92	80	7.40	1.35	-	0	1.09	2.7	1.15	105
30	7.50	1.10	-	0.11	1.08	2.1	1.07	73	7.42	1.10	-	0	1.09	1.2	0.96	78	7.35	1.30	-	0	1.09	1.7	1.23	105
40	7.40	0.38	1.2	-	1.09	94	0.05	20	7.50	0.60	3.19	-	1.01	70	0.03	50	7.50	1.50	2.2	-	0.42	8.2	0.54	75
50	7.30	0.34	1.0	-	1.10	96	0.06	15	7.40	0.55	3.10	-	1.03	78	0.05	40	7.55	3.10	2.2	-	0.53	9.2	0.61	80
60	7.45	0.30	1.1	-	1.10	96	0.02	5	7.39	0.67	3.12	-	1.01	74	0.14	35	7.60	3.10	2.2	-	0.41	7.1	0.51	70
70	7.40	0.40	1.4	-	1.10	98	0	0	7.45	0.75	3.24	-	1.11	98	0	0	7.05	0.58	2.5	-	1.08	97	0	10
80	7.30	0.42	1.4	-	1.09	99	0.04	0	7.50	0.70	3.15	-	1.04	88	0	10	7.40	0.70	2.2	-	0.79	83	0.23	40
90	7.45	0.45	1.0	-	1.09	98	0	0	7.30	0.77	3.07	-	1.09	94	0	8	7.15	0.64	2.6	-	1.00	90	0.12	25

Table A 10. Manganese concentration as a function of pE and pH

pH 6.0 pE	pH 7.0 pE	pH 8.0 pE	pH 6.0 Mn^{2+} Moles/L	pH 7.0 Mn^{2+} Moles/L	pH 8.0 Mn^{2+} Moles/L
9.24	7.24	5.24	1	1	1
12.24	10.24	8.24	10^{-6}	10^{-6}	10^{-6}
15.24	14.24	11.24	10^{-12}	10^{-15}	10^{-12}
19.24	17.24	15.24	10^{-20}	10^{-20}	10^{-20}
34.24	32.24	20.24	10^{-50}	10^{-50}	10^{-30}
-8.60	-8.60	-8.60	$10^{35.68}$	$10^{31.68}$	$10^{35.68}$

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CODE VERSION: MINTEQK1A      DATE OF CALCULATIONS:  19-DEC-89      TIME:  18:40:25

*****INTERNAL DOCUMENTATION FOR CODE MODIFICATIONS TO THE MINTEQ GEOCHEMICAL MODEL*****
        ONLY THE TWELVE MOST RECENT MODIFICATIONS WILL BE DESCRIBED

                12/01/82 ORIGINAL VERSION OF MINTEQ CODE  COPIED  FROM A. FELMY (MINTEQ.FOR;12);
                  PREPARED FOR EPA AND DOCUMENTED IN FELMY
                  EPA REPORTS (NTIS PB84-157148 and PB84-157155)
              **  12/17/82 K. KRUPKA ADDED ROUTINES AND FORMATS FOR PRINTING VAX-SYSTEM DATE AND TIME
                  FOR THE EXECUTION OF A MINTEQ RUN
              **  12/17/82 K. KRUPKA ADDED PARAMETERS 9 (KKDAV) AND 10(KKTR) RESPECTIVELY: 1) TO JUST USE THE
                  DAVIES EQUATION FOR ACTIVITY COEFFICIENT  CALCULATIONS
                  AND 2) TO NOT PRINT THE INITIAL DATA BASE FOR THE AQUEOUS  SPECIES
              **   1/18/83 FROM A. FELMY, IF (ABS(V).GE.38) IN *SOLIDX*, SET C(I) = 0.00
              **   1/28/83 K. KRUPKA ADDED CORRECTIONS TO *SOLIDX* THAT WERE LISTED IN MEMO
                   FROM A. FELMY (MEMO NOT DATED, ABOUT 1/25/83)
              **   2/07/83 K. KRUPKA ADDED STATEMENTS TO *IAP* TO BY-PASS TEMPERATURE CORRECTIONS TO
                   MIN OR MAX LOG K VALUES THAT EQUAL ZERO
              **   4/11/83 K. KRUPKA ADDED CHANGES FROM 4/5/83 MEMO FROM A. FELMY, WHICH
                   DESCRIBES MODIFIICATIONS TO SECTION THAT CALCULATES PERCENT DISTRIBUTION OF COMPONENTS
              **   5/12/83 K. KRUPKA ADDED CHANGES:
                   A. C. COWAN MEMO OF 4/18/83 FOR MINTEQ TO HANDLE 50 COMPONENTS; CHANGES TO
                      SUBROUTINES COMMON, CONVERG, MAIN, AND SOLVE
                   B. A. FELMY MEMO OF 5/6/83 CONCERNING ROUND-OFF ERROR AND CHANGES TO SUBROUTINE OUTPUT
                   C. SUBROUTINE IAP - FOR NO BLANK PAGE AT 52 COUNT
                   D. SUBROUTINE INPUT - TO HANDLE MAX OF 12 COMPONENTS IN REACTION OF NEW SPECIES OR SOLID

CALCIUM SPECIATION
CONDNS. pH 7,MNSO4=0.02mm NaHCO3=3mm, PO4=10mg/l, CaCl2=100 mg/l as CaCO3
T =   20.00 MOL      0.00
0 0 0 1 3 0 0 0 0 0
0    0.00    0.00    0.00    0.00
    500  3.000E-03    0.00
    140  3.000E-03    0.00
    330  3.000E-03    0.00
    580  1.000E-04    0.00
    150  1.000E-03    0.00
    732  2.000E-05    0.00
    470  2.000E-05    0.00
    471  0.000E+00    0.00
    180  2.000E-03    0.00
      1  0.000E+00    0.00
 H2O HAS BEEN INSERTED AS A COMPONENT
  3    3
    330  7.000E+00    0.00
      1  2.180E+01    0.00
4714700  0.000E+00    0.00
INPUT DATA BEFORE TYPE MODIFICATIONS
   ID        NAME        ACTIVITY GUESS  LOG GUESS   ANAL TOTAL
    500  NA                  1.000E+00       0.000   3.000E-03
    140  CO3                 1.000E+00       0.000   3.000E-03
    330  N                   1.000E+00       0.000   3.000E-03
    580  PO4                 1.000E+00       0.000   1.000E-04
    150  CA                  1.000E+00       0.000   1.000E-03
    732  SO4                 1.000E+00       0.000   2.000E-05
    470  MN+2                1.000E+00       0.000   2.000E-05
    471  MN+3                1.000E+00       0.000   0.000E+00
    180  CL                  1.000E+00       0.000   2.000E-03
      1  E                   1.000E+00       0.000   0.000E+00
      2  H2O                 1.000E+00       0.000   0.000E+00
```

CODE VERSION: MINTEQK1A DATE OF CALCULATIONS: 19-DEC-89 TIME: 18:40:27

ALL SPECIES CONSIDERED IN THIS PROBLEM

SPECIES: TYPE I - COMPONENTS

ID	NAME	DH	LOGK	MIN LOGK	MAX LOGK	Z	DHA	DHB	GFW
500	NA	0.0000	0.0000	0.000	0.000	1.00	4.00	0.08	22.9898
140	CO3	0.0000	0.0000	0.000	0.000	-2.00	5.40	0.00	60.0094
180	CL	0.0000	0.0000	0.000	0.000	-1.00	3.00	0.01	35.4530
580	PO4	0.0000	0.0000	0.000	0.000	-3.00	5.00	0.00	94.9714
150	CA	0.0000	0.0000	0.000	0.000	2.00	6.00	0.17	40.0800
732	SO4	0.0000	0.0000	0.000	0.000	-2.00	4.00	-0.04	96.0616
470	MN+2	0.0000	0.0000	0.000	0.000	2.00	6.00	0.00	54.9380
471	MN+3	0.0000	0.0000	0.000	0.000	3.00	9.00	0.00	54.9380

SPECIES: TYPE II - COMPLEXES

ID	NAME	DH	LOGK	MIN LOGK	MAX LOGK	Z	DHA	DHB	GFW
3305800	KNPO4 -2	-3.5300	12.3460	0.000	0.000	-2.00	5.00	0.00	95.9790
3305801	KH2PO4 -	-4.5200	19.5530	0.000	0.000	-1.00	5.40	0.00	96.9870
3305802	H3PO4 AQ	-2.6200	21.7000	0.000	0.000	0.00	0.00	0.00	97.9951
3300020	K OH-	13.3450	-13.9980	0.000	0.000	-1.00	3.50	0.00	17.0074
1503300	KCAOH +	14.5350	-12.5980	0.000	0.000	1.00	6.00	0.00	57.0870
1501400	KCAHCO3 +	1.7900	11.3300	0.000	0.000	1.00	6.00	0.00	101.0970
1501401	KCACO3 AQ	4.0300	3.1500	0.000	0.000	0.00	0.00	0.00	100.0890
1507320	KCASO4 AQ	1.4700	2.3090	0.000	0.000	0.00	0.00	0.00	136.1410
1505800	KCAHPO4 AQ	-0.2300	15.0850	0.000	0.000	0.00	0.00	0.00	136.0590
1505801	KCAPO4 -	3.1000	6.4590	0.000	0.000	-1.00	5.40	0.00	135.0510
1505802	KCAH2PO4 +	-1.1200	20.9600	0.000	0.000	1.00	5.40	0.00	137.0670
5001400	KNACO3 -	8.9110	1.2680	0.000	0.000	-1.00	5.40	0.00	82.9990
5001401	KNAHCO3 AQ	0.0000	10.0800	0.000	0.000	0.00	0.00	0.00	84.0070
5007320	KNASO4 -	1.1200	0.7000	0.000	0.000	-1.00	5.40	0.00	119.0510
5005800	KNAHPO4 -	0.0000	12.6360	0.000	0.000	-1.00	5.40	0.00	118.9690
4701800	KMNCL +	0.0000	0.6070	0.000	0.000	1.00	5.00	0.00	90.3910
4701801	KMNCL2 AQ	0.0000	0.0410	0.000	0.000	0.00	0.00	0.00	125.8440
4701802	KMNCL3 -	0.0000	-0.3050	0.000	0.000	-1.00	5.00	0.00	161.2970
4703300	KMNOH +	14.3990	-10.5900	0.000	0.000	1.00	5.00	0.00	161.2970
4703301	KMN(OH)3 -1	0.0000	-34.8000	0.000	0.000	-1.00	5.00	0.00	105.9600
4707320	KMNSO4 AQ	2.1700	2.2600	0.000	0.000	0.00	0.00	0.00	150.9990
4701400	KMNHCO3 +	0.0000	11.6000	0.000	0.000	1.00	5.00	0.00	115.9550
3301400	KHCO3 -	-3.6170	10.3300	0.000	0.000	-1.00	5.40	0.00	61.0170
3301401	KH2CO3 AQ	-2.2470	16.6810	0.000	0.000	0.00	0.00	0.00	62.0250
3307320	KHSO4 -	4.9100	1.9870	0.000	0.000	-1.00	4.50	0.00	97.0690

SPECIES: TYPE III - FIXED SOLIDS

ID	NAME	DH	LOGK	MIN LOGK	MAX LOGK	Z	DHA	DHB	GFW
2	H2O	0.0000	0.0000	0.000	0.000	0.00	0.00	0.00	18.0153
1	E	0.0000	21.8000	0.000	0.000	-1.00	0.00	0.00	0.0000
330	H	0.0000	7.0000	0.000	0.000	1.00	9.00	0.00	1.0080
4714700	MN+3/MN+2	25.7600	-25.5070	0.000	0.000	0.00	0.00	0.00	0.0000

SPECIES: TYPE V - DISSOLVED SOLIDS

ID	NAME	DH	LOGK	MIN LOGK	MAX LOGK	Z	DHA	DHB	GFW
5015000	ARAGONITE	2.6150	8.3600	0.000	0.000	0.00	0.00	0.00	100.0894
5015001	CALCITE	2.5850	8.4750	8.560	0.000	0.00	0.00	0.00	100.0894
6015001	GYPSUM	-0.2610	4.8480	0.000	0.000	0.00	0.00	0.00	172.1722
4150000	HALITE	-0.9180	-1.5820	0.000	0.000	0.00	0.00	0.00	58.4428
6050001	MIRABILITE	-18.9870	1.1140	0.000	0.000	0.00	0.00	0.00	322.1942
3050000	NATRON	-15.7450	1.3110	0.000	0.000	0.00	0.00	0.00	286.1420
6050002	THENARDITE	0.5720	0.1790	0.000	0.000	0.00	0.00	0.00	142.0412

5050001	THERMONATR	2.8020	-0.1250	0.000	0.000	0.00	0.00	0.00	124.0043
2047000	PYROLUSITE	29.1800	-15.8610	0.000	-16.038	0.00	0.00	0.00	86.9368
2047001	BIRNESSITE	0.0000	-18.0910	0.000	0.000	0.00	0.00	0.00	86.9368
2047002	MSUTITE	0.0000	-17.5040	0.000	0.000	0.00	0.00	0.00	86.9368
3047100	BIXBYITE	15.2450	0.6110	2.226	0.430	0.00	0.00	0.00	157.8742
3047000	HAUSMANNITE	80.1400	-61.5400	0.000	0.000	0.00	0.00	0.00	228.8116
2047003	PYROCROITE	22.5900	-15.0880	0.000	-15.381	0.00	0.00	0.00	88.9528
2047100	MANGANITE	0.0000	0.2380	0.000	0.000	0.00	0.00	0.00	87.9448
5047000	RHODOCHROSIT	2.0790	10.4100	11.019	9.993	0.00	0.00	0.00	114.9474
4147000	MNCL2, 4H2O	-17.3800	-2.7100	0.000	0.000	0.00	0.00	0.00	197.9052
6047000	MNSO4	15.4800	-2.6690	0.000	0.000	0.00	0.00	0.00	150.9996
6047100	MN2(SO4)3	39.0600	5.7110	0.000	0.000	0.00	0.00	0.00	398.0608
7047000	MN3(PO4)2	-2.1200	23.8270	0.000	0.000	0.00	0.00	0.00	354.7568
7047001	MNHPO4(C)	0.0000	25.4000	0.000	0.000	0.00	0.00	0.00	150.9174
2015000	LIME	46.2650	-32.7970	0.000	0.000	0.00	0.00	0.00	0.0000
2015001	PORTLANDITE	30.6900	-22.6750	0.000	0.000	0.00	0.00	0.00	0.0000
5050007	TRONA	-8.4400	11.3690	11.480	0.000	0.00	0.00	0.00	226.0260
7015003	HYDROXYAPATI	38.9240	39.3820	44.232	0.000	0.00	0.00	0.00	502.3210
6015000	ANHYDRITE	3.7690	4.6370	0.000	0.000	0.00	0.00	0.00	136.1416

SPECIES: TYPE VI - SPECIES NOT CONSIDERED

ID	NAME	DH	LOGK	MIN LOGK	MAX LOGK	Z	DHA	DHB	GFW
4700021	KHNO4 -2	150.0200	-118.4400	0.000	0.000	-2.00	5.00	0.00	118.9350
4700020	KHNO4 -	176.6200	-127.8240	0.000	0.000	-1.00	3.00	0.00	118.9350
3301404	CH4(GAS)	-61.0000	41.0800	0.000	0.000	0.00	0.00	0.00	16.0432
3301403	CO2(GAS)	-0.5300	18.1600	0.000	0.000	0.00	0.00	0.00	41.0100
3300021	O2(AQ) SATO	0.0000	-45.5400	0.000	0.000	0.00	0.00	0.00	31.9988
3300022	O2(AQ) CALC	133.8300	-85.9800	0.000	0.000	0.00	0.00	0.00	31.9988
3300023	O2(GAS)	136.6300	-83.1200	0.000	0.000	0.00	0.00	0.00	0.0000

CHARGE BALANCE: UNSPECIATED
SUM OF CATIONS= 8.040E-03 SUM OF ANIONS = 8.340E-03
PERCENT DIFFERENCE = 1.831E+00 (ANIONS - CATIONS)/(ANIONS + CATIONS)

CODE VERSION: MINTEQK1A DATE OF CALCULATIONS: 19-DEC-89 TIME: 18:40:27

TERATIONS DURING SOLVE

ITER	NAME	TOTAL MOL	DIFF FXN	LOG ACTVTY
1	NA	3.000E-03	-2.956E-03	-4.52288
2	NA	3.000E-03	-8.568E-04	-2.68787
3	NA	3.000E-03	3.044E-04	-2.52899
4	NA	3.000E-03	-6.967E-05	-2.56878
5	NA	3.000E-03	-3.715E-06	-2.55842
6	PO4	1.000E-04	2.843E-07	-9.94098

ODE VERSION: MINTEQK1A DATE OF CALCULATIONS: 19-DEC-89 TIME: 18:40:27

ITERATIONS= 6: SOLID PYROLUSITE PRECIPITATES

CODE VERSION: MINTEQK1A DATE OF CALCULATIONS: 19-DEC-89 TIME: 18:40:27

TERATIONS DURING SOLVE

ITER	NAME	TOTAL MOL	DIFF FXN	LOG ACTVTY
7	NA	3.000E-03	-2.306E-04	-2.55816
8	NA	3.000E-03	2.479E-04	-2.52347

9	PO4	1.000E-04	5.191E-07	-9.93980

ODE VERSION: MINTEQK1A DATE OF CALCULATIONS: 19-DEC-89 TIME: 18:40:27

ITERATIONS= 9: SOLID HYDROXYAPATI PRECIPITATES

CODE VERSION: MINTEQK1A DATE OF CALCULATIONS: 19-DEC-89 TIME: 18:40:27

TERATIONS DURING SOLVE

ITER	NAME	TOTAL MOL	DIFF FXN	LOG ACTVTY
10	NA	3.000E-03	-2.300E-04	-2.55806
11	NA	3.000E-03	2.558E-04	-2.52345
12	CO3	3.000E-03	5.378E-06	-6.02391
13	NA	3.000E-03	-6.423E-06	-2.55900
14	SO4	2.000E-05	-3.400E-08	-4.88429

OUTPUT DATA: ITERATIONS = 14

ID	NAME	ANAL MOL	CALC MOL	ACTIVITY	LOG ACTVTY	GAMMA	NEW LOGK	DIFF FXN
500	NA	3.000E-03	2.996E-03	2.768E-03	-2.55785	0.923723	0.0345	-7.074E-08
140	CO3	3.000E-03	1.294E-06	9.479E-07	-6.02326	0.732359	0.1353	-5.494E-08
180	CL	2.000E-03	2.000E-03	1.843E-03	-2.73459	0.921281	0.0356	-4.985E-08
580	PO4	1.000E-04	1.877E-10	9.254E-11	-10.03369	0.493106	0.3071	4.509E-08
732	SO4	2.000E-05	1.804E-05	1.308E-05	-4.88355	0.724801	0.1398	-1.738E-09
150	CA	1.000E-03	9.413E-04	6.937E-04	-3.15885	0.736924	0.1326	0.000E+00
470	MN+2	2.000E-05	3.877E-30	2.851E-30	-29.54499	0.735321	0.1335	0.000E+00
2	H2O	0.000E+00	-4.655E-05	9.998E-01	-0.00009	1.000000	0.0001	0.000E+00
471	MN+3	0.000E+00	5.106E-34	2.667E-34	-33.57403	0.522225	0.2821	0.000E+00
1	E	0.000E+00	4.000E-05	1.585E-22	-21.80000	1.000000	21.8000	0.000E+00
330	H	3.000E-03	-5.737E-04	1.000E-07	-7.00000	0.930360	7.0000	0.000E+00

SPECIES: TYPE I - COMPONENTS

ID	NAME	CALC MOL	ACTIVITY	LOG ACTVTY	GAMMA	NEW LOGK	DN
500	NA	2.996E-03	0.0027679	-2.55785	0.923723	0.034	0.000
140	CO3	1.294E-06	0.0000009	-6.02326	0.732359	0.135	0.000
180	CL	2.000E-03	0.0018425	-2.73459	0.921281	0.036	0.000
580	PO4	1.877E-10	0.0000000	-10.03369	0.493106	0.307	0.000
150	CA	9.413E-04	0.0006937	-3.15885	0.736924	0.133	0.000
732	SO4	1.804E-05	0.0000131	-4.88355	0.724801	0.140	0.000
470	MN+2	3.877E-30	0.0000000	-29.54499	0.735321	0.134	0.000
471	MN+3	5.106E-34	0.0000000	-33.57403	0.522225	0.282	0.000

SPECIES: TYPE II - COMPLEXES

ID	NAME	CALC MOL	ACTIVITY	LOG ACTVTY	GAMMA	NEW LOGK	DN
3305800	KHPO4 -2	3.111E-05	0.0000227	-4.64356	0.730347	12.527	-3.530
3305801	KH2PO4 -	4.070E-05	0.0000377	-4.42418	0.925084	19.643	-4.520
3305802	H3PO4 AQ	4.994E-10	0.0000000	-9.30094	1.001320	21.732	-2.620
3300020	K OH-	7.419E-08	0.0000001	-7.16492	0.921963	-14.130	13.345
1503300	KCAOH +	1.244E-09	0.0000000	-8.93865	0.926018	-12.746	14.535
1501400	KCAHCO3 +	1.503E-05	0.0000139	-4.85644	0.926018	11.359	1.790
1501401	KCACO3 AQ	8.403E-07	0.0000008	-6.07501	1.001320	3.107	4.030
1507320	KCASO4 AQ	1.769E-06	0.0000018	-5.75178	1.001320	2.290	1.470
1505800	KCAHPO4 AQ	7.848E-06	0.0000079	-5.10466	1.001320	15.087	-0.230
1505801	KCAPO4 -	1.826E-07	0.0000002	-6.77229	0.925084	6.454	3.100
1505802	KCAH2PO4 +	6.536E-07	0.0000006	-6.21854	0.925084	21.008	-1.120
5001400	KNACO3 -	4.067E-08	0.0000000	-7.42451	0.925084	1.190	8.911
5001401	KNAHCO3 AQ	3.150E-06	0.0000032	-5.50111	1.001320	10.079	0.000
5007320	KNASO4 -	1.898E-07	0.0000002	-6.75541	0.925084	0.720	1.120

5005800	KNAHPO4 -	1.198E-07	0.0000001	-6.95554	0.925084	12.670	0.000
4701800	KMNCL +	2.299E-32	0.0000000	-31.67258	0.924448	0.641	0.000
4701801	KMNCL2 AQ	1.062E-35	0.0000000	-34.97317	1.001320	0.040	0.000
4701802	KMNCL3 -	9.558E-39	1.0000000	0.00000	0.924448	-0.271	0.000
4703300	KMNOH +	5.236E-34	0.0000000	-33.31509	0.924448	-10.736	14.399
4703301	KMN(OH)3 -1	0.000E+00	1.0000000	0.00000	0.924448	-34.766	0.000
4707320	KMNSO4 AQ	6.364E-33	0.0000000	-32.19567	1.001320	2.232	2.170
4701400	KMNHCO3 +	1.164E-31	0.0000000	-30.96824	0.924448	11.634	0.000
3301400	KHCO3 -	2.439E-03	0.0022562	-2.64662	0.925084	10.410	-3.617
3301401	KH2CO3 AQ	5.407E-04	0.0005414	-3.26650	1.001320	16.756	-2.247
3307320	KHSO4 -	1.197E-10	0.0000000	-9.95632	0.923637	1.962	4.910

SPECIES: TYPE III - FIXED SOLIDS

ID	NAME	CALC MOL	LOG MOL	NEW LOGK	DH
2	H2O	-4.655E-05	-4.332	0.000	0.000
1	E	4.000E-05	-4.398	21.800	0.000
330	H	-5.737E-04	-3.241	7.000	0.000
4714700	MN+3/MN+2	2.000E-05	-4.699	-25.829	25.760

SPECIES: TYPE IV - PRECIPITATED SOLIDS

ID	NAME	CALC MOL	LOG MOL	NEW LOGK	DH
2047000	PYROLUSITE	2.000E-05	-4.699	-16.226	29.180
7015003	HYDROXYAPATI	6.475E-06	-5.189	38.895	38.924

SPECIES: TYPE V - DISSOLVED SOLIDS

ID	NAME	CALC MOL	LOG MOL	NEW LOGK	DH
6015001	GYPSUM	6.437E-04	-3.191	4.851	-0.261
4150000	HALITE	1.371E-07	-6.863	-1.571	-0.918
6050001	MIRABILITE	2.245E-09	-8.649	1.351	-18.987
3050000	NATRON	2.333E-10	-9.632	1.508	-15.745
6050002	THENARDITE	1.488E-10	-9.827	0.172	0.572
5050001	THERMONATR	5.022E-12	-11.299	-0.160	2.802
5015000	ARAGONITE	1.287E-01	-0.890	8.292	2.615
2047001	BIRNESSITE	1.364E-02	-1.865	-18.091	0.000
2047002	NSUTITE	5.270E-02	-1.278	-17.504	0.000
3047100	BIXBYITE	1.871E-25	-24.728	0.420	15.245
3047000	HAUSMANNITE	0.000E+00	-51.577	-62.542	80.140
2047003	PYROCROITE	1.215E-31	-30.916	-15.370	22.590
2047100	MANGANITE	4.611E-13	-12.336	0.238	0.000
5047000	RHODOCHROSIT	6.543E-26	-25.184	10.384	2.079
4147000	MNCL2, 4H2O	3.110E-38	-37.507	-2.493	-17.380
6047000	MNSO4	5.116E-38	-37.291	-2.863	15.480
6047100	MN2(SO4)3	0.000E+00	-76.576	5.223	39.060
7047000	MN3(PO4)2	0.000E+00	-84.849	23.854	-2.120
7047001	MNHPO4(C)	6.627E-22	-21.179	25.400	0.000
2015000	LIME	2.922E-23	-22.534	-33.375	46.265
2015001	PORTLANDITE	6.058E-13	-12.218	-23.059	30.690
5050007	TRONA	5.679E-16	-15.246	11.475	-8.440
5015001	CALCITE	1.836E-01	-0.736	8.446	2.585
6015000	ANHYDRITE	3.528E-04	-3.453	4.590	3.769

SPECIES: TYPE VI - SPECIES NOT CONSIDERED

ID	NAME	CALC MOL	LOG MOL	NEW LOGK	DH
4700021	KMNO4 -2	2.184E-07	-6.661	-120.315	150.020
4700020	KMNO4 -	2.646E+05	5.423	-130.032	176.620
3301404	CH4(GAS)	0.000E+00	-208.580	41.843	-61.000
3301403	CO2(GAS)	1.391E-02	-1.857	18.167	-0.530
3300021	O2(AQ) SATO	0.000E+00	69.660	-45.540	0.000
3300022	O2(AQ) CALC	3.522E+27	27.547	-87.653	133.830
3300023	O2(GAS)	2.354E+30	30.372	-84.828	136.630

CODE VERSION: MINTEQK1A DATE OF CALCULATIONS: 19-DEC-89 TIME: 18:40:27

PERCENTAGE DISTRIBUTION OF COMPONENTS

NA	99.9	PERCENT BOUND IN SPECIES #	500	NA
CO3	81.3	PERCENT BOUND IN SPECIES #3301400		KHCO3 -
	18.0	PERCENT BOUND IN SPECIES #3301401		KH2CO3 AQ
CL	100.0	PERCENT BOUND IN SPECIES #	180	CL
PO4	38.6	PERCENT BOUND IN SPECIES #3305800		KHPO4 -2
	50.5	PERCENT BOUND IN SPECIES #3305801		KH2PO4 -
	9.7	PERCENT BOUND IN SPECIES #1505800		KCAHPO4 AQ
SO4	90.2	PERCENT BOUND IN SPECIES #	732	SO4
	8.8	PERCENT BOUND IN SPECIES #1507320		KCASO4 AQ
CA	97.3	PERCENT BOUND IN SPECIES #	150	CA
	1.6	PERCENT BOUND IN SPECIES #1501400		KCAHCO3 +
MN+2	96.4	PERCENT BOUND IN SPECIES #	470	MN+2
	2.9	PERCENT BOUND IN SPECIES #4701400		KMNHCO3 +
H2O	98.4	PERCENT BOUND IN SPECIES #3300020		K OH-
	1.6	PERCENT BOUND IN SPECIES #1503300		KCAOH +
MN+3	100.0	PERCENT BOUND IN SPECIES #	471	MN+3

E

N

2.2	PERCENT BOUND IN SPECIES #3305801	KH2PO4 -
66.6	PERCENT BOUND IN SPECIES #3301400	KHCO3 -
29.5	PERCENT BOUND IN SPECIES #3301401	KH2CO3 AQ

IDX	NAME	AQUEOUS MASS	SORBED MASS
		--------MOL/KG--------	
500	NA	3.000E-03	0.000E+00
140	CO3	3.000E-03	0.000E+00
180	CL	2.000E-03	0.000E+00
580	PO4	8.062E-05	0.000E+00
732	SO4	2.000E-05	0.000E+00
150	CA	9.676E-04	0.000E+00
470	MN+2	4.024E-30	0.000E+00
2	H2O	7.544E-08	0.000E+00
471	MN+3	5.106E-34	0.000E+00
1	E	0.000E+00	0.000E+00
330	H	3.660E-03	0.000E+00

CHARGE BALANCE: SPECIATED
SUM OF CATIONS = 4.895E-03 SUM OF ANIONS 4.581E-03
PERCENT DIFFERENCE = 3.311E+00 (ANIONS - CATIONS)/(ANIONS + CATIONS)
NONCARBONATE ALKALINITY = 0.000E+00
IONIC STRENGTH = : 5.730E-03

CODE VERSION: MINTEQK1A DATE OF CALCULATIONS: 19-DEC-89 TIME: 18:40:27

SATURATION INDICES FOR ALL MINERALS AND SOLIDS

ID	NAME	SAT INDEX	LOG K	MIN LOGK	MAX LOGK	LOG IAP	DN
6015000	ANHYDRITE	-3.453	4.590	0.000	0.000	-8.042	3.769
5015000	ARAGONITE	-0.890	8.292	0.000	0.000	-9.182	2.615
5015001	CALCITE	-0.736	8.446	8.528	0.000	-9.182	2.585
6015001	GYPSUM	-3.191	4.851	0.000	0.000	-8.043	-0.261
4150000	HALITE	-6.863	-1.571	0.000	0.000	-5.292	-0.918
6050001	MIRABILITE	-8.649	1.351	0.000	0.000	-10.000	-18.987
3050000	NATRON	-9.632	1.508	0.000	0.000	-11.140	-15.745
6050002	THENARDITE	-9.827	0.172	0.000	0.000	-9.999	0.572
5050001	THERMONATR	-11.299	-0.160	0.000	0.000	-11.139	2.802
2047000	PYROLUSITE	0.000	-16.226	0.000	-16.403	16.226	29.180
2047001	BIRNESSITE	-1.865	-18.091	0.000	0.000	16.226	0.000
2047002	NSUTITE	-1.278	-17.504	0.000	0.000	16.226	0.000
3047100	BIXBYITE	-24.728	0.420	2.035	0.239	-25.148	15.245
3047000	HAUSMANNITE	-51.577	-62.542	0.000	0.000	10.965	80.140
2047003	PYROCROITE	-30.916	-15.370	0.000	-15.663	-15.545	22.590
2047100	MANGANITE	-12.336	0.238	0.000	0.000	-12.574	0.000
5047000	RHODOCHROSIT	-25.184	10.384	10.993	9.967	-35.568	2.079
4147000	MNCL2, 4H2O	-37.507	-2.493	0.000	0.000	-35.015	-17.380
6047000	MNSO4	-37.291	-2.863	0.000	0.000	-34.429	15.480
6047100	MN2(SO4)3	-76.576	5.223	0.000	0.000	-81.799	39.060
7047000	MN3(PO4)2	-84.849	23.854	0.000	0.000	-108.702	-2.120
7047001	MNHPO4(C)	-21.179	25.400	0.000	0.000	-46.579	0.000
2015000	LIME	-22.534	-33.375	0.000	0.000	10.841	46.265
2015001	PORTLANDITE	-12.218	-23.059	0.000	0.000	10.841	30.690
5050007	TRONA	-15.246	11.475	11.586	0.000	-26.720	-8.440

7015003 HYDROXYAPATI	0.000	38.895	43.745	0.000	-38.895	38.924

VITA

Daniel Christodoss was born in Madras, India on May 17, 1957. He graduated with a B.S. in Civil Engineering from Madras University and M.S. in Civil-Public Health Engineering from Bharathiyar University. In May 1986, he emigrated to the United States to join his family. In fall of 1986, he began his graduate studies in Civil Engineering at the University of Tennessee, Knoxville. He graduated with a Doctor of Philosophy in Civil Engineering in August, 1990.

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