



The effect of corrosion control treatments and biofilm disinfection on unlined ferrous pipes
by Calvin Glenn Abernathy

A thesis submitted in partial fulfillment Of the requirements for the degree of Doctor of Philosophy in
Civil Engineering
Montana State University
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Abstract:

The occurrence of microbially related water quality problems has long been a concern to consumers and to water suppliers. Microbially related water quality problems are of particular interest because ferrous materials have been found to support larger populations of attached microorganisms (biofilms) even in the presence of disinfectants. These systems are now being required to implement corrosion control programs to reduce the quantities of lead and copper that leach from plumbing materials into the finished water. Many utilities have reservations about the implementation of a corrosion control program because most corrosion inhibitors contain phosphorus, which is an essential nutrient for microbial growth.

It is therefore the purpose of this research to investigate the numerous interactions between disinfectants (free chlorine and monochloramine) and several corrosion control methods and determine how they influence microbial growth in distribution systems.

To investigate these numerous interactions, studies were conducted using bench-scale and pilot-scale facilities, chemostats, and various other laboratory systems. Bench-scale facilities consisted of continuous flow annular reactors using unlined ductile iron or unlined mild steel materials. Pilot-scale facilities consisted of a 5-loop system of 4-inch mild steel pipe located at the Bozeman Water Treatment Plant. A series of experiments were conducted, using each type of facility, to evaluate the effect that various combinations of disinfectant and corrosion control treatments would have on distribution biofilms.

Results from these experiments have demonstrated that use of an effective corrosion control treatment will typically reduce microbial populations within the distribution system. Our studies have shown that corrosion products have a significant influence on the amount of microorganisms that a pipe material can support. Goethite (α -FeOOH), the most common corrosion product found in distribution systems, is of particular importance because it is able to adsorb and transform humic substances to more bioavailable forms, resulting in increased substrate for attached microorganisms. This study has demonstrated that an effective corrosion control program will reduce the amount of goethite formed on a ferrous pipe, and will consequently reduce the amount of bioavailable carbon on the surface and reduce habitat for problematic microorganisms.

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APPROVAL

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

The occurrence of microbially related water quality problems has long been a concern to consumers and to water suppliers. Microbially related water quality problems are of particular interest because ferrous materials have been found to support larger populations of attached microorganisms (biofilms) even in the presence of disinfectants. These systems are now being required to implement corrosion control programs to reduce the quantities of lead and copper that leach from plumbing materials into the finished water. Many utilities have reservations about the implementation of a corrosion control program because most corrosion inhibitors contain phosphorus, which is an essential nutrient for microbial growth.

It is therefore the purpose of this research to investigate the numerous interactions between disinfectants (free chlorine and monochloramine) and several corrosion control methods and determine how they influence microbial growth in distribution systems.

To investigate these numerous interactions, studies were conducted using bench-scale and pilot-scale facilities, chemostats, and various other laboratory systems. Bench-scale facilities consisted of continuous flow annular reactors using unlined ductile iron or unlined mild steel materials. Pilot-scale facilities consisted of a 5-loop system of 4-inch mild steel pipe located at the Bozeman Water Treatment Plant. A series of experiments were conducted, using each type of facility, to evaluate the effect that various combinations of disinfectant and corrosion control treatments would have on distribution biofilms.

Results from these experiments have demonstrated that use of an effective corrosion control treatment will typically reduce microbial populations within the distribution system. Our studies have shown that corrosion products have a significant influence on the amount of microorganisms that a pipe material can support. Goethite (α -FeOOH), the most common corrosion product found in distribution systems, is of particular importance because it is able to adsorb and transform humic substances to more bioavailable forms, resulting in increased substrate for attached microorganisms. This study has demonstrated that an effective corrosion control program will reduce the amount of goethite formed on a ferrous pipe, and will consequently reduce the amount of bioavailable carbon on the surface and reduce habitat for problematic microorganisms.

Chapter 1

Introduction

For the past 20 years, the United States government has been implementing drinking water regulations with the intent of reducing the health risk associated with drinking water. For the most part these regulations have focused on increased microbial disinfection, reducing the amount of disinfection by-products and reducing the leaching of lead and copper from distribution piping. In the years to come, new regulations will be promulgated that will not only lower the maximum contaminant levels (MCLs) of various disinfection by-products, but for the first time place a maximum limit on chlorine residuals found in distribution systems. In view of these new regulations, many utilities are concerned about maintaining chlorine residuals high enough to control biofilms and the possible impacts of increased microbial growth resulting from phosphorus based corrosion inhibitors.

Although the federal regulations have changed significantly in the past 20 years and will continue to change well into the next millennium, microbial biofilms will still be present in water distribution systems. Biofilms have been shown to be responsible for positive coliforms in water samples along with causing taste and odor complaints from consumers (LeChevallier, et al 1996; van der Wende and Characklis 1990; AWWA 1996). In the years to come, the water industry will be implementing numerous treatment changes to stay one step ahead of the

regulations. In many cases, utilities will be using a trial-and-error approach to stay in regulatory compliance without knowing the impact a treatment change may have on the biostability of the finished water. Some questions that are frequently pondered by water suppliers are:

- Will the addition of phosphorus based corrosion inhibitors increase microbial growth of distribution biofilms?
- Will lower chlorine residuals be able to effectively control microbial regrowth in the distribution system?
- Will chloramines be strong enough to control microbial regrowth events even though it is a weaker disinfectant?

In view of the above listed concerns, a better understanding is needed about the interactions between pipe materials, disinfectants, and corrosion inhibitors, on distribution biofilms. It is therefore the purpose of this thesis to investigate and discuss many of these interactions, and hopefully provide better guidance on how treatment changes may affect distribution system biofilms.

1.1 Goals and Objectives

The main goal of this work is to gain a better working knowledge of the interactions between pipe materials, organics, corrosion inhibitors and how each of these influence the disinfection of distribution biofilms. Since the complete inactivation of distribution biofilms is not possible, this thesis will focus on the effect that corrosion control treatments have on the control of biofilms on unlined ferrous pipes.

1.2 Experimental Approach

To investigate the numerous interactions between corrosion control treatments and the disinfection of distribution biofilms, a four-step approach was implemented. This approach consisted of (a) a comprehensive literature review, (b) bench-scale studies utilizing annular reactors, (c) pilot-scale studies, and (d) ancillary laboratory experiments. Results from these four steps brought to light several new relationships between corrosion products, bioavailable carbon, and distribution biofilms. Regulation or control of the formation rates of corrosion products may prove to be a key factor in reducing water quality problems associated with distribution biofilms.

Chapter 2

Literature Review

The removal or inactivation of microorganisms in potable water is perhaps the leading health concern of consumers. Although the inactivation and removal of microorganisms from the finished water leaving a water treatment plant may appear to be simple, maintaining low levels of microorganisms in the distribution system is seldom, if at all, accomplished even in the presence of a disinfectant residual. The presence of microorganisms in water distribution systems is widespread because the microorganisms are able to accumulate and colonize on the interior surfaces of drinking water pipes. Once attached, they develop a physical and chemical structure that enables them to modify the microenvironment of the pipe surface in a manner that allows them to optimize their metabolism and become highly resistant to disinfectants (Characklis and Marshall 1990; LeChevallier, et al 1988).

In consideration of the numerous water quality problems associated with microorganisms in water supply, a better understanding of how implementation of processes to meet the federal regulations influences distribution biofilms so that water suppliers can develop more efficient ways to minimize water quality problems. It is therefore the purpose of this chapter to: (a) discuss the federal regulations and (b) discuss the numerous interactions between pipe materials,

organics, disinfectants, corrosion control methods and how each of these components affect the formation and inactivation of distribution biofilms.

2.1 Regulatory Impacts

The 1986 and 1996 Safe Drinking Water Act (SDWA) Amendments will require many water utilities to modify current treatment and distribution practices. The goal of these regulations is to reduce the microbial and chemical health risk of the finished water by increasing disinfection efficacy along with reducing the concentrations of lead and copper, disinfection byproducts, and disinfectant residuals within the distribution system. Although these regulations will result in lower health risk, many utilities will use a trial-and-error approach to compliance, and may actually increase water quality problems associated with the presence of microorganisms in the distribution system if improperly addressed.

In view of the above, it is therefore the purpose of this section to discuss the existing and proposed SDWA regulations, and define how irrational implementation may result in increased microbial related water quality problems. Regulations that will be addressed will include the Surface Water Treatment Rule, Lead and Copper Rule, and the Disinfectant and Disinfection Byproduct Rule.

2.1.1 Surface Water Treatment Rule

The assumption in developing the Surface Water Treatment Rule (SWTR) was that surface waters and groundwater under the direct influence of surface

waters are at risk of contamination by *Giardia lamblia* and other protozoa, viruses, and pathogenic microorganisms (Bryant, et al 1992). The goal of this rule was to provide a minimum level of protection from illnesses caused by these organisms by specifying a minimum 3-log (99.9 percent) inactivation and/or removal of *Giardia* cysts and a 4-log (99.99 percent) inactivation and/or removal of enteric viruses prior to final distribution. The SWTR also established a minimum disinfectant residual (either free or total chlorine) of 0.2 mg/L entering the distribution system and requires each utility to maintain a detectable residual throughout the distribution system.

As a result of the SWTR, the microbial water quality supplied by water suppliers has improved, primarily from increased disinfection at the water treatment plant. Increased disinfection efficacy will minimize the possible "breakthrough" of microorganisms from the treatment system, and will likely reduce the quantity of microorganisms that enter the distribution system.

One possible adverse impact of the SWTR occurs when utilities increase disinfectant dosages or change primary disinfectants to comply with the "CT" requirements of the SWTR. In many cases it has been found that an increase in disinfectant dosage - particularly with the strong oxidants such as ozone, chlorine dioxide, and free chlorine - results in increased bioavailable organics in the finished water (Bryant, et al 1992). The increase of bioavailability of organics may result in increased microbial growth within the distribution system, even

though disinfection efficacy was increased at the water treatment plant. Additional information on this subject can be found in Section 2.4 of this chapter.

2.1.2 Lead and Copper Rule

The Lead and Copper Rule (LCR) was promulgated in June 1991 and requires utilities to maintain lead and copper concentrations at the consumer tap below an action level of 15 $\mu\text{g/L}$ and 1.3 mg/L respectively (AWWA 1992). In the event that the lead and/or copper levels exceed the specified action limit, the water supplier must implement a response plan that will minimize the leaching of lead and copper from pipes and plumbing fixtures. The response plan is typically to implement a corrosion control program that interferes with the corrosion process, resulting in reduced leaching of lead and copper from piping and plumbing materials.

A corrosion control plan typically includes the use of pH adjustment of the finished water with sufficient alkalinity to promote the coating of the interior surface of pipes and plumbing materials with calcium carbonate (CaCO_3), or by applying a corrosion inhibitor (AWWA 1992). The selection and implementation of corrosion control programs should be done with caution, because they can have an impact on both the formation of disinfection byproducts and possibly increase microbial growth in the distribution system (AWWA 1992). Of particular concern of these corrosion control techniques are: (a) the increase in total trihalomethane (TTHM) formation resulting from higher pH values (Symons, et al 1982) and (b) the fact that most corrosion inhibitors contain phosphorus which is

an essential nutrient for microbial growth (Brock, et al 1994). It has also been demonstrated numerous times that the implementation of a corrosion control program reduces biofilm densities (Schreppel and Geiss 1996; Lowther and Moser 1984). Discussions about how these corrosion control techniques may increase microbial related water quality problems are presented in Section 2.6 of this chapter.

2.1.3 Disinfectant and Disinfection Byproduct Rule

The proposed Disinfectant/Disinfection Byproduct Rule (D/DBPR) is expected to lower the current THM levels and establish many new limits on various other disinfection byproducts and disinfectants in the finished water. This rule will likely have the most dramatic impact on water quality because it will apply to almost all water suppliers, regardless of size, and for the first time establish a maximum disinfectant residual in the distribution system. In summary, the goal of the D/DBPR is to optimize the removal of organic carbon, minimize the formation of disinfection byproducts, and to minimize disinfectant dosages. The implementation of the D/DBPR will drastically reduce the chemical health risk associated with disinfection, but may also reduce both primary and secondary disinfection efficacies.

The implementation of the D/DBPR may cause widespread microbial water quality problems if not addressed properly by water suppliers. Perhaps the highest at risk are the smaller utilities that currently serve less than 10,000 people. These utilities do not have to comply with current TTHM limits, but will

soon be required to meet TTHM levels as low as 80 $\mu\text{g/L}$ and maintain disinfectant residuals less than 4 mg/L in the distribution system. Many of these utilities will struggle with coliform violations during the warmer months when microbial activity is at its highest level, and may not be able to control water quality problems with disinfectant residuals less than 4 mg/L and still comply with TTHM limits.

A second group of utilities that will possibly have adverse microbial water quality problems are those utilities that currently have TTHM levels between 80 and 100 $\mu\text{g/L}$. Many of these utilities will attempt to lower disinfectant residuals to reduce disinfection byproduct levels, only to result in reduced control of existing distribution biofilms.

A third group of utilities that may have problems with the delicate balance between disinfection byproducts and microbial inactivation will be the utilities that modify current primary disinfection practices by using more powerful disinfectants such as ozone or chlorine dioxide. The popularity of these powerful disinfectants is rapidly gaining because they are known to produce fewer regulated disinfection byproducts and are more effective at inactivating *Cryptosporidium*. (DeMers L.D. and Renner 1992; AWWA 1998). Although the use of these primary disinfectants will likely result in lower disinfection byproducts in the finished water, these disinfectants are known to increase the bioavailability of organics for downstream treatment processes or in the distribution system

(Pontius 1990; Langlais, et al 1991). Additional information on this subject can be found in Section 2.4 of this chapter.

2.2 Physical, Chemical and Biological Properties of Distribution Biofilms

Disinfectants such as free chlorine or monochloramine have been used for nearly 100 years to reduce microbial populations in potable water supplies. Both free chlorine and monochloramine can be highly efficient at inactivating microorganisms in the bulk fluid, but have been found to be up to 2400 times less efficient at inactivating distribution biofilms (LeChevallier, et al 1988; McMath, et al 1997; Geldreich 1996). Low inactivation efficacy of biofilms can be attributed to the physical and chemical properties of a biofilm which enable the microorganisms to accumulate nutrients and to develop resistance mechanisms to various disinfectants (Chen, et al 1993; van der Wende and Characklis 1990; LeChevallier, et al 1996; LeChevallier 1990; Geldreich 1996).

2.2.1 The Structure of Distribution Biofilms

In general, biofilms consists of four components. The first three components include a consortium of microorganisms, extracellular polymeric substances (EPS) excreted by the microorganisms, and water (Characklis and Marshall 1990). The fourth component can be classified as organic and inorganic particles that adhere to the EPS and may originate from the bulk fluid, the pipe surface, or from inactivated cells from within the biofilm (LeChevallier, et al 1996; LeChevallier 1990; van der Wende and Characklis 1990; LeChevallier, et al 1993). EPS production will vary in composition and quantity depending on

the bacteria present and may be influenced by environmental conditions (Koudjonou, et al 1997). The development and accumulation of these four components creates a variety of niches that favor the metabolisms of aerobic, facultative, and anoxic microorganisms (van der Wende and Characklis 1990; Geldreich 1996), EPS, and the accumulation of corrosion products and particulates exert a significant disinfectant demand and provides a shield that protects microorganisms from lethal levels of disinfectants (LeChevallier, et al 1996; van der Wende and Characklis 1990; Geldreich 1996; LeChevallier, et al 1993).

2.2.2 Types of Microorganisms Found in Distribution Biofilms

As result of the numerous niches formed within a biofilm, a distribution system can support a variety of microorganisms as described above. Microorganisms found in distribution biofilms may include coliforms, actinomyces, molds, fungi, nitrifying bacteria, iron oxidizing bacteria, sulfate reducing bacteria (SRBs), and possibly even *Giardia* cysts or *Cryptosporidium* oocysts (LeChevallier 1990; AWWA 1996; Geldreich 1996; Keevel 1997; Camper 1994). Possible water quality problems associated with these microorganisms are identified in Table 2.1.

Table 2.1 Problematic Microorganisms in Water Distribution Systems

Type of Microorganism	Infrastructure or Water Quality Problem
Coliforms	Positive samples may be a violation of the Total Coliform Rule for large utilities and a violation of the Total Coliform Rule for small utilities.
Actinomycetes, Molds, and Fungi	Produce earthy-musty-moldy taste and odor compounds. Commonly found in surface waters.
Iron Bacteria	Oxidize soluble iron to precipitate forms increasing the mass of corrosion products on pipe walls and pump casings. Excessive iron deposits causes increased pipe friction and lower pump efficacy.
Sulfate Reducing Bacteria (SRBs)	Reduces sulfate to hydrogen sulfide creating rotten egg taste and odor. Increases corrosion rates.
Nitrifying Bacteria	Oxidizes ammonia to nitrate. Consumes alkalinity, which may result in pH reduction.
Protozoans	Will not reproduce in biofilm, but may reside in biofilm.

2.3 Interactions Between Pipe Materials and Distribution Biofilms

Most water distribution lines constructed today utilize polyvinyl chloride (PVC), cement lined ductile iron, or prestressed concrete cylinder pipes (PCCP). However, prior to the 1940's when these modern materials were not universally available, most water distribution systems were constructed with unlined mild steel and unlined cast-iron pipes. Although these materials are seldom used today, they currently comprise about 22 percent of all distribution pipes in the

United States(LeChevallier 1997). For many of the larger water distribution systems (>50,000 people), the average age of the oldest section of the distribution system is typically greater than 50 years (Haas 1998). In view of this, it can be concluded that these distribution systems will have substantial quantities of unlined cast iron pipes. In many older cities, unlined cast-iron and unlined ductile-iron pipes may consist of more than 80 percent of the entire distribution system.

The materials used in water distribution systems appear to be one of the most important factors that influence the proliferation of distribution biofilms (Camper, et al 1996). In a recent survey (LeChevallier, et al 1996), it was found that water distribution systems that contain large quantities of unlined cast-iron and unlined ductile-iron pipes frequently experience problems with coliform violations and taste and odor complaints(LeChevallier, et al 1996; van der Wende and Characklis 1990; van der Kooij and Oorhuizen 1997). Researchers have also found that pipe materials support different quantities of microorganisms even when the influent water quality is the same for each material (Chen, et al 1993; Camper, et al 1996; Ollos, et al 1997; Delanoue, et al 1997). These researchers have documented that unlined mild steel, followed by unlined cast-iron, and unlined ductile-iron surfaces will support significantly higher biofilm densities than non-ferrous materials (LeChevallier 1997; Delanoue, et al 1997).

2.3.1 Pipe Material Properties

In consideration of the facts presented above, one must ponder why unlined mild steel, unlined cast-iron and unlined ductile-iron pipes are capable of supporting higher biofilm densities than non-ferrous materials. The answer to this question is likely to be related to the amount iron present in each material. A typical mild steel will contain approximately 99.12 percent iron by weight, while cast-iron and ductile-iron contain 93.18 and 92.66 percent respectively (Singley and Ahmadi 1985). Although the differences between these percentages may appear to be insignificant, the amount of exposed iron surface area is substantial when the specific gravity of the non-ferrous materials are taken into consideration. The exposed non-ferrous materials amount to 1.1 percent of the total area for mild steel and 17 and 18.5 percent for cast-iron and ductile-iron pipes, respectively (Singley and Ahmadi 1985). Exposed iron is critical because the formation of iron based corrosion products is directly related to release of dissolved Fe^{2+} from the pipe surface. Corrosion products exert a chlorine demand and can accumulate nutrients for the growth of microorganisms (van der Wende and Characklis 1990; LeChevallier, et al 1996; LeChevallier, et al 1993). Corrosion products are of interest because systems with significant quantities of corrosion product mass have been found to have substantially higher microbial densities (Rice, et al 1991; Herson, et al 1991; van der Kooij and Oorhuizen 1997; McMath, et al 1997; Crayton, et al 1997; Martin, et al 1982; LeChevallier, et al 1991; LeChevallier, et al 1993; Camper 1994).

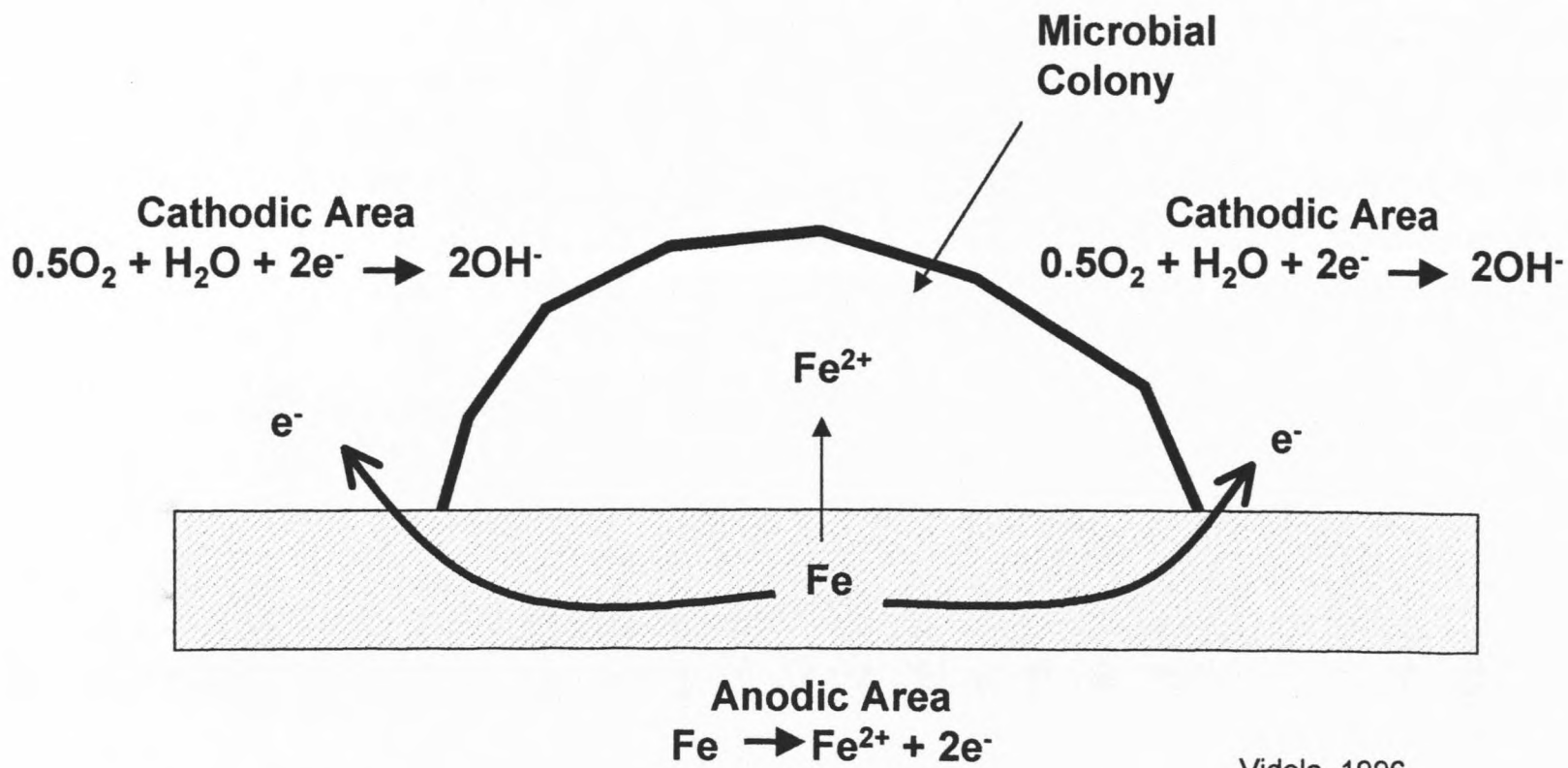
2.3.2 Formation of Corrosion Products

The formation of corrosion products in water distribution systems results from the release of Fe^{2+} ions from the pipe surface that react with various electron acceptors such as carbonate, oxygen, and free chlorine in the bulk fluid (Singley and Ahmadi 1985). Dissolved iron (Fe^{2+}) can be released from the pipe by either microbiologically influenced corrosion (MIC) or by chemical induced corrosion. MIC is caused by the chemical gradient that develops between the pipe surface beneath a microbial colony and the bulk fluid. The oxygen gradient creates an electrochemical cell that causes the pipe to release a Fe^{2+} ion and two electrons as illustrated in Figure 2.1 (Videla 1996).

Chemically induced corrosion is the result of an electrochemical potential differences between the ions present in the bulk fluid and the pipe surface, which promotes the release of the more thermodynamically stable form of iron (Fe^{2+}) and electrons from the pipe surface. Once Fe^{2+} is released, it reacts with various electron acceptors to form precipitated corrosion products, or chelates with organic compounds in the bulk fluid or the biofilm matrix (Gu, et al 1994; Parfitt, et al 1977; Benjamin, et al 1990; Weber 1988).

2.3.3 Physical/Chemical Properties of Corrosion Products

Goethite ($\alpha\text{-FeOOH}$) and magnetite (Fe_3O_4) are the most common types of corrosion products found on iron pipe surfaces in water distribution systems (Singley and Ahmadi 1985; Smith, et al 1996). The presence of goethite, the



Videla, 1996

Figure 2.1 Microbially Influenced Corrosion

most abundant corrosion product, is of interest because it is capable of adsorbing organics from the bulk fluid (Gu, et al 1994; Chang, et al 1997; Benjamin, et al 1993; Benjamin and Li 1997; Benjamin, et al 1990; Parfitt, et al 1977; Tipping and Cooke 1982; Characklis 1989). There have even been a few studies where iron oxides have been used as a filter medium to remove natural organic matter (NOM) from water supplies (Benjamin, et al 1993; Benjamin and Li 1997). Considering that corrosion products are iron oxides, the corrosion products on a pipe surface are capable of adsorbing organics from the bulk fluid, hence, providing a higher concentration of carbon on the pipe surface than in the bulk fluid (van der Wende and Characklis 1990). It is hypothesized that these adsorbed organics exert a substantial chlorine demand along with increasing the bioavailability of carbon substrates for microorganisms. The interactions between organics and corrosion products are discussed in more detail in Section 2.4.

2.4 Interactions Between Organics and Distribution Biofilms

The role and significance of organic compounds in drinking water is of concern because many are precursors for various disinfection byproducts such as THM's, and that many of the microorganisms present in distribution biofilms require the use of organic carbon for metabolism and/or cell synthesis (Camper 1994). This section will discuss the role of dissolved organic compounds typically found in finished water and discuss how they influence the formation of distribution biofilms.

2.4.1 Types of Organics in Finished Water

The amount of total organic carbon (TOC) in finished water is often used as a measure for appraising a water's potential to form disinfection byproducts and to support microbial growth in the distribution system. In many situations this appraisal works reasonably well for assessing the disinfectant byproduct potential of a water, but can be inaccurate for predicting a water's ability to promote excessive growth of microorganisms in the distribution system. The shortfall of using TOC as an indicator of a water's ability to support biofilms is that only a small fraction of TOC can be used as a carbon source for microbial growth and energy (Geldreich 1996). This small amount of TOC can be classified as the bioavailable portion of TOC, and will change after rain events and seasonally (Trussell 1998). In view of this, it is possible to have a decrease in TOC and have an increase in bioavailable carbon in the distribution system.

In an attempt to quantify the bioavailable portion of TOC, several researchers have developed methods that measure the bioavailability of carbon in water. Results from these studies can be used to assess a water's potential to support microorganisms in the distribution system. These methods utilize bioassays and are defined as the biodegradable organic carbon (BDOC) and assimilable organic carbon (AOC). An overview of these bioassays are described by Huck and Camper (Huck 1990; Camper 1994).

The BDOC is that portion of the TOC in water that can be mineralized by heterotrophic microorganisms (Camper 1994). BDOC can be determined by

measuring the difference in TOC between the influent and effluent of a packed bed bioreactor (Lucena, et al 1990). The change in TOC is defined as the BDOC and is typically less than 0.6 mg/L and may be less than 0.1 mg/L for a high quality water. Due to the low levels of BDOC, the accuracy of TOC equipment must be very high and all glassware must be thoroughly cleaned to obtain statistically reliable results.

The AOC has been defined as the portion of BDOC that can be converted to cell mass and is expressed as $\mu\text{g/L}$ acetate equivalents (van der Kooij and Hijnen 1984). The procedure to measure biomass production uses prepared cultures of *Pseudomonas fluorescens* (P17) and *Spirillum* (NOX) (van der Kooij and Hijnen 1984). The procedure is time consuming and can take up to 20 days to obtain results. This procedure is considered by many to be excessively labor intensive and may not be entirely representative of the bioavailable carbon, because it only uses two specific microorganisms which may not have similar metabolisms as the microorganisms in the distribution system.

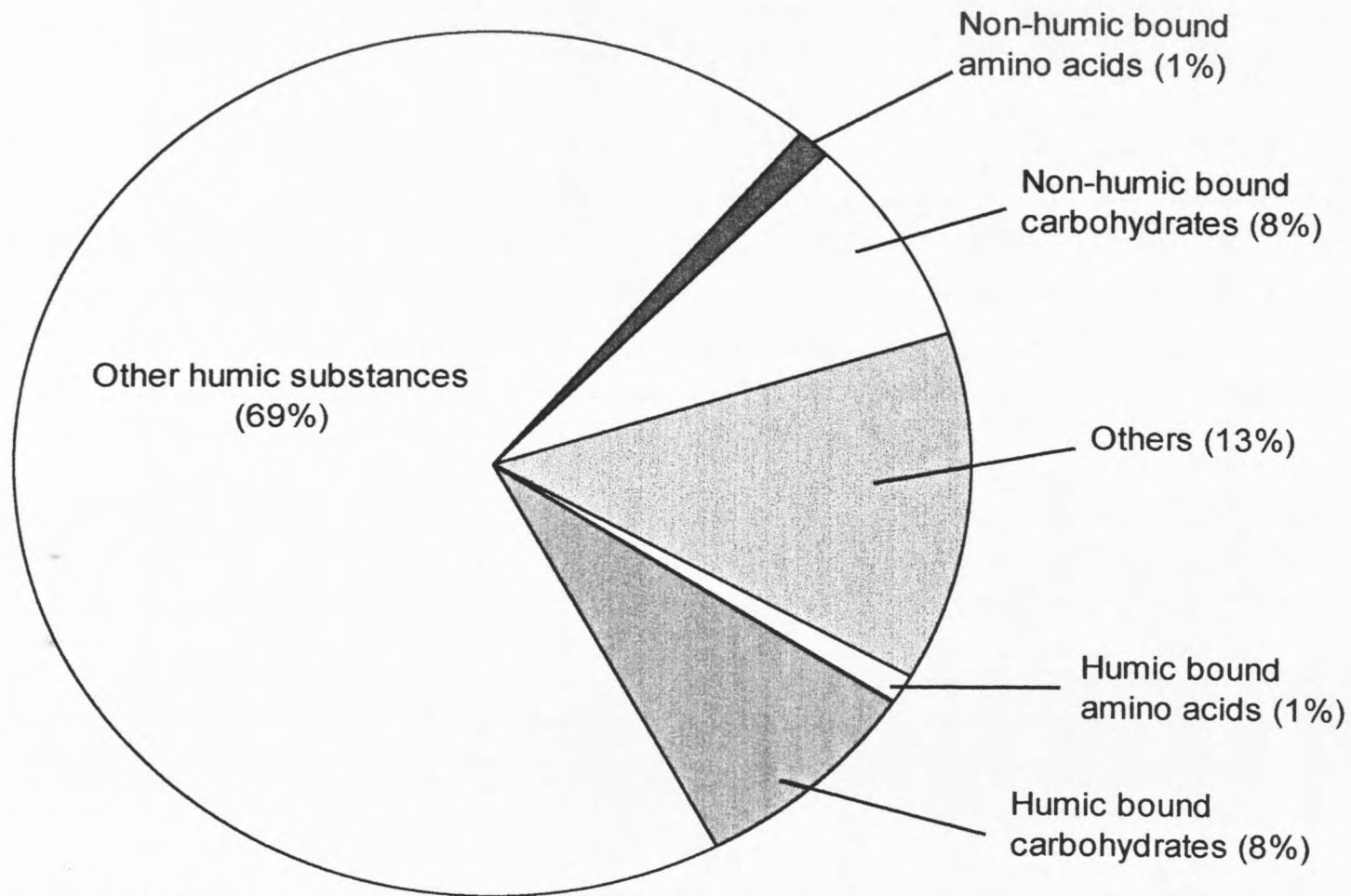
Many researchers and water suppliers have used these to determine relationships between BDOC and AOC concentrations and the occurrence of coliforms in distribution samples. These studies have found that AOC levels greater than 10-15 $\mu\text{g/L}$ typically supported heterotrophic microbial growth in distribution systems (van der Kooij 1992), while AOC levels greater than 50 $\mu\text{g/L}$ always supported heterotrophic growth (LeChevallier 1990; Laurent, et al 1997).

It has also been shown that some coliforms are unable to grow in waters containing AOC concentrations less than 50 $\mu\text{g/L}$ (LeChevallier 1990).

In view of the above, it is clear that the amount of bioavailable carbon present in the bulk fluid may have a profound affect on a water's biostability. However, as addressed in the Section 2.3 and in the concluding sections, the biostability of a water should be based on numerous factors that include material composition of the substratum, organics, disinfectant type and residual, and ions present in the finished water (Laurent, et al 1997; Trussell 1998).

To obtain a better working knowledge of BDOC and AOC, the types of organics that are utilized by microorganisms in water distribution systems must be considered. The types of organics commonly found in finished water include humic and non-humic substances. Typically, up to 90 percent humic substances are fulvic acids, with the remaining components consisting of humic acids and humin (Benjamin, et al 1993; Beckett 1990; Chang 1992). The non-humic substances may include carbohydrates, proteins, and lipids (Ollos, et al 1997).

As illustrated in Figure 2.2, humic substances and humic-bound organics comprise the majority of organics found in a finished water (Kaplan, et al 1994). Humic substances are naturally occurring organic materials that result from the decomposition of vegetative material and residues (Benjamin, et al 1993; Lovley, et al 1996; Stumm and Morgan 1996; Owen, et al 1993). They are long-chain molecules having molecular weights ranging from 500 to 5,000 g/mole (Stumm and Morgan 1996). In the bulk fluid, humic substances are found in tightly coiled



Kaplan 1994

Figure 2.2 Major Groups of TOC Available for Microbial Growth in Drinking Water

structures, which decreases their bioavailability to suspended microorganisms (Chang 1992). However, there are several physical/chemical pathways that are capable of transforming the structure of humic substances to forms that increase the bioavailability of these compounds, resulting in an increase in BDOC and AOC levels without an increase in TOC.

2.4.2 Transformation of TOC Bioavailability by Disinfectants

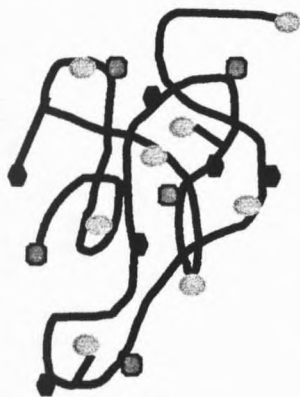
The use of disinfectants to inactivate pathogens and control microbial water quality is widespread in most of the world. Disinfectants such as ozone, chlorine dioxide, and free chlorine are used in water treatment processes for a variety of reasons. Although these disinfectants can be highly efficient at inactivating suspended microorganisms, they also react with various organic and inorganic compounds present in the water. The reactions of these disinfectants with humics substances are of concern because; (a) they may lead to the formation of trihalomethanes, and (b) they may transform the structure of humics to smaller more bioavailable molecules (Bryant, et al 1992). As a result, the BDOC and AOC levels increase, perhaps leading to elevated microbial growth in the distribution system (Volk, et al 1997; van der Kooij, et al 1998). The transformation of TOC to a more bioavailable form by disinfectants provides one explanation of why the addition of a disinfectant sometimes increases microbial populations in downstream processes or in the distribution system.

2.4.3 Transformation of TOC Bioavailability by Corrosion Product Adsorption

Adsorbed humic substances is perhaps the most overlooked component of corrosion products. Humic substances are some of the most powerful metal-binding agents found in natural organic matter (NOM) (Glaus, et al 1995). The mechanisms by which humic substances adsorb to corrosion products have been proposed to involve: (a) anion exchange, (b) ligand exchange-surface complexation, (c) hydrophobic interaction, (d) hydrogen bonding, (e) cation bridging, and (f) electrostatic interactions (Gu, et al 1994; Glaus, et al 1995; Varadachari, et al 1997; Chang 1992; Stumm and Morgan 1996; Kummert and Stumm 1980; Davis 1982; Weber, et al 1983; Tipping 1981; Tipping and Cooke 1982; Parfitt, et al 1977; Tipping, et al 1981).

The most common adsorption mechanism is thought to be ligand exchange between the hydroxyl (OH^-) molecule of goethite ($\alpha\text{-FeOOH}$) and the carboxylate groups (COO^-) of humic substances as illustrated in Figure 2.3 (Parfitt, et al 1977; Gu, et al 1994; Varadachari, et al 1997; Chang, et al 1997). Once adsorbed, humic substances collapse on the surface, allowing for maximum points of interaction and ligand exchange with goethite (Gu, et al 1994; Chang 1992; Stumm and Morgan 1996). As a result of this collapse, the humic molecules becomes uncoiled, increasing the bioavailability of sugars and peptides previously unavailable to microorganisms (Gu, et al 1994). The tails of the adsorbed humic substances may also bond with other humic molecules in the bulk fluid, increasing the mass of humics at the corrosion product-bulk fluid

Humic Substance in Bulk Fluid



- sugar
- ◆ peptide
- carboxylate

Humic Substance Reacting with Goethite

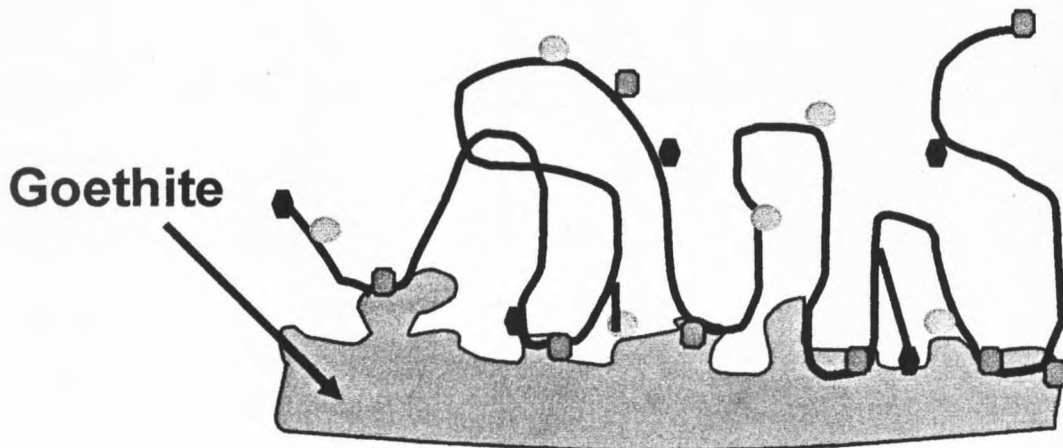
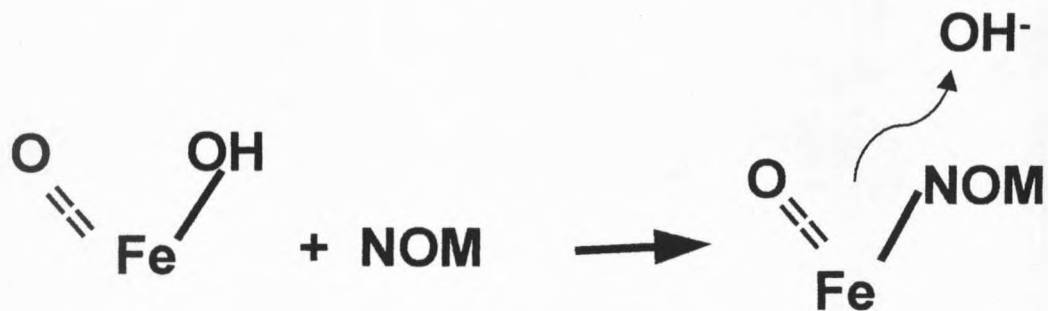


Figure 2.3 Humic Substance Interaction with Iron Oxides

interface (Gu, et al 1994), and once again increasing the bioavailability of organics for microorganisms.

Adsorbed carbon on corrosion products is likely to produce the highest concentration of bioavailable carbon in the water distribution system. As with other systems, a large portion of the adsorbed organics are irreversibly attached while others are loosely attached (Gu, et al 1994). The detachment of these loosely bound humics can be enhanced by surfactants that are excreted by many microorganisms commonly found in distribution biofilms (Georgiou, et al 1992). The increased solubility of these organics by microbial surfactants represents another pathway a biofilm system uses to increase the bioavailability of organic carbon.

As illustrated in the preceding paragraphs and summarized in Figure 2.4, the transformation of bound organic carbon to bioavailable forms has numerous pathways. In view of the pathways that occur within the biofilm/corrosion product matrix, it can be concluded that analytical techniques such as BDOC and AOC will underestimate the amount of bioavailable carbon that can be used as a carbon substrate by biofilms.

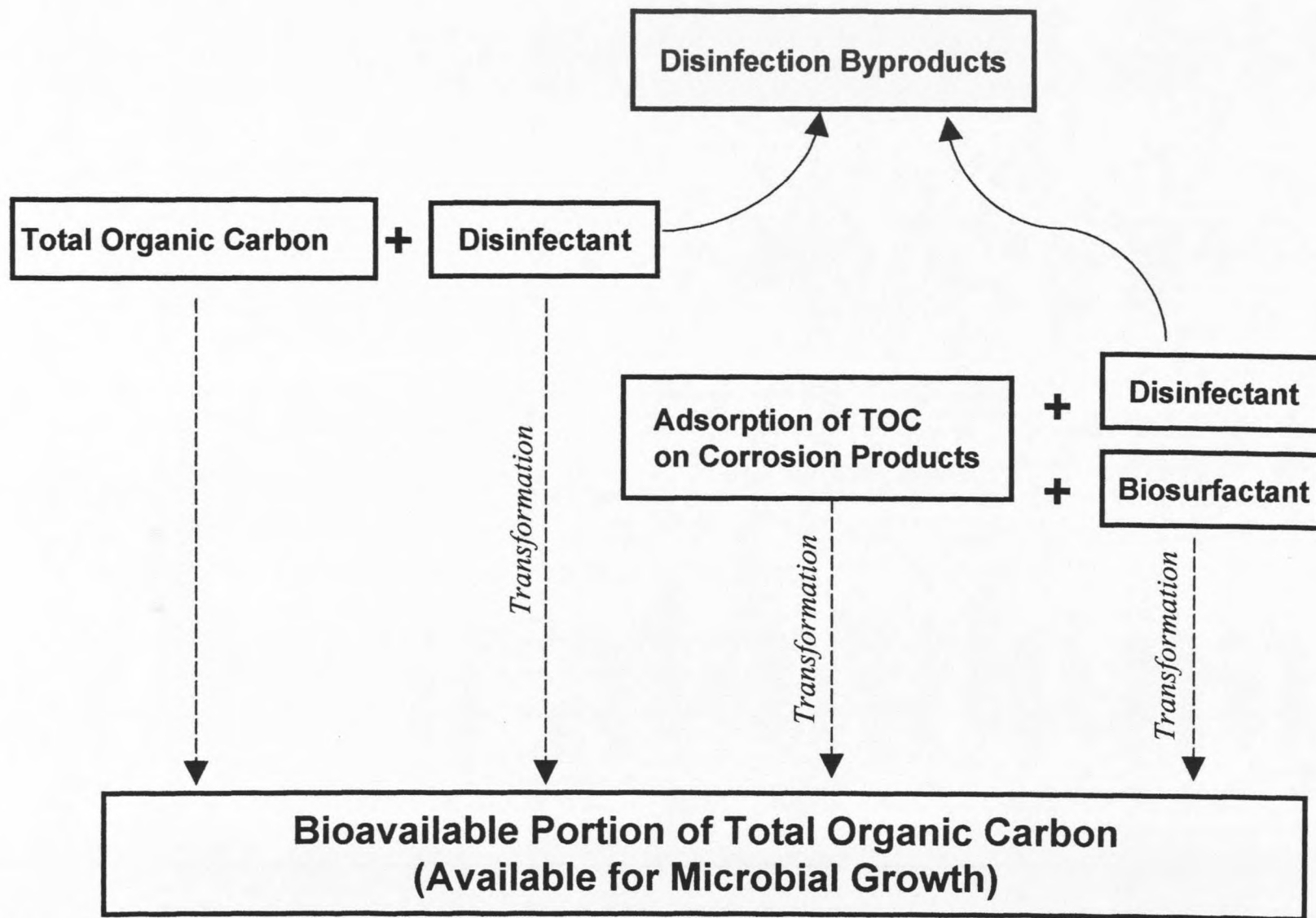


Figure 2.4 Biotransformation Pathways of Total Organic Carbon

2.5 Interactions Between Disinfectants and Distribution Biofilms

Secondary disinfectants have been used in the United States to provide protection against cross-connections and to control the growth of microorganisms in the distribution system. Although most water systems maintain detectable disinfectant residuals throughout the distribution system, biofilms continue to grow and create water quality problems. The presence of biofilms promotes positive coliform occurrences in water samples and cause taste and odor complaints from consumers.

Free chlorine and monochloramine are the most commonly used secondary disinfectants in the United States (Bryant, et al 1992). In most cases, these disinfectants are capable of minimizing the occurrence of coliforms, but neither has been able to completely eliminate the presence of biofilms in the distribution system. The disinfection efficacy of these two disinfectants is different for cell inactivation in the bulk fluid versus the attached microorganisms within the biofilm/EPS/corrosion product matrix. Free chlorine is considered to be the superior disinfectant for inactivating microorganisms in the bulk fluid, but monochloramine, a weaker disinfectant, is typically the superior disinfectant for inactivating biofilms (Olson 1996; Ollos, et al 1997; Griebe, et al 1994; Srinivasan, et al 1995). To explain why a weaker disinfectant is superior at inactivating biofilms, the reactivity of disinfectants in the bulk fluid and biofilms must be taken into consideration.

2.5.1 Microbial Inactivation in the Bulk Fluid by Disinfectants

The mechanisms of disinfectants on bulk fluid microorganisms have been known for many years. Microorganisms that are suspended in the bulk fluid are exposed to disinfectants from every possible angle (LeChevallier, et al 1988). As a result of this exposure, the disinfectant with the highest oxidizing strength will be quickest and most efficient disinfectant. In view of this, free chlorine has been found to be the most efficient bulk fluid secondary disinfectant, because it is a stronger oxidant than monochloramine, although the disinfection kinetics will vary depending on: (a) type of microorganism, (b) age of microorganism, and (c) the nutrient concentrations of the bulk fluid (LeChevallier, et al 1988; Carson, et al 1972).

The differences in efficacy between these two disinfectants can be attributed to the reactivity of the disinfectant with the specific components of the cell wall of a microorganism. Free chlorine will oxidize virtually every component of a bacterial cell, which results in a quick destruction of the cell wall. Monochloramine reacts specifically with nucleic acids, tryptophan, and sulfur-containing amino acids and is not known to react with EPS or sugars which results in a much slower death (van der Wende and Characklis 1990; LeChevallier 1997). The slow reactivity of monochloramine is the reason why it is seldom recognized as a primary disinfectant (Olson 1996).

2.5.2 Disinfection of Distribution Biofilms

The objective of an effective biofilm disinfection scheme is to provide a lethal concentration of disinfectant to inactivate attached microorganisms. This is seldom accomplished in a distribution biofilm because of the mass transfer limitations created by the EPS and corrosion products that embed the microbial cells of a biofilm (LeChevallier 1990; Chen and Stewart 1996; LeChevallier, et al 1991). This section will present information on the causes of mass transfer limitations and discuss how biofilms resist disinfectants.

Overcoming mass transfer limitations is the key to minimizing the presence and problems caused by distribution biofilms. These mass transfer limitations are the result of fast consumption of the disinfectant near the surface of the biofilm/bulk fluid interface along with diffusion restrictions caused by corrosion products and EPS (van der Wende and Characklis 1990; Koudjonou, et al 1997; Martin, et al 1982; LeChevallier, et al 1993; Srinivasan, et al 1995; DE Beer, et al 1994). The reaction limitation is caused by the consumption of chlorine with EPS, corrosion products, and the numerous organics adsorbed to the corrosion products (Gatel, et al 1998; Srinivasan, et al 1995; Koudjonou, et al 1997). The consumption of chlorine by these components and the diffusion limitation caused by the porosity of these components severely restricts the penetration of a lethal dose of chlorine to the inner core of a corrosion tubercle. The inner core region of a corrosion tubercle is thought to be void of oxygen,

creating a niche for microorganisms such as coliforms and sulfate reducing bacteria (SRBs) (Lovley, et al 1996; AWWA 1996; LeChevallier, et al 1993).

To overcome diffusion/reaction mass transfer limitations, many utilities have attempted to increase the disinfectant residual in the bulk fluid, which enables the disinfectant to penetrate deeper into the biofilm/corrosion product matrix. This approach has worked for a number of systems, but may not be an acceptable solution if TTHM concentrations exceed allowable levels. LeChevallier (LeChevallier 1990) summarized numerous cases where utilities increased chlorine residuals and were not successful at reducing coliform levels in water samples. To complicate matters, the proposed Disinfectant/Disinfection Byproduct Rule (D/DBPR) will for the first time establish a maximum disinfectant residual in the distribution system of 4 mg/L and will lower allowable TTHM levels from 100 $\mu\text{g/L}$ to 80 $\mu\text{g/L}$.

Another approach to overcoming these diffusion/reaction limitations is to use a disinfectant that is not as reactive with EPS, organics, and corrosion products. Many researchers and utilities have found that monochloramine closely fits these criteria and has been successfully implemented in numerous cases (LeChevallier, et al 1996; LeChevallier 1997; Camper, et al 1997; Griebe, et al 1994). Monochloramine has about the same diffusivity as free chlorine and is not as reactive with organics, EPS, or corrosion products (LeChevallier 1990; van der Wende and Characklis 1990). The low reactivity of monochloramine enables it to penetrate deeper in the biofilm/corrosion product matrix and provide

a higher degree of biofilm inactivation (LeChevallier 1990). The lower reactivity of monochloramine also allows utilities to more easily maintain higher disinfectant residuals in the outer extremes of the distribution system without producing significant levels of TTHMs (LeChevallier 1997).

As previously discussed, the use of disinfectants can actually increase the bioavailability of organics in the bulk fluid and in the biofilm/corrosion product matrix. At low disinfectant residuals the diffusion/reaction limitations restrict the penetration of the disinfectant to the extreme depths of the biofilm/corrosion product matrix. The reactivity of the disinfectants with corrosion products and other matter creates increased chloride levels, which have been shown to accelerate corrosion (Videla 1996; Singley and Ahmadi 1985). As a result, the combination of these mechanisms creates a system that becomes self-sustaining for microorganisms within the biofilm/corrosion product matrix.

Although the use of disinfectants can cause an increase in corrosion product formation, there will be a disinfectant residual level in which the diffusion/reaction limitations are exceeded, enabling the disinfectant to penetrate deeper in the biofilm/corrosion product matrix. The deeper penetration increases the inactivation of microorganisms resulting in a decrease in biofilm density. This disinfectant level can be defined as the threshold residual and will change dependent on the pipe material and water quality.

2.6 Interactions Between Corrosion Inhibitors and Distribution Biofilms

Corrosion control has been used in industry for a number of years to minimize the impact of corrosion related water quality problems, extend the useful life of pipe materials, and to reduce energy requirements in pump/pipeline systems. In the drinking water industry, corrosion control is used to minimize the leaching potential of lead and copper into the finished water as required by the Lead and Copper Rule (AWWA 1992). In most cases, water utilities use either corrosion inhibitors or pH adjustment as a method of corrosion control. This research will focus on the use of two corrosion inhibitors (zinc orthophosphate and polyphosphate) and pH adjustment and evaluate how each may affect the formation of distribution biofilms.

2.6.1 Adverse Water Quality Concerns Caused by Corrosion Control Methods

There are several water quality changes associated with the implementation of a corrosion control program. These water quality changes may lead to conditions that may result in increased levels of microorganisms in the distribution system. These problems are associated with the reduced disinfectant efficacy of free chlorine at high pH values, and the possible increase microbial growth by the addition of phosphorus based corrosion inhibitors.

Utilities that use pH adjustment as a corrosion control method face two potential water quality problems. These problems include: (a) increased TTHM levels and, (b) reduction in disinfection efficacy of free chlorine. Increases in

TTHM levels may occur after pH adjustment because the formation rate of TTHM typically increases with increasing pH (Symons, et al 1982). Although TTHM increases may not be substantial, even a small increase may cause some utilities to be in violation of the current or future TTHM limits. Another problem with pH adjustment may be the reduced disinfection efficacy of free chlorine at higher pH values (Snoeyink and Jenkins 1980; AWWA 1998; Pontius 1990; Montgomery 1985). This is the result of a shift in equilibrium between hypochlorous acid (HOCl) and hypochlorite ion (OCl⁻) (Stumm and Morgan 1996; Pontius 1990; Snoeyink and Jenkins 1980; AWWA 1998). At pH values below 7.50, free chlorine is a stronger disinfectant because most of the free chlorine is in the form of HOCl. At pH values above 7.50, OCl⁻ a much weaker disinfectant is the dominant species, resulting in lower disinfectant demands but a less efficient disinfectant.

The use of corrosion inhibitors is also of concern to water suppliers because most are phosphorus based. Phosphorus is an essential nutrient for microbial growth. The fear of phosphorus originates from the wastewater industry where phosphorus is the limiting nutrient for phototrophic (use light as an energy source) microorganisms such as algae. Since distribution biofilms are carbon limited (LeChevallier 1990; Camper, et al 1996), the addition of phosphorus will seldom result in increased microbial levels, unless the finished water is phosphorus limited (Haas, et al 1988) or exposed to sunlight in uncovered finished water reservoirs (LeChevallier, et al 1996). It has also been found that

the total organic carbon increases downstream of uncovered finished water storage reservoirs (LeChevallier, et al 1996). The increase in TOC is likely the result of endogenous respiration and decay of phototrophic microorganisms once they enter the light-free distribution system.

Another possible concern about the use of zinc orthophosphate is the presence of zinc in wastewater effluents (Geldreich 1996). Zinc levels in wastewater effluents, in many cases, limits the dose of zinc orthophosphate in the drinking water. If the zinc orthophosphate dose is not adequate, the user is required to change to a different corrosion control program to maintain compliance with the Lead and Copper Rule. As a result of these problems, several corrosion inhibitor manufacturers have changed the formulation of zinc orthophosphate, so that it now contains less zinc.

2.6.2 Mechanisms of Corrosion Control Methods

The process of corrosion is a natural chemical reaction where elements in the pipe material are transformed to a more thermodynamically stable state. Corrosion can be minimized by reducing the rate at which ions such as Fe^{+2} , lead, and copper are released from the pipe surface. Corrosion control can be accomplished by making it more difficult for these molecules to either approach or vacate the vicinity of a cathode and anode, or by altering the electrical potential of the surface (Benjamin, et al 1990).

The two most common mechanisms that can be implemented to interfere with the corrosion process are (a) coating the surface with a compound that limits the transport of molecules from the pipe surface, or (b) altering the surface chemistry of the pipe. The first mechanism is defined as precipitation, while the latter is defined as passivation. Both mechanisms are discussed in the following paragraphs.

The most commonly practiced precipitation method is accomplished by controlling the pH of the finished water. In the pH adjustment method, the pH of the bulk fluid is raised to a level that saturates the water with calcium carbonate (CaCO_3) provided that adequate alkalinity and calcium is present. Once saturation is reached, the pipe surface is coated with a layer of CaCO_3 , which forms a diffusion-limited barrier between the pipe surface and the bulk fluid. The diffusion-limited barrier minimizes the release rate of Fe^{+2} molecules from the pipe surface, hence, reducing the corrosion rate. This process is controlled by maintaining a near zero Langelier Saturation Index (LSI), which is a measure of the number of pH units away from the saturation pH of CaCO_3 (Pontius 1990; Singley 1981; Singley and Ahmadi 1985). The LSI can be determined by a variety of spreadsheet programs. (Trussell 1998; Holm and Schock 1998) pH adjustment, with sufficient alkalinity, can also stabilize monochloramine residuals in the distribution system.

Another possible benefit of pH adjustment is that some microorganisms are inhibited by pH. Provided that the pH required to achieve CaCO_3

precipitation is high enough to inhibit microorganisms, a reduction in microbial populations may result. This may be particularly attractive if commonly found coliforms, such as *Klebsiella pneumoniae*, are inhibited by high pH levels. *Klebsiella pneumoniae* is commonly found in soils and is known to remove iron from solution by attacking the organic portion of iron-organic molecules (Alexander 1977). It has also been found that *Klebsiella pneumoniae*, the most common coliform found in water distribution systems (Geldreich 1996), is inhibited by pH values above 9.0 (Martin, et al 1982). In view of this inhibition, many utilities that have old pipes with poor joints, high water tables, and water hammer problems (LeChevallier 1998) may find pH adjustment as an attractive management approach to minimize the growth and survival of *Klebsiella pneumoniae* in the distribution system. It is therefore possible that pH adjustment will not only minimize leaching of iron, lead and copper, but also selectively inhibit the growth of commonly found coliforms in distribution systems.

Most of the corrosion inhibitors used today utilize passivation to minimize the corrosion rate. This process forms a chemical scale on the pipe surface mainly from the reaction of phosphate (PO_4) with Fe^{+2} and Fe^{+3} molecules to form a Fe-PO_4 . The FePO_4 film is a more thermodynamically stable form of corrosion product, and is not easily converted to other forms of corrosion products that have carbon adsorption capabilities. The presence of this film on the pipe surface develops a protective stable layer that minimizes the diffusion rate of Fe^{+2} from the pipe surface, hence, reducing the corrosion rate.

The use of corrosion inhibitors may also cause short-term coliform problems in the distribution system. These problems are the result of the action of phosphates on existing corrosion tubercles and the formation of FePO_4 at the pipe surface. As a result of the PO_4 interactions, the cohesive strength of corrosion tubercles are much lower, resulting in rapid sloughing (Geldreich 1996). Since coliforms are frequently found in these corrosion tubercles, coliform excursions may be experienced. Frequent flushing and controlled increases of disinfectant residuals may minimize the impact of these sloughing events soon after the addition of the corrosion inhibitor (Geldreich 1996).

As discussed above, the use of corrosion control practices such as pH adjustment and phosphorus based corrosion inhibitors change the type of corrosion products normally found on pipe materials. The use of these corrosion control methods will reduce the amount of goethite ($\alpha\text{-FeOOH}$) formed along with changing the electrostatic surface characteristics of these materials. The electrostatic surface charge is of significance because the charge regulates the rate of adsorption of humic substances to the pipe surface (Stumm and Morgan 1996; Chang 1992; Beckett 1990) along with the electrostatic adhesion of microorganisms to the surface (Stumm and Morgan 1996).

2.6.3 Use of Corrosion Indices

For many years, researchers have attempted to develop an index that will quantify the interactions between a pipe material and finished water that result in corrosion. Since it has been found that systems with high corrosion rates and

unlined pipe typically have biofilm related water quality problems, the use of a corrosion index could be a valuable tool to evaluate the efficacy of a corrosion control program. Indexes commonly used include the Langelier Saturation Index (LSI)(Singley 1981; Pontius 1990; Singley and Ahmadi 1985; LeChevallier, et al 1993), Riddick Index (RI)(Singley 1981; Pontius 1990), and the Larson Index (LI) (Singley 1981; Pontius 1990; Singley and Ahmadi 1985). These indexes may be used to estimate a water's corrosion potential prior to the implementation of a corrosion control program. However, they should not be used to evaluate the effectiveness of a corrosion inhibitor. An evaluation of each index will be discussed in the following paragraphs.

The Langelier Saturation Index (LSI) is probably the most used and improperly used index in the water industry. The LSI is an indicator for the saturation of CaCO_3 in a water. The LSI should be used to determine if CaCO_3 is precipitating on the pipe surface and not be used if a corrosion inhibitor is present. LSI should also be used with caution if high levels of sulfate (SO_4^{2-}) are present, because the formation of CaSO_4 will lead to inaccurate results (Singley 1981) and an ineffective corrosion control program. Use of LSI should also be avoided in very soft-low alkalinity water, because it is well known that these waters cannot be supersaturated with CaCO_3 , regardless of how high the pH is raised (Singley 1981).

The Riddick Index (RI) is an empirical equation that considers many factors that contribute to corrosion. This index provides values that can be used

to quantify the corrosion potential of a water. The empirical equation is as follows (Pontius 1990):

$$RI = \frac{75}{Alk} \left[CO_2 + \frac{1}{2} (hardness - Alk) + Cl^- + 2NO_3^- \left(\frac{10}{SiO_2} \right) \left(\frac{DO+2}{DO_{sat}} \right) \right] \quad (1)$$

where hardness and alkalinity (ALK) are in mg/L as CaCO₃, NO₃ is in mg/L as nitrogen, and the remaining parameters in mg/L (Singley 1981; Pontius 1990). Values of RI less than 25 indicate noncorrosive water, 26 to 50 indicate a moderately corrosive water, 51 to 75 a corrosive water, and values greater than 75 very corrosive water (Singley 1981; Pontius 1990). The use of the RI should be limited to soft water (Singley 1981), and should not be used to evaluate the efficacy of a corrosion inhibitor, because it does not take into consideration the effects of the passivating properties of phosphate.

The Larson Index (LI) has been used by a number of utilities as a measure of corrosion potential (LeChevallier, et al 1991; LeChevallier, et al 1993). This index evaluates the effects of chlorides (Cl⁻), sulfates (SO₄⁼) and bicarbonate (HCO₃⁼) on corrosion (Pontius 1990; Singley 1981). Chlorides have been found to break down passive films (Videla 1996), while sulfate levels create a high potential for microbially influenced corrosion by sulfate reducing bacteria. The Larson Index (LI) can be determined by evaluating the following equation where all concentrations are expressed in moles/L.

$$LI = \frac{[Cl^-] + 2[SO_4^-]}{[HCO_3^-]} \quad (2)$$

German regulations (DIN 50930, 1980) recommend that the LI be less than 1.0 (Singley and Ahmadi 1985). Researchers from the American Water Works Service Company, Inc. have also found that monochloramine was more effective with a LI less than 1.0, while free chlorine was much less efficient at inactivating biofilms at LI greater than 0.5 (LeChevallier, et al 1991; LeChevallier, et al 1993).

The use of the Larson Index can provide a indication of long-term effects of corrosion and as an indicator for determining disinfection efficacy. However, as with the previous indexes, it does not provide any information about the formation of passivating films of corrosion inhibitors, and it also does not address the precipitation formation of CaCO_3 .

2.7 Biofilm Modeling Systems

The use of computer models to mathematically simulate dynamic systems has been widespread for the past 15 years. The use of these models has provided substantial advances in decision-making, design, and rapid evaluation of numerous chemical and/or biological systems. These models are capable of simulating many complex conditions using a variety of analytical and numerical techniques. The accuracy of these models is limited to systems with respect to the microbial community, reactor configuration, kinetic expressions, and substrate concentration ranges for which they were designed. (Wanner and Gujer 1986)

2.7.1 Requirements of a Biofilm Model

As stated above, it is essential that a model be capable of accurately portraying the numerous physical, chemical, and biological reactions that occur within the system to be modeled. This is particularly true for the complex interactions that occur within bulk fluid and biofilm systems. Systems that need to be accounted for in an oligotrophic biofilm model include: (a) the physical, chemical and biological activity in the bulk fluid, (b) external mass transfer resistance between the bulk fluid and the biofilm, (c) detachment of microorganisms from the biofilm to the bulk fluid, (d) diffusion of disinfectants, and nutrients into the biofilm, (e) chemical and biological reactions within the biofilm, (f) physical and chemical reactions with inorganic compounds within the biofilm/corrosion product matrix, and (g) the physical and chemical reactions that occur between the biofilm and the substratum (Characklis and Marshall 1990; Weber and DiGiano 1996).

Incorporation of these criteria will likely result in a model for many systems, provided that: (a) the biological and chemical kinetics, (b) absence of unaccounted for inorganic materials such as corrosion products, and (c) water quality conditions (both biological and chemical), are nearly constant. The accuracy of a model is determined by comparing the results of the model with data from a prototype or full-scale system.

2.7.2 Deficiencies of Existing Biofilm Models

As previously discussed, many biofilm models can be used to accurately simulate the net affect of numerous environmental factors. These models are effective because they are used within the substrate ranges and kinetic ranges of the system. Models for high substrate systems can be simplified by neglecting many of the insignificant kinetic and surface interactions that have very little effect on the overall accuracy of the model. However, when low substrate systems such as those found in drinking water systems are modeled, these small kinetic and surface interactions can not be eliminated because they will likely significant and would have notable effects on the accuracy of the model. Items that are typically neglected in high substrate systems but can not be omitted in a low substrate system include:

- the effect of substratum on the formation of distribution biofilms as discussed in Section 2.3 of this chapter.
- the consumption of organic substrates by corrosion products as discussed in Section 2.3 of this chapter.
- the changes in the bioavailability of humic substances adsorbed to corrosion products as discussed in Section 2.4 of this chapter.
- the effects of biosurfactants on the availability of humic substances adsorbed to corrosion products as discussed in Section 2.4 of this chapter.
- the changes in the microbial niches caused by corrosion tubercles as discussed in Section 2.2 of this chapter.

- the changes in microbial growth rates (kinetics) associated with the numerous types of microorganisms present in the numerous niches found in a corrosion product/biofilm.
- the effect of EPS (chlorine demand, diffusion resistance, and nutrient accumulation) on biofilm disinfection (LeChevallier 1990; van der Wende and Characklis 1990; Koudjonou, et al 1997).
- the biotransformation of carbon by disinfectants as discussed in Section 2.4 of this chapter.

As discussed above, the simplification of a biofilm model – by eliminating many reactions that are insignificant in high substrate models – will not be able to accurately predict/simulate the microbial and nutrient conditions present in a distribution biofilm. In view of this, it is clear that an accurate model for distribution biofilms will need to include these components. This will result in a highly complex model that will require substantial field measurements and verification.

2.8 Key Findings

As presented above, a distribution biofilm is a unique system that has many physical, chemical, and biological properties that aid in the protection and survival of microorganisms. In retrospect, these properties enable the distribution system to serve as a plug flow reactor that is highly reactive with chlorine, adsorbs and accumulates carbon and other nutrients, and supports copious quantities of attached microorganisms. Several of the key features presented in this section are listed below:

- Low disinfectant inactivation efficacy of distribution biofilms can be attributed to the physical and chemical properties of a biofilm which enable the microorganisms to accumulate nutrients and to develop diffusion/reaction resistance mechanisms to disinfectants.
- Biofilms consist of a consortium of microorganisms, EPS produced by microorganisms, water, and organic and inorganic substances adsorbed from the bulk fluid or substratum. The biofilm/corrosion product matrix develops a variety of niches that favor the metabolisms of aerobic, facultative, and anoxic microorganisms.
- Biofilms can be home to various microorganisms that include heterotrophic bacteria, coliforms, actinomyces, molds, fungi, nitrifying bacteria, iron oxidizing bacteria, sulfate reducing bacteria, and possibly act as a reservoir for *Giardia* cysts and/or *Cryptosporidium* oocysts.
- The presence of microorganisms may lead to taste and odor complaints by consumers and violations of the Safe Drinking Water Act (coliforms).
- Distribution systems that contain large quantities of unlined cast-iron pipe typically have the most problems with biofilm related water quality problems.
- Non-ferrous pipe materials typically support fewer microorganisms than ferrous materials.

- The presence of corrosion products on a pipe surface creates mass transfer limitations of oxygen and disinfectants. These conditions may lead to the formation of facultative and/or anoxic zones, which are known to support coliforms and sulfate reducing bacteria.
- Total organic carbon measurements do not accurately predict a water's potential to support microbial growth in the distribution system.
- The amount of bioavailable total organic carbon is only a small fraction of the total organic carbon.
- The majority of bioavailable carbon is comprised of humic substances, carbohydrates, and amino acids.
- Goethite (α -FeOOH), the most common corrosion product found on distribution pipes, is known to adsorb humic substances from the bulk fluid.
- Organic carbon can be in either the solute or adsorbed forms.
- Non-bioavailable total organic carbon can be transformed into bioavailable carbon by reacting with disinfectants, adsorbing to corrosion products, and from biosurfactant reactions.
- BDOC and AOC measurements will not totally quantify the amount of carbon that is bioavailable within a biofilm.

- Free chlorine is the superior disinfectant for inactivating microorganisms in the bulk fluid.
- Monochloramine is a superior disinfectant for inactivating distribution biofilms on ferrous materials, because it is less reactive with corrosion products, organics, and EPS.
- Using pH control as a corrosion control method may cause elevated levels of TTHMs in the distribution system. The efficacy of free chlorine is reduced at higher pHs due to a shift in equilibrium between HOCl and OCl⁻.
- pH levels above 9.0 may inhibit the growth of *Klebsiella pneumoniae*, the most common coliform found in water distribution systems.
- The use of the Langelier Saturation Index (LSI) is most appropriate when pH adjustment is used as a corrosion control method, and should not be used in conjunction with corrosion inhibitors.
- With few exceptions, heterotrophic microorganisms found in the water distribution system are carbon limited, not phosphorus limited. The addition of phosphorus based corrosion inhibitors will not typically result in increased microbial levels unless the finished water is exposed to sunlight in an uncovered reservoir.

- Widespread sloughing events may occur in the distribution system shortly after the addition of corrosion inhibitors due to the "softening" of existing corrosion tubercles.
- The use of corrosion indices such as the Riddick Index (RI) and the Larson Index (LI) are not appropriate in assessing the efficacy of a corrosion control program, because they do not account for the passivating properties of phosphate.

Chapter 3

Materials and Methods

The purpose of this chapter is to: (a) describe the materials and methods used to collect, quantify, and statistically evaluate data, and (b) describe the facilities used to conduct bench-scale, pilot-scale, and laboratory studies. Details on the specific experimental designs are described in the relative chapters associated with bench-scale (Chapter 4), pilot-scale (Chapter 5), and laboratory studies (Chapter 6).

3.1 Microbial and Chemical Measurement Techniques

Microbial bulk fluid and biofilm measurements were taken using sterile techniques and analyzed using the spread plate method as described in Section 9215 of Standard Methods.

3.1.1 Bulk Fluid Measurements

Bulk fluid samples were collected in empty sterile test tubes. For bulk fluid samples collected from disinfected systems, a small amount of sodium thiosulfate was added to the test tube prior to collection to neutralize any disinfectant present. Dilutions (10^{-1} , 10^{-2}) were then prepared, using a 1-ml pipette (P-1000 as distributed by Fisher Scientific) into sterile test tubes, each containing 9-ml of sterile water. Quantification of samples was then determined by plating 100 μ l or 1 ml of the appropriate dilution on triplicate plates

of R2A or mT7. Heterotrophic plate counts (HPCs) were quantified using R2A media and incubated for 7 days at room temperature, while coliforms were quantified on mT7 media and incubated at 35°C in a Lab-line Imperial III incubator for 24 hours. After incubation, colonies were counted and the number of colony forming units (CFU) per ml determined by the following equation:

$$\frac{CFU}{cm^3} = \frac{\text{ColonyCount}}{\text{dilution} \cdot mls} \quad (3)$$

3.1.2 Biofilm Density Measurements

Biofilm samples were collected from annular reactor coupons or slides and from coupons from the pilot-scale facilities by scraping all corrosion products and biofilm into a 100-ml beaker containing 10-ml of sterile water. For biofilm samples collected from disinfected systems, a small amount of sodium thiosulfate was added to the 10-ml of sterile water prior to collection to neutralize any disinfectant present. The biofilm/corrosion product slurry was then poured into a sterile test tube and transported to the laboratory for processing. Biofilm samples were homogenized, using a Janke & Kunkel Model T25S1 Homogenizer, for 2 minutes at 20,000 rpm to disperse bacteria and corrosion products prior to preparing dilutions (10^{-1} , 10^{-2} , 10^{-3} , 10^{-4} , and 10^{-5}). Heterotrophic and coliform populations for the biofilm samples were quantified by the spread plate method as described in Section 9215 of Standard Methods, using triplicate plates of R2A and mT7 agar plates respectively. R2A plates were incubated for 7 days at room temperature and mT7 plates incubated at 35°C in a Lab-line Imperial III

incubator. After incubation, the plates were counted and the biofilm density determined by evaluating the following equation:

$$\frac{CFU}{cm^2} = \frac{\frac{ColonyCount}{dilution}}{mls(cm^2)} \quad (4)$$

3.1.3 Chemical Measurements

In addition to microbial samples, numerous other physical and chemical parameters were routinely analyzed using the methods described in Table 3.1. Flow rates and temperature were routinely monitored and adjusted while numerous chemical parameters were also analyzed.

3.1.4 Corrosion Product Mass Measurements

Corrosion product masses were determined by filtering the corrosion product/biofilm slurry, as described in Section 3.1.2, on Watman 3 filter paper and measured on a Mettler AE 200 balance. Filters were initially rinsed and oven dried at 105°C for at least 2 hours and the initial weight recorded. After filtering the corrosion product/biofilm slurry, the filters were again dried 105°C for at least 2 hours and the final weight measured. The difference between the two weight measurements represents 90 percent of the total corrosion product mass on the slide. The remaining 10 percent of corrosion product mass were used in preparing dilutions as described in Section 3.1.2.

Table 3.1 Chemical Analysis Methods and Equipment

Chemical Parameter, units	Method	Equipment
pH	Section 4500 of Standard Methods	Accumet Model 50, Fisher Scientific
Total Chlorine, mg/L	DPD Method. Hach Method 8021	Hach DR 2000 Spectrophotometer
Free Chlorine, mg/L	DPD Method. Hach Method 8167	Hach DR 2000 Spectrophotometer
Magnesium and Calcium Hardness, mg/L as CaCO ₃	Calmagite Colorimetric Method. Hach Method 8030	Hach DR 2000 Spectrophotometer
Alkalinity, mg/L as CaCO ₃	Section 2320 of Standard Methods	50-ml burette and 0.036 N Sulfuric Acid
Nitrate Nitrogen, mg/L	Cadmium Reduction Method. Hach Method 8039	Hach DR 2000 Spectrophotometer
Phosphorus, mg/L	Orthophosphate Method. Hach Method 8048	Hach DR 2000 Spectrophotometer
Sulfate, mg/L	Sulfa Ver 4 Method. Hach Method 8051	Hach DR 2000 Spectrophotometer
Dissolved and Total Iron, mg/L	Ferrozine Method. Hach Method 8147	Hach DR 2000 Spectrophotometer (Dissolved iron filtered with a 0.2 µm filter)
Chloride, mg/L	Mercuric Thiocyanate Method. Hach Method 8113	Hach DR 2000 Spectrophotometer
Silica, mg/L	Silicomolybdate Method. Hach Method 8185	Hach DR 2000 Spectrophotometer
Total Organic Carbon, mg/L	Infrared Combustion Method. Standard Method 5310	Shimadzu Model TOC-5000A Total Organic Carbon Analyzer

3.1.5 Statistical Methods

The objective of the statistical analysis was to determine if a specific treatment significantly increases or decreases biofilm densities when compared against another treatment system. For these experiments, two controls were used. The first control was a non-chlorinated (or non-chloraminated) system while the second control was a chlorinated (or chloraminated) system, without the use of any type of corrosion control method. In all experiments, organic and nutrient feeds were constant for each system. Some experiments incorporated variable disinfectant dosages, while other experiments utilized constant disinfectant feeds but with variable dosages of corrosion inhibitors. Since one of the goals of this project was to determine the numerous interactions between pipe materials, disinfectants, and corrosion inhibitors on distribution biofilms, a multiple comparison analysis of variance was utilized.

Prior to conducting the statistical analysis, all microbial data were \log_{10} transformed to stabilize the variance. Data were then analyzed using Fisher's Multiple Comparison Tests with MINITAB™ software using all microbial data collected during the last 4 weeks of the experiment. The last 4 weeks represents steady state conditions. Experiments that utilized the laboratory style annular reactors (see Section 3.3), multiple samples were collected at the end of the experiment and statistically analyzed as described above.

3.2 Chemostat Operation

Prepared cultures of coliforms were introduced to all field-type annular reactors (Chapter 4), two of the pilot-scale experiments (Chapter 5), and the pH inhibition experiment (Chapter 6). Coliforms used were originally isolated from coliform outbreaks in distribution systems. Coliforms included *Klebsiella pneumoniae*, *Klebsiella oxytoca*, *Enterobacter aerogenes*, *E. cloacae*, and *Escherichia coli*. These cultures were maintained as frozen stocks at -70°C .

3.2.1 Coliform Culture Preparation and Conditioning

Isolated colonies were obtained for each coliform by streaking frozen stocks of each coliform on R2A agar. Batch cultures of each coliform were prepared by placing an isolated colony of the respective coliforms in a sterile 250-ml flask containing 100-ml of sterile water containing 2500 $\mu\text{g C/L}$ substrate (equal carbon amounts from sodium acetate, sodium benzoate, propionaldehyde, parahydroxybenzoic acid, and ethanol), 500 $\mu\text{g/L}$ of nitrate (potassium nitrate), and 500 $\mu\text{g/L}$ of phosphate (equal molar amounts of potassium phosphate and potassium phosphate monobasic). Each batch culture was then placed in a shaking incubator for 20 hours at room temperature. Five mls from each batch culture were then placed in another sterile 250-ml flask, using the same nutrients described above, and incubated again for 20 hours.

Klebsiella pneumoniae cultures used in pH inhibition studies (Chapter 6) were prepared by placing an isolated colony in a sterile test tube containing 10

ml of sterile 1% R2A broth for 20 hours. One ml of the culture was then transferred to a sterile 250-ml flask containing 100 ml of sterile 0.05% R2A broth and incubated in a shaking incubator for 20 hours at room temperature.

3.2.2 Chemostat Startup

Prior to chemostat startup, each chemostat, associated solution bottles and tubing were autoclaved. Chemostats were inoculated with 5 ml of each culture when a 4.4 L chemostat was used (bench-scale and pilot-scale studies) and 1ml of *Klebsiella pneumoniae* for the 500 ml chemostats used in the pH inhibition studies. Nutrient feeds (carbon substrate, nitrogen, phosphorus, or R2A broth) were introduced at 10% of the concentration used in the last batch culture, at a flow rate that would produce a growth rate of 0.05 hr^{-1} (20-hour residence time). A 20 hour residence time was used because it has been found that coliforms grown at low growth rates and low nutrient conditions are more resistant to the environmental conditions found in a water distribution system (Camper, et al 1991; LeChavallier, et al 1988; Camper 1995). Each chemostat was mixed and aerated using filtered ($0.2 \mu\text{m}$ filter) air supplied by an aquarium pump. Chemostats were operated for approximately 4 days to establish steady-state conditions prior to inoculation of the bench-scale and pilot-scale facilities or for pH adjustment for the pH inhibition studies. A typical chemostat setup is presented in Figure 3.1.

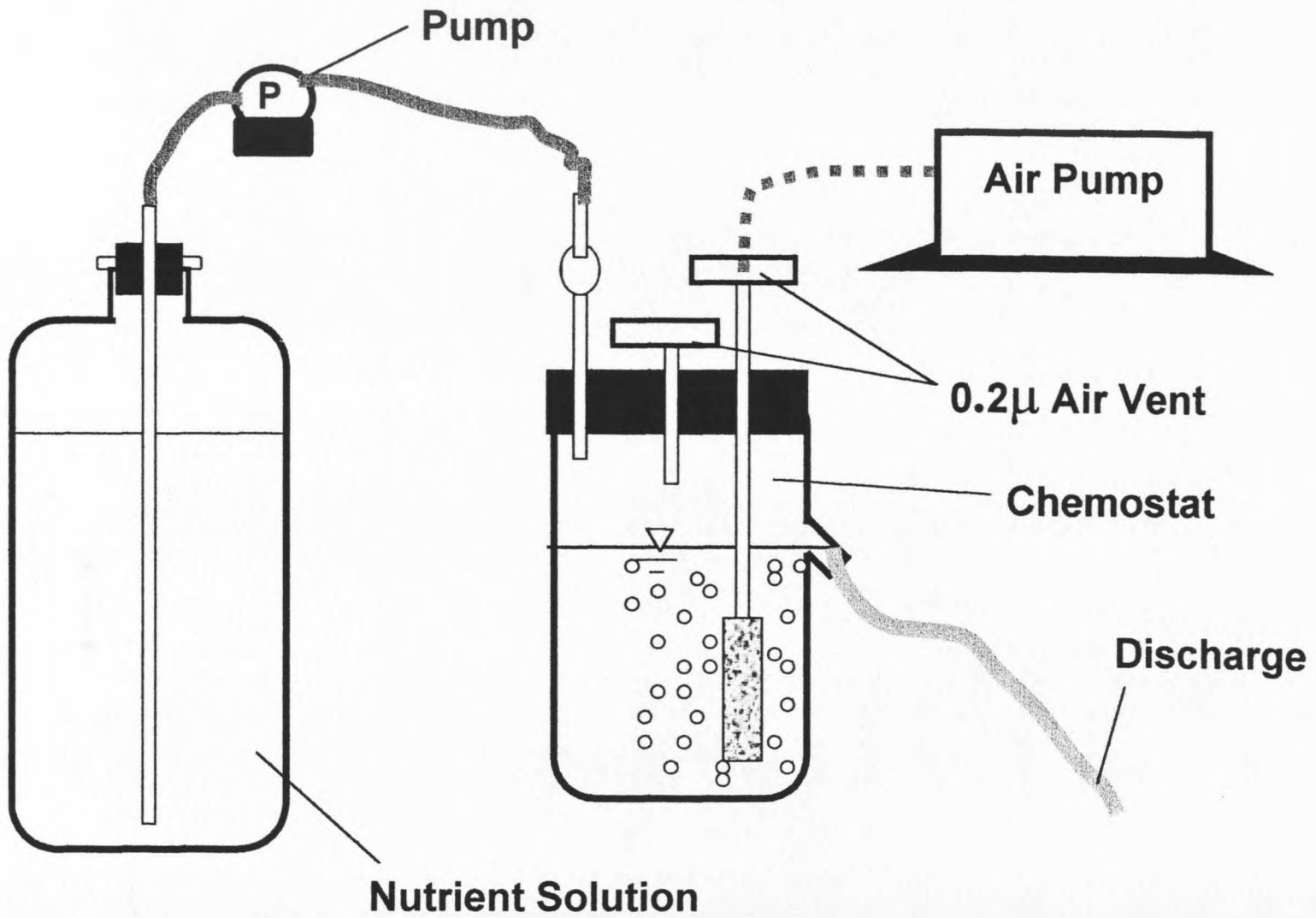


Figure 3.1 Typical Chemostat Schematic

3.3 Bench-scale Studies

Bench-scale experiments reported here employed two different types of annular reactors. These reactors were either the field type (Model 920WD) or the laboratory type (Model 920LJ) as manufactured by BioSurface Technologies Corporation (Bozeman, Montana) and illustrated in Figure 3.2. Each reactor consists of a stationary outer cylinder and a rotating inner cylinder. The outer cylinder for the field type units is constructed of unlined ductile-iron pipe with 30 removable coupons each with a surface area of 1.27 cm^2 . The outer cylinders of the laboratory units were made of glass with 20 removable mild-steel slides, each with a surface area of 19.05 cm^2 , were located on the rotating inner cylinder of the laboratory units. In both reactor types, the inner cylinder rotates to simulate shear stresses that would be present on a pipe surface at low velocities. Low shear stresses were used to simulate low flow conditions in distribution systems that have been found to be problematic locations for the formation of biofilms.

The total liquid volume of each reactor is 1,100 ml (0.29 gal.) which provides a high surface area to volume ratio. Due to the high surface area to volume ratio, the annular reactors are highly biased towards surface interactions associated with microbial attachment/detachment (biofilms) and chemical reactions. As a result, annular reactors will have higher disinfectant demands and higher microbial counts in the bulk fluid than an actual distribution system. Bench-scale studies using the field type reactors used a hydraulic residence time of 120 minutes, while the lab style reactors utilized a hydraulic residence time of



a) Field Type Annular Reactor



b) Lab Type Annular Reactor

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Figure 3.2 Field Type and Lab Type Annular Reactors

90 minutes to maintain control of disinfectant residuals. As result of the short residence time, any increase in microbial populations in the effluent will be from the detachment of microorganisms from the biofilm (van der Wende and Characklis 1990; Camper 1995).

The annular reactors were operated in parallel, to allow multiple conditions to be evaluated simultaneously. Experiments used three, four or six annular reactors to evaluate the interactions between disinfectants and corrosion inhibitors within distribution biofilms. In each experiment, pretreated dilution water and associated chemical feeds were introduced to each reactor to produce a hydraulic residence time of 2 hours for the field type annular reactors and 90 minutes for the laboratory style annular reactors. Dilution water was pretreated by a granular activated carbon (GAC) filter to remove disinfectant residual followed by a biological active carbon (BAC) filter to remove available biodegradable organic matter (BOM) from Bozeman tap water. The dilution water also provided a continuous inoculum of adapted microorganisms to each reactor. Various chemical feeds were then introduced to the reactors by a series of chemical solutions of disinfectant, nutrients, and corrosion inhibitor. A typical schematic of the annular reactor system is presented in Figure 3.3.

There are several features of the annular reactors that are problematic because the small liquid volume and corresponding high surface area leads to noisy bulk fluid measurements (both chemical and microbial) due to sloughing

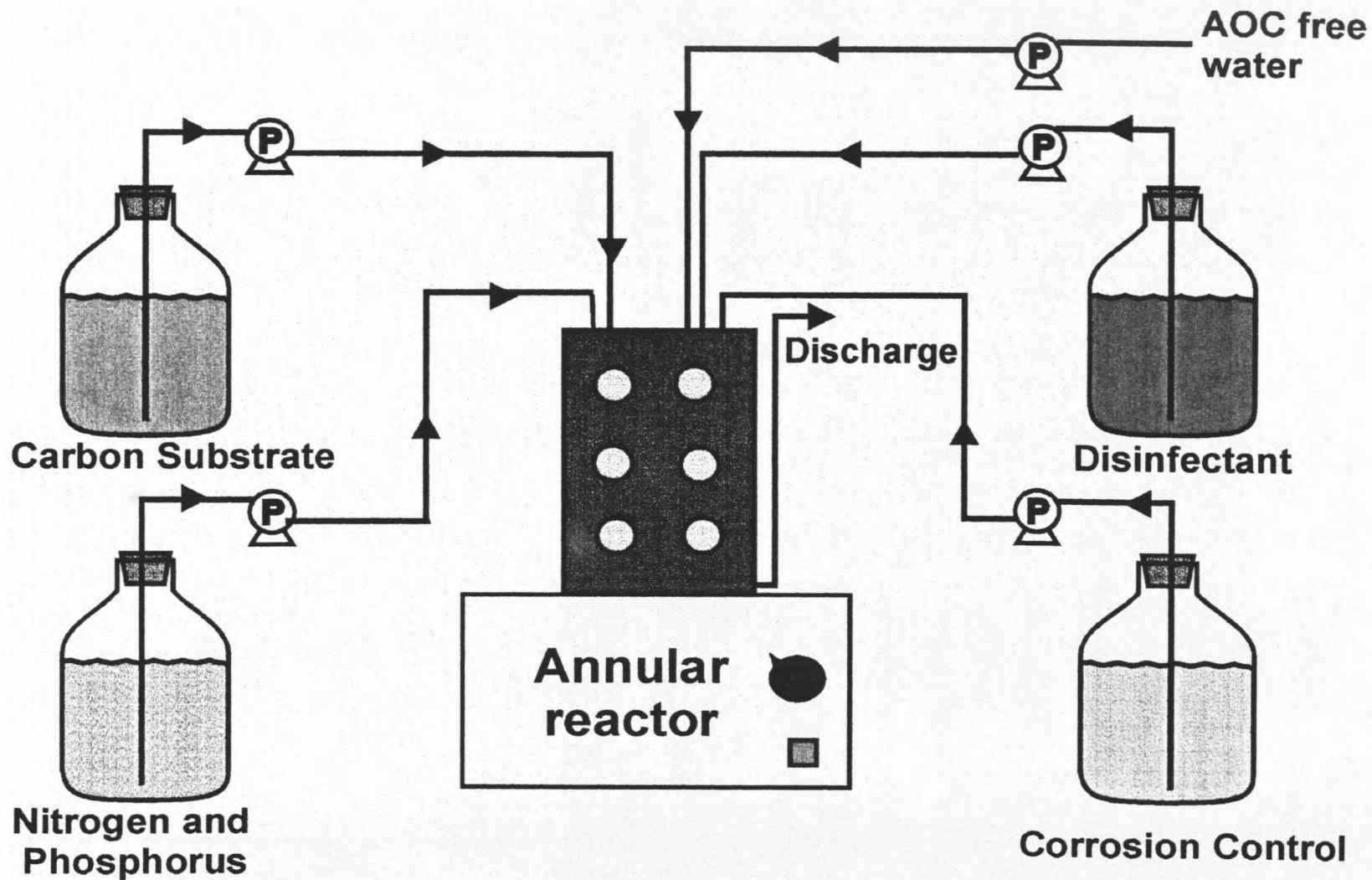


Figure 3.3 Typical Annular Reactor System

events. Another problem is the reactors (both the field and laboratory models) are constructed of polycarbonate and metal surfaces. Past research has shown that these materials will support different microbial populations under the same nutrient conditions (Chen, et al 1993; Camper, et al 1996; Ollos, et al 1997; Delanoue, et al 1997; Camper 1995), which means that they will have different effects on the performance of the annular reactor.

3.3.1 Bench-scale Startup Procedures

Prior to the startup of the bench-scale reactors, each reactor was cleaned to remove any buildup of corrosion products from previous experiments. Field type reactors were bead-blasted and washed with a mild detergent, while the lab style reactors were hand cleaned and refurbished with new mild steel slides. Once clean, the reactors (excluding the experiments conducted using the laboratory style reactors) were inoculated with 1,100 ml of effluent from a 4.4 L chemostat containing five coliform cultures (*Klebsiella pneumoniae*, *K. oxytoca*, *Enterobacter aerogenes*, *E. cloacae*, and *Escherichia coli*) and allowed to operate in a chemostat mode for 24 hours. Coliforms were added so that they could colonize the reactor surfaces prior to introduction of other non-coliform heterotrophic microorganisms present in the dilution water.

After inoculation, dilution water and nutrients (carbon, nitrogen and phosphorus) were added to the reactors for one week to establish a healthy population of biofilm in each reactor. On the seventh day biofilm samples (collected from the removable coupons) and bulk fluid samples were collected

and assayed for coliforms and heterotrophic microorganisms. After the first sampling, the addition of disinfectant (free chlorine or monochloramine) and corrosion inhibitor were initiated. Bulk fluid and biofilm samples were collected the following day and periodically over the duration of the experiment to determine the effect of the disinfectants and corrosion control on bulk fluid and biofilms within the reactors.

3.4 Pilot-scale Studies

Pilot-scale studies were conducted using facility at the City of Bozeman Water Treatment Plant (WTP). This system was designed to simulate physical conditions of drinking water distribution systems and has the capability of controlling flow rate, water temperature, and hydraulic residence time. The system also has the capability of simulating various chemical properties of a finished water system by the addition of organic substrates, nutrients (nitrogen and phosphorus), disinfectants (free chlorine or monochloramine), corrosion inhibitors (zinc orthophosphate or polyphosphate), and pH control.

3.4.1 Pretreatment Facilities

The pretreatment facilities are designed to dechlorinate the finished water from the Bozeman WTP and remove trace organics and biodegradable organic matter (BOM). Pretreatment facilities consist of a granular activated carbon (GAC) filter for the removal of chlorine and trace organics, and two biological active carbon (BAC) filters to remove any available BOM from the finished water.

Once pretreated, the water is transported to an insulated 0.208 m³ (55-gallon) reservoir for temperature control prior to distribution to the five pipe loops. A schematic of the pretreatment system is presented in Figure 3.4.

3.4.2 Pipe Loop System

The pipe loop system consists of five 12.18 m (40 ft) sections of 10.16 cm (4-inch) mild steel pipe and 18.41m (60.4 ft) of 3.81cm (1-1/2 inch) diameter mild steel pipe. Each pipe loop contains 80 flush-mounted coupons (with an 8.84 cm² surface area) for biofilm sampling, an insulated and temperature controlled recycle tank, a 0.1514 m³/min (40 gpm) recycle pump and associated valves, flow monitor, and sample spouts. Each pipe loop also has chemical feed facilities for the addition of organic substrates, nutrients, disinfectant, and corrosion inhibitor. A pH controller (Chemcadet pH meter/controller, Cole-Parmer) and caustic feed pump were used on one pipe loop when pH control was used as a corrosion control method. A schematic of these facilities is presented in Figure 3.5.

The pilot loop system operated in a recycle mode with a hydraulic residence time of 120 minutes at a temperature of 20°C. As with the annular reactor studies presented in Section 3.3, the short residence time minimizes microbial growth in the bulk fluid. As a result of this short residence time, any increase in microbial cell counts (either viable or inactivated) can be attributed to detachment of biofilm organisms from the pipe walls.

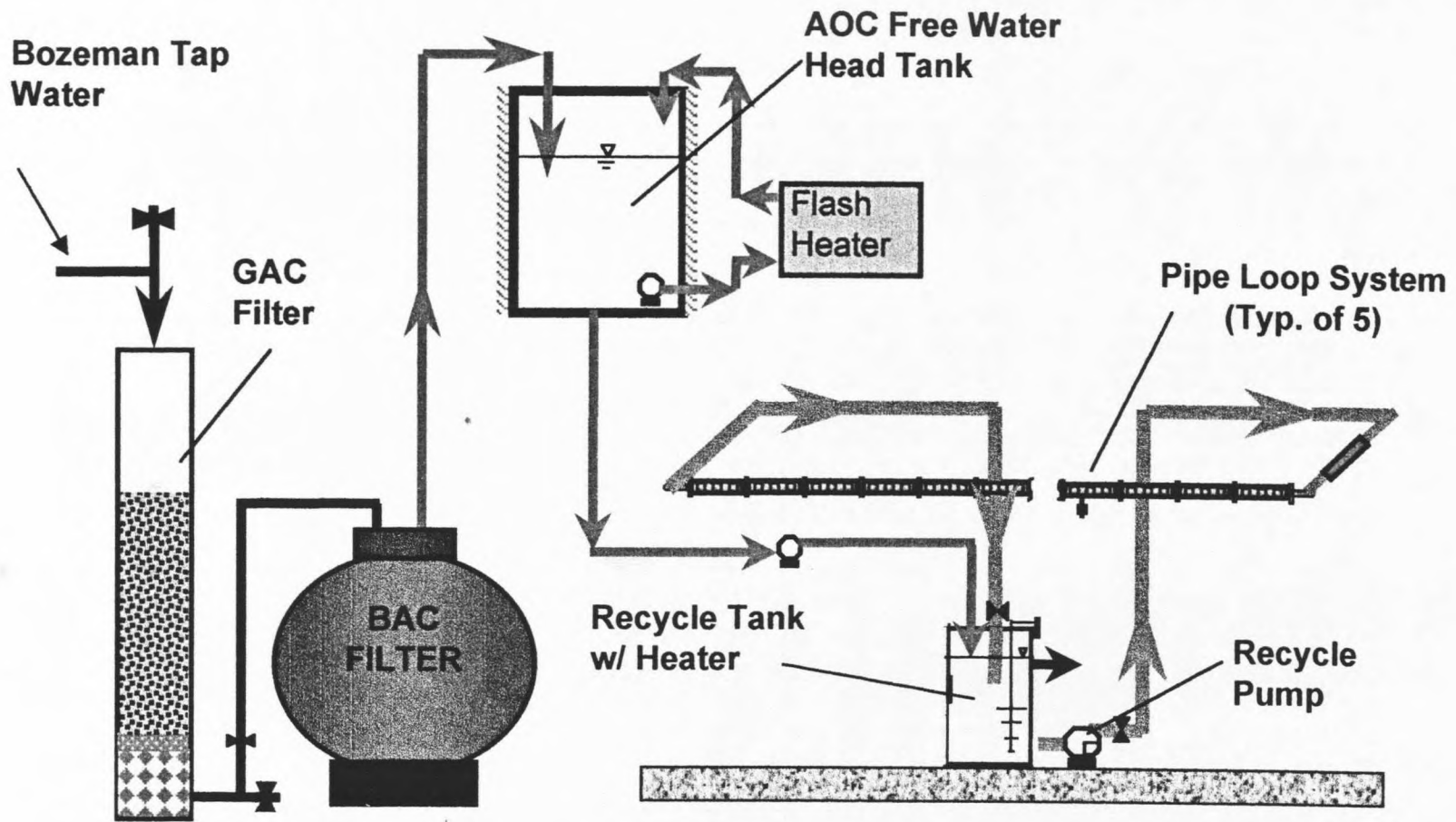


Figure 3.4 Pretreatment Facilities for the Pilot-plant System

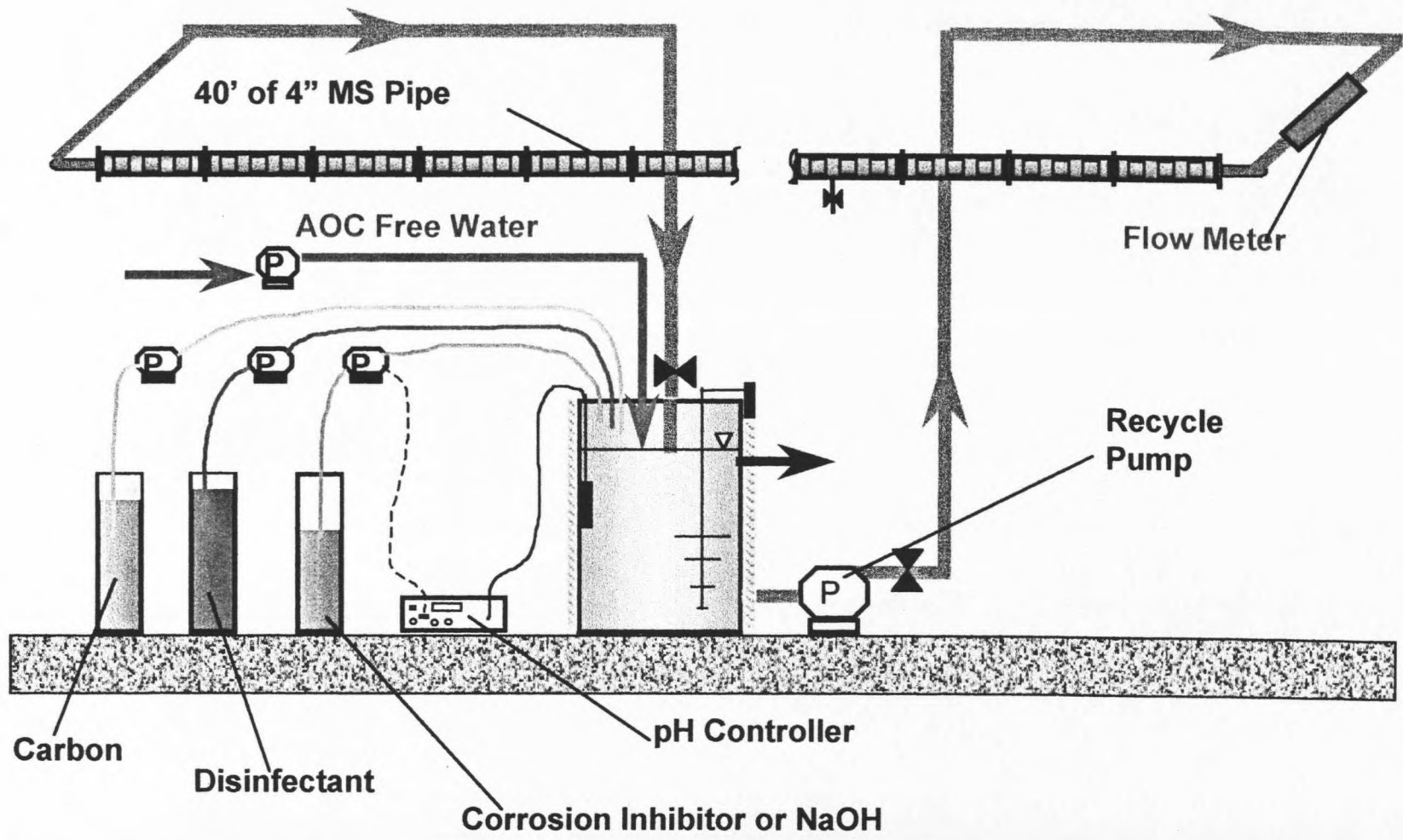


Figure 3.5 Schematic of Pilot-scale Distribution System

In normal operation, water was delivered from the main reservoir to each recycle tank by a dedicated vane pump at a flow rate of $0.0026 \text{ m}^3/\text{min}$ (0.68 gpm). Carbon substrate, disinfectant, and corrosion inhibitor are then continuously added to the recycle tank by peristaltic pumps. A recycle pump circulates the water into the pipe loop at a flow rate of $0.1514 \text{ m}^3/\text{min}$ (40 gpm) to produce a flow rate of 0.305 m/s (1 ft/sec). An overflow outlet in the recycle tank regulates the hydraulic residence time of the system.

3.4.3 Pilot-plant Startup Procedures

Prior to the startup of the pilot plant facilities, all coupons are removed and bead blasted to remove any corrosion products accumulated on the surface, chemical feed pumps are recalibrated, tubing is replaced, and the recycle pumps/valves are adjusted to provide the proper flow rates. Once calibrated, each pipe loop was operated with dilution water (at 20°C) and organic substrate and nutrient feed for 3 or 4 weeks to create a natural biofilm on all surfaces. Following this period, effluent from a 4.4 liter chemostat containing five coliform cultures (*Klebsiella pneumoniae*, *K. oxytoca*, *Enterobacter aerogenes*, *E. cloacae*, and *Escherichia coli*) operated at a residence time of 20 hours was introduced to the main reservoir for 5 days.

At the conclusion of the inoculation period, bulk fluid and biofilm samples were collected from each loop to quantify initial bulk fluid and biofilm density. After the first sampling, the disinfectant (free chlorine or monochloramine), corrosion inhibitor (zinc orthophosphate or polyphosphate), or pH adjustment (for

pH corrosion control method) were initiated. Bulk fluid and biofilm samples were collected the following day and periodically over the next 12 weeks to determine the effect of the disinfectants and corrosion control treatments on distribution biofilms.

With a few exceptions, the mechanics of pilot-scale facilities are similar to the annular reactor system previously described. The pilot-scale system also provides a high surface area to volume ratio and a single material (mild steel) with the exception of cast-iron pumps and valves. The pilot-scale facilities are operated in a recycle mode with a mean hydraulic residence time of 120 minutes. The higher volumes and flow rates provide a significantly higher degree of control for chemical feeds such as carbon substrates, nutrients, corrosion inhibitors, and disinfectants. The short hydraulic residence time minimizes microbial growth in the bulk fluid.

3.5 Miscellaneous Laboratory Studies

In addition to bench-scale and pilot-scale studies, several laboratory studies were conducted to determine the humic adsorption capacities of corrosion products and the disinfectant demand of disinfectants (free chlorine and monochloramine) corrosion products.

3.5.1 Batch-scale Adsorption Studies of GAC and Corrosion Products

Adsorption isotherms were determined by adding known masses of adsorptive material (GAC, magnetite, and corrosion products) to several media bottles containing a buffered humic substance solution. Magnetite (Fe_3O_4 , Aldrich Chemical Company, Cat. No. 31006-9) and uncharacterized corrosion products were collected from a field style annular reactor. Corrosion products were used because siderite (FeCO_3) and goethite ($\alpha\text{-FeOOH}$) are not commercially available or practical to make in the laboratory. GAC was also used because of its known high adsorption capacity and was used as a base-line material.

The humic substance solution was prepared from humic material supplied by the International Humic Substances Society and buffered using 200 mg of potassium bicarbonate per liter, of solution and the pH adjusted to 7.5 units using a sodium hydroxide and/or sulfuric acid solution. The humic solution was stored in a walk-in cooler.

100-ml media bottles (Corning Cat. No. 1395-100) were used to contain the corrosion product mass or GAC and humic substance solution. All glassware was acid washed and glass fired at 550°C for at least 8 hours to remove any carbon that may be present. Bottle tops were boiled in a 5% potassium persulfate solution to oxidize any surface carbon present. Bottle tops were rinsed in ultrapure water and wrapped in aluminum foil prior to use.

Adsorption isotherms were determined by placing known masses of material (GAC, magnetite, and corrosion products) into the media bottles filled with the buffered humic substance solution. Media bottles were then placed on a shaker table and vigorously mixed for 48 hours to allow the adsorptive media to reach equilibrium with the humic substances in the bulk fluid. One control (media bottle without any adsorptive material present) was utilized for each experiment. After shaking, each bottle was centrifuged at 10,000 rpm for 15 minutes to separate the particulate/colloidal material from the bulk fluid. Total organic carbon (TOC) samples were then collected and measured on a Dohrman DC-80 Total Organic Carbon Analyzer.

3.5.2 Disinfectant Demand Studies

Disinfectant demands of corrosion products were determined using corrosion product samples collected from a mild steel annular reactor surface at the Bozeman Water Treatment Plant. Corrosion product samples were collected by scraping the attached corrosion products from the pipe surface. After collection, the corrosion products were air-dried and stored in an air tight media bottle at room temperature.

Demand studies were conducted in 125-ml serum bottles (Wheaton No. 223748) with teflon-lined septa (Wheaton 224223-01). Serum bottles and septa were soaked in a 25 mg/L chlorine solution for 48 hours prior to the experiment to remove any disinfectant demand of the glass or teflon. Immediately prior to use,

all serum bottles and septa were rinsed with ultrapure water (TOC less than 40 $\mu\text{g/L}$) to remove any traces of disinfectant.

Disinfectant solutions were prepared using ultrapure water buffered with the addition of 200 mg of KHCO_3 per liter of solution in addition to household bleach (for free chlorine solution) or household bleach and ammonium chloride (for monochloramine solution). A 4:1 ratio of $\text{Cl}_2:\text{NH}_3$ was used for the monochloramine solution. Chlorine and monochloramine solutions were prepared to produce a disinfectant residual of approximately 5 mg/L and the pH adjusted to 7.5 units with the addition of sodium hydroxide or a sulfuric acid solution. Both disinfectant solutions were stored for at least 24 hours to remove any disinfectant demand of the water prior to use.

Chapter 4

Bench-scale Studies

Bench-scale laboratory tests were conducted to determine the long-term effect of disinfectants and corrosion inhibitors on the formation of distribution biofilms on pipe materials. The experiments presented in this chapter were designed to provide insight into the numerous interactions between organics, disinfectants, and corrosion inhibitors on pipe materials.

Bench-scale experiments presented in this section utilized both free chlorine and monochloramine as secondary disinfectants. These studies utilized low disinfectant residuals to simulate future trends in disinfection that will minimize the formation of various disinfection byproducts. These experiments also evaluated the use of polyphosphate and zinc orthophosphate as corrosion control methods. Although there are several other corrosion control methods used by the drinking water industry, these two inhibitors are the most commonly used methods. pH adjustment was not utilized during bench-scale experiments due to the difficulty in controlling pH at low flow rates.

4.1 Bench-scale Studies with Free Chlorine without Corrosion Control

The purpose of this study was to determine the effects of various free chlorine residuals on the formation of distribution biofilms. This study is of particular interest because in many situations, the addition of free chlorine

actually increases biofilm levels even though a free chlorine residual is present in the bulk fluid (Camper 1995).

4.1.1 Experimental Design

To determine the effects of various levels of free chlorine on distribution biofilms, six laboratory style annular reactors were used, each receiving the same nutrient and hydraulic conditions but operating with different effluent and bulk fluid free chlorine residuals. To simulate worst case conditions, mild steel slides were used as a biofilm substratum. This experiment was conducted in three steps. The first step was the inoculation step in which microorganisms were allowed to attach and grow on the substratum without the presence of free chlorine for 30 days. The second step was the addition of free chlorine to five of the reactors (one reactor used as a non-chlorinated control) at various levels up to 0.3 mg/L with the last reactor maintained and effluent and bulk fluid chlorine residual of approximately 1.25 mg/L for a period of 52 days. Specific operating conditions for this step are identified in Table 4.1.

At the conclusion of the second step, effluent and bulk fluid chlorine residuals were increased to approximately 0.75 mg/L with the last reactor again operated at a free chlorine residual of approximately 1.25 mg/L for a period of 76 days. Specific operating conditions for this step are identified in Table 4.2. The entire experiment was conducted during the winter months when water quality was nearly constant and not affected by spring runoff. Typical finished water

quality changes in Bozeman, MT are illustrated in Table 4.3. A schematic of the experimental setup is presented in Figure 4.1.

Table 4.1 Operational Conditions of Bench-scale Study (Step 2) Using Variable Free Chlorine Residuals without Corrosion Control

Reactor	Residence Time, minutes	Influent Carbon supplement, mg/L	Influent Phosphate and Nitrate added, $\mu\text{g/L}$ each	Average Effluent Free Chlorine Residual, mg/L
1	90	0.25	100	0.00
2	90	0.25	100	0.04
3	90	0.25	100	0.09
4	90	0.25	100	0.12
5	90	0.25	100	0.21
6	90	0.25	100	1.25

Table 4.2 Operational Conditions of Bench-scale Study (Step 3) Using Variable Free Chlorine Residuals without Corrosion Control

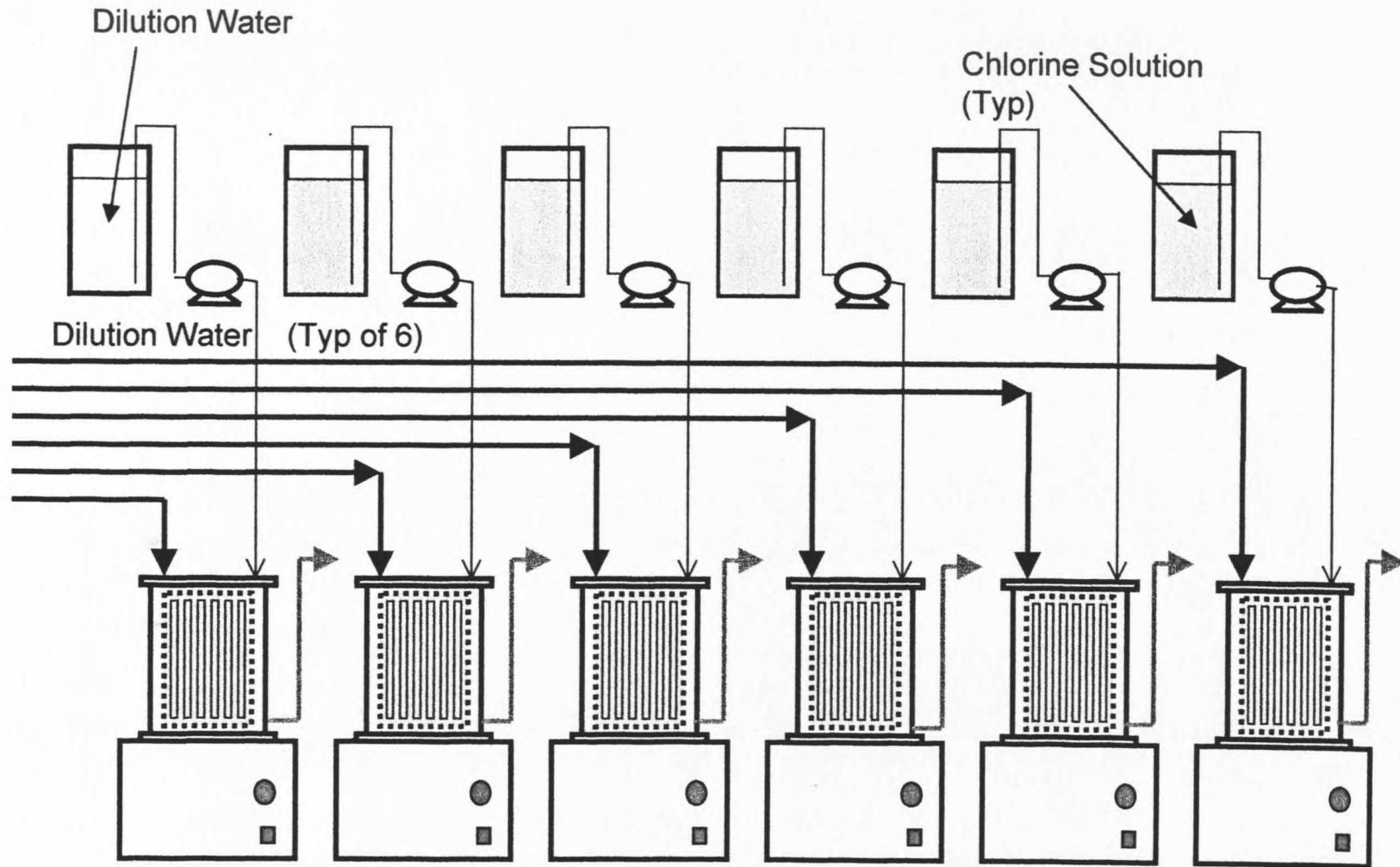
Reactor	Residence Time, minutes	Influent Carbon supplement, mg/L	Influent Phosphate and Nitrate added, $\mu\text{g/L}$ each	Average Effluent Free Chlorine Residual, mg/L
1	90	0.25	100	0.00
2	90	0.25	100	0.12
3	90	0.25	100	0.58
4	90	0.25	100	0.75
5	90	0.25	100	0.54
6	90	0.25	100	1.22

Table 4.3 Seasonal Finished Water Quality Changes in Bozeman, MT

Months	Total Hardness, mg/L as CaCO ₃	Alkalinity, mg/L as CaCO ₃	Total Dissolved Solids, mg/L
January - April	95 - 116	93 - 109	97 - 114
May - June	68 - 94	53 - 99	73 - 94
July - October	68 - 105	54 - 76	72 - 114
November - December	97 - 106	95 - 100	107 - 117

4.1.2 Results

At the conclusion of each chlorination step, slides were removed from each reactor and analyzed for biofilm density and corrosion product density. As illustrated in Figure 4.2, under some conditions it is possible to have an increase in biofilm density with an increase in chlorine residual. This increase in biofilm density with an increase in chlorine residual can be attributed to: (a) the increased release of Fe⁺² from the pipe surface resulting from increased chloride levels, (b) increased corrosion product formation associated with the presence of powerful oxidants such as free chlorine, and (c) an increase in bioavailability of organic substrates (both free and adsorbed) resulting from chemical oxidation of organics by chlorine. It can also be observed from Figure 4.2 that once the chlorine residual exceeds approximately 0.75 mg/L, the biofilm densities begin to decrease. This chlorine residual which results in a decrease in biofilm density can be defined as the threshold residual. The threshold residual will vary from



**Figure 4.1 Bench-scale Studies with Free Chlorine without Corrosion Control
Process Flow Schematic**

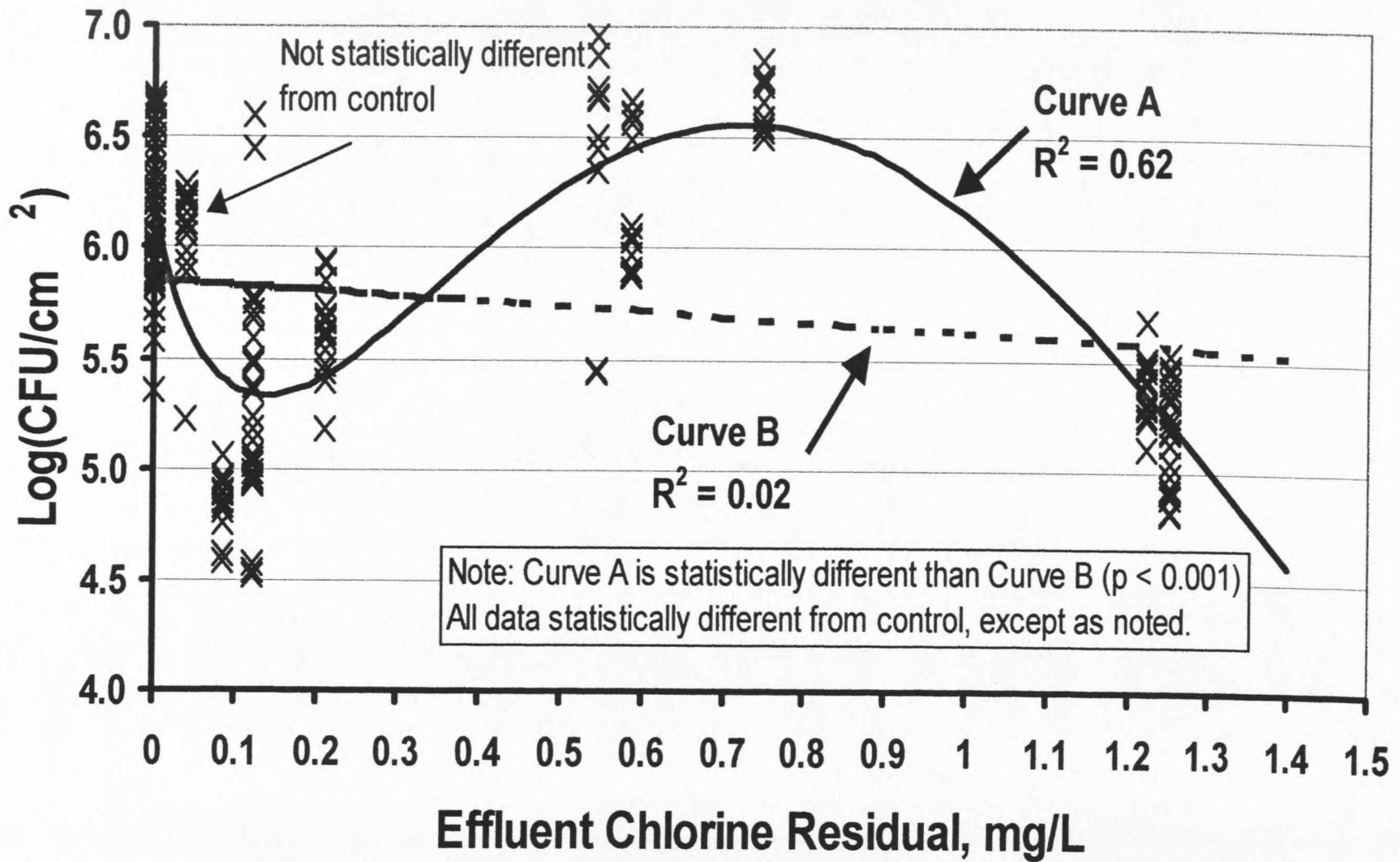


Figure 4.2 Biofilm Density as a function of Chlorine Residual

site-to-site and will likely change with the physical and chemical properties of the water.

In addition to biofilm density comparisons, evaluations of corrosion product mass densities were performed. Results from these evaluations are presented in Figure 4.3. Biofilm density (CFU/cm²) and corrosion product density (mg/cm²) typically increased with increased chlorine residuals up to the threshold level (approximately 0.75 mg/L chlorine residual). Once the chlorine residual was maintained at levels above the threshold, biofilm densities began to decrease even though corrosion product density continued to increase. The increase in disinfectant efficacy can be attributed to bulk fluid chlorine residuals being high enough to overcome the reaction/diffusion limited mass transfer limitations of the corrosion product/biofilm matrix, hence, allowing for deeper penetration of the disinfectant into the corrosion product/biofilm matrix.

In view of Figure 4.2 and Figure 4.3, one important observation is that the mass of corrosion products present on a surface influences the biofilm density that can be supported by a pipe surface at a given chlorine residual, provided that the chlorine residual in the bulk fluid is less than the threshold residual previously defined. The sensitivity of corrosion product mass at various chlorine residuals can be determined by evaluating the microbial yield (CFU/cm²) as a function of corrosion product mass as a function of chlorine residual. Data for the development of the reaction rates were obtained by combining data from statistically insignificant chlorine concentrations from the two chlorinated steps

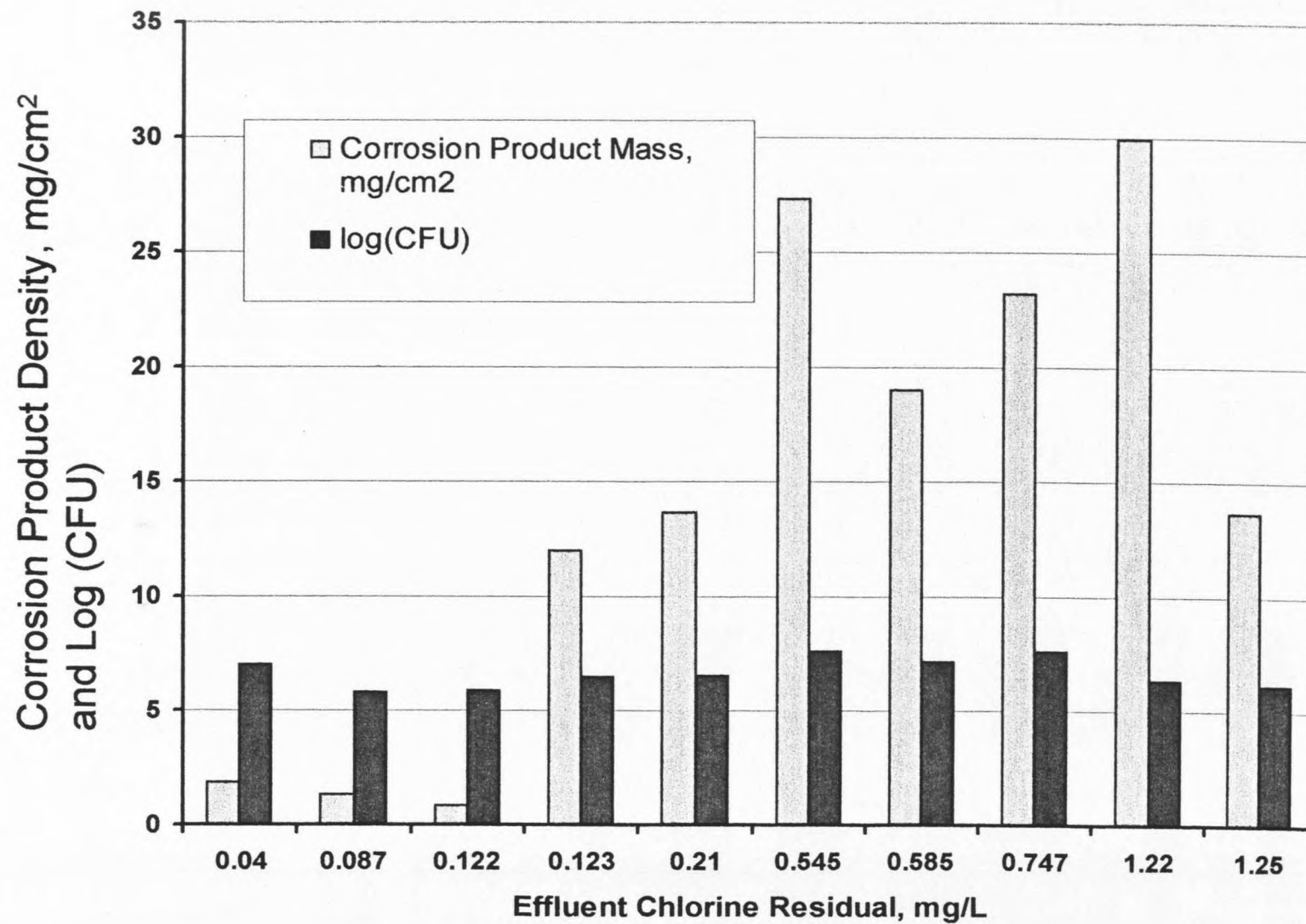


Figure 4.3 Corrosion Product Mass and Biofilm Populations at various Chlorine Residuals

previously described. Data were then plotted and a yield (the slope of line of best fit) determined by the Least Squares Method. Results from these evaluations are presented graphically in Figure 4.4 and summarized in Table 4.4.

As illustrated in Figure 4.4 and Table 4.4, corrosion product mass has an influence on the amount of microorganisms that can be supported by a pipe surface at a given chlorine residual. The significance of corrosion product mass was highest at the lower chlorine residuals and less significant at higher chlorine residuals. Based on these observations, it can be concluded that for distribution systems maintaining low chlorine residuals, it is essential that corrosion rates be held at a minimum if biofilm related water quality problems are to be minimized.

4.2 Bench-scale Studies Comparing Free Chlorine and Monochloramine without Corrosion Control.

The use of monochloramine as a secondary disinfectant is rapidly becoming widespread in the water industry because it is less reactive with pipe materials and does not form as many undesirable disinfection byproducts as free chlorine (LeChevallier 1997; Montgomery 1985; Pontius 1990; Bryant, et al 1992). Although monochloramine is considered to be a weaker disinfectant, it has been demonstrated that it is more effective at inactivating distribution biofilms because it is less reactive with EPS and corrosion products (LeChevallier 1990; van der Wende and Characklis 1990; Chen, et al 1993), allowing it to penetrate deeper into the corrosion product/biofilm matrix (LeChevallier, et al 1996; LeChevallier 1997; Camper, et al 1997).

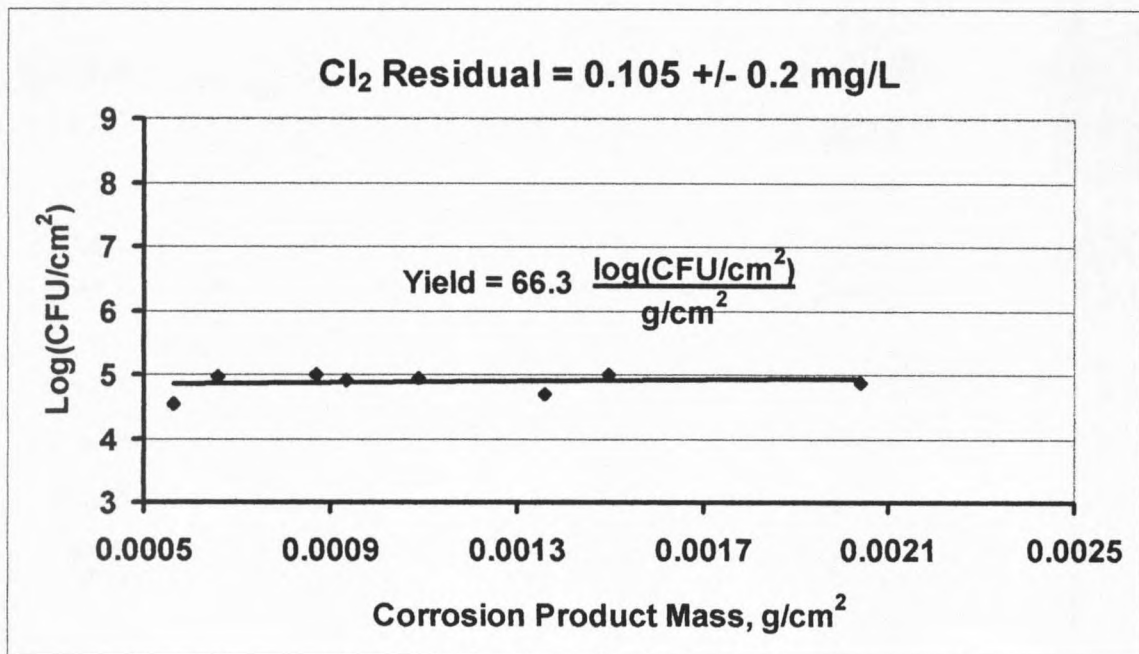
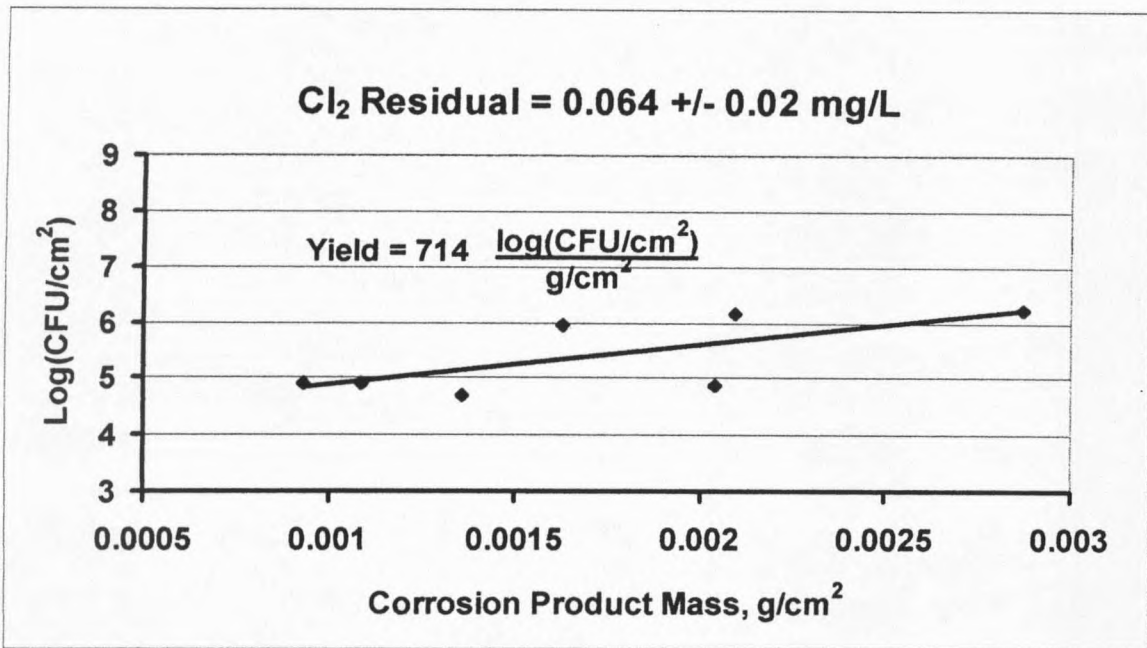


Figure 4.4 Biofilm density as a function of corrosion products and Cl₂ residual

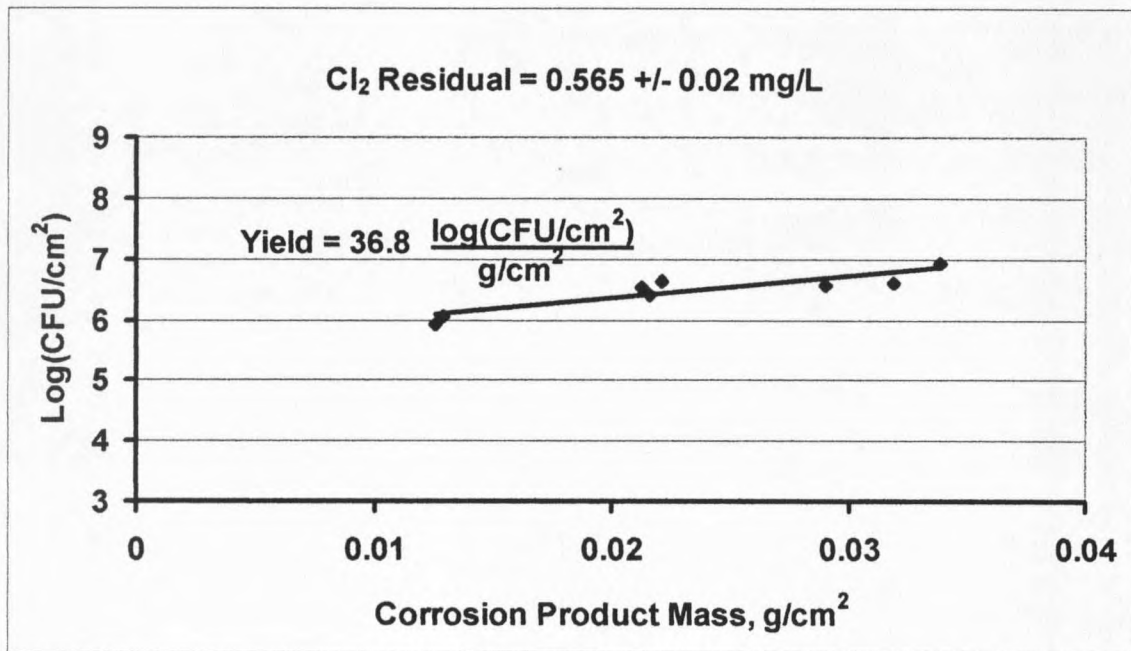
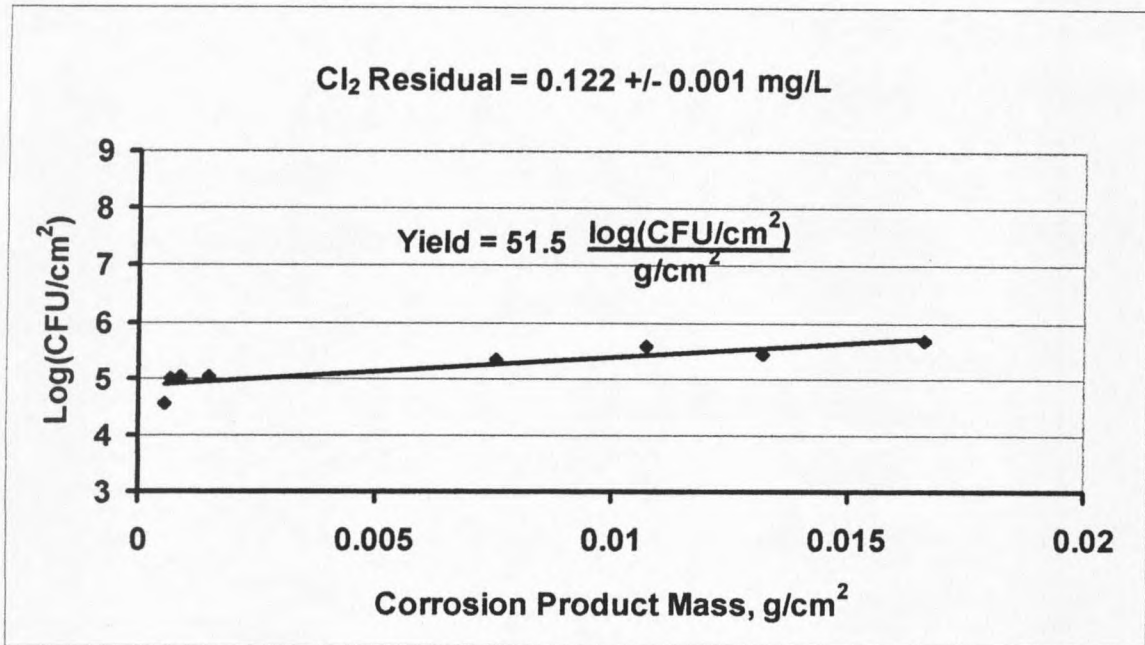


Figure 4.4 Biofilm density as a function of corrosion products and Cl_2 residual

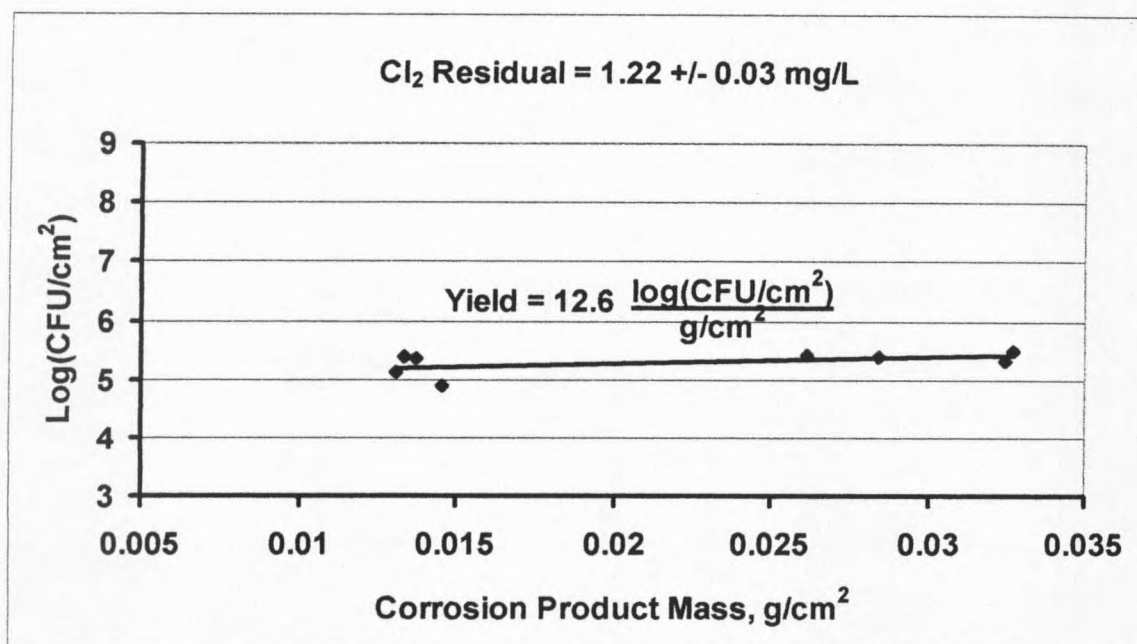


Figure 4.4 Biofilm density as a function of corrosion products and Cl_2 residual

Table 4.4 Biofilm Density Yields at Various Bulk Fluid Chlorine Residual Levels without the use of Corrosion Inhibitors

$$\text{Log}\left(\frac{\text{CFU}}{\text{cm}^2}\right) = Y\left(\frac{\text{g}}{\text{cm}^2}\right)$$

Free Chlorine Residual, mg/L	Yield, Y, $\log(\text{CFU}/\text{cm}^2)/(\text{g}/\text{cm}^2)$	Significance of Yield as compared to zero
0.064 +/- 0.02 mg/L	714	Not significant, p = 0.075
0.105 +/- 0.2 mg/L	66.3	Not significant, p = 0.64
0.122 +/- 0.001 mg/L	51.5	Significant, p = 0.002
0.565 +/- 0.02 mg/L	36.8	Significant, p = 0.003
1.22 +/- 0.03 mg/L	12.6	Not significant, p = 0.156

Note: Yield will vary depending on water quality and pipe material

4.2.1 Experimental Design

This experiment utilized three field type annular reactors and was conducted to provide a side-by-side comparison between a non-chlorinated control, monochloramine, and free chlorine. For the two disinfected reactors, the same influent disinfectant (free chlorine or monochloramine) and nutrient feeds were used in each reactor. A summary of the experimental design is presented in Table 4.5.

4.2.2 Results

As illustrated in Figure 4.5, the monochloramine reactor produced the lowest biofilm density at the conclusion of the experiment. However, it must be

noted that the monochloramine feed solution was buffered with phosphorus, which likely produced results that would not be representative of monochloramine used in an actual water treatment facility.

Table 4.5 Operational Conditions of Bench-scale Study Comparing Free Chlorine and Monochloramine without Corrosion Control

Parameter	Control Reactor	NH ₂ Cl Reactor	Free Cl ₂ Reactor
Residence Time, minutes	120	120	120
Carbon supplement, mg/L [ⓐ]	0.25	0.25	0.25
Influent Monochloramine feed, mg/L	None	3.25	None
Influent Free Chlorine feed, mg/L	None	None	3.25

[ⓐ] In addition to background carbon present in dilution water

As a result of the elevated phosphorus levels in the monochloramine solution, these results should not be used to conclude that monochloramine is a superior disinfectant for the inactivation of distribution biofilms. However, this experiment did provide some insight about the significance of corrosion products on a pipe surface and the role of phosphorus used in most corrosion inhibitors. These observations became evident when the physical condition of the unlined cast-iron pipe reactors was inspected at the conclusion of the experiment. As illustrated in Figure 4.6, the reactor receiving monochloramine had some type of

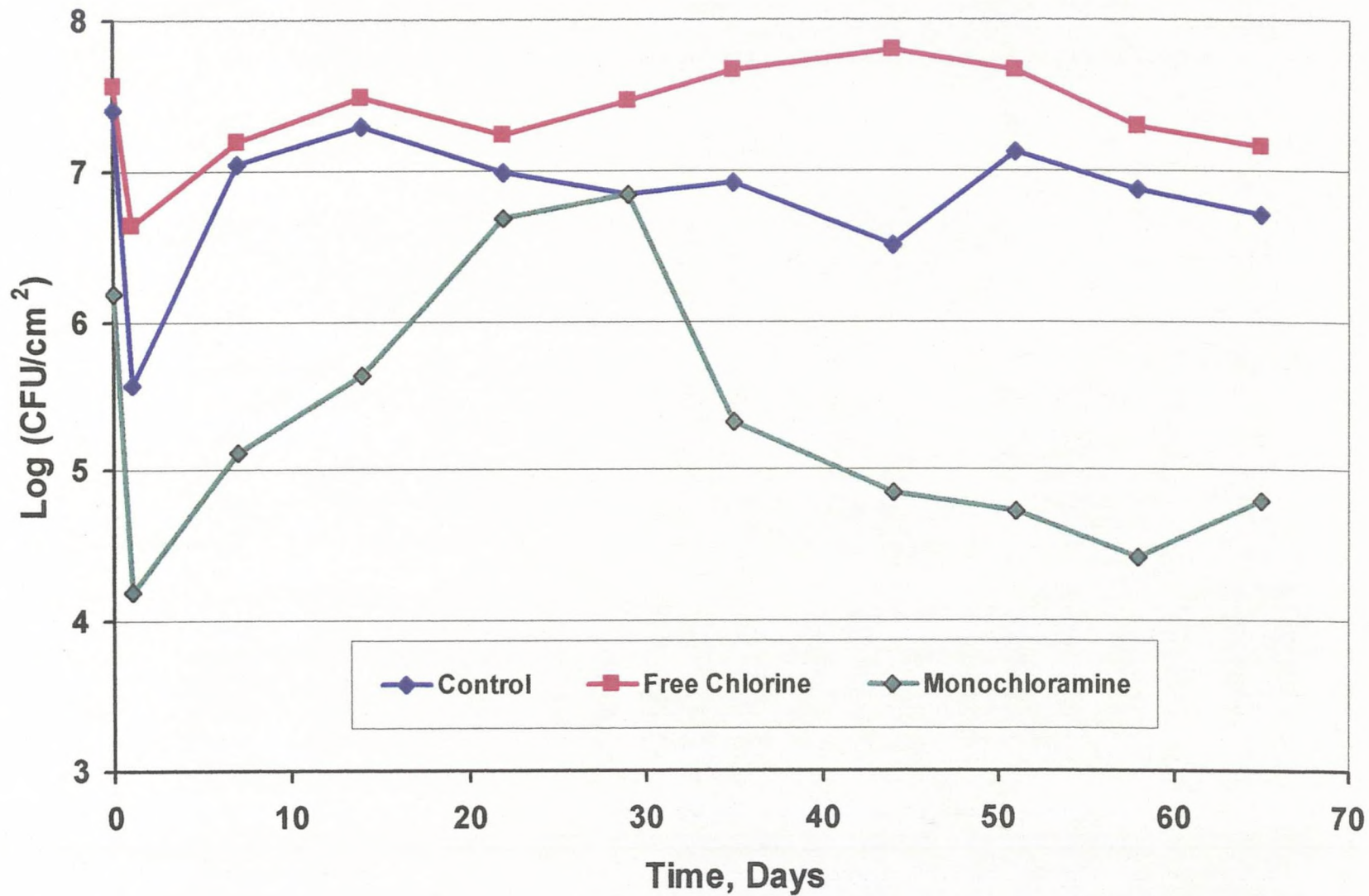
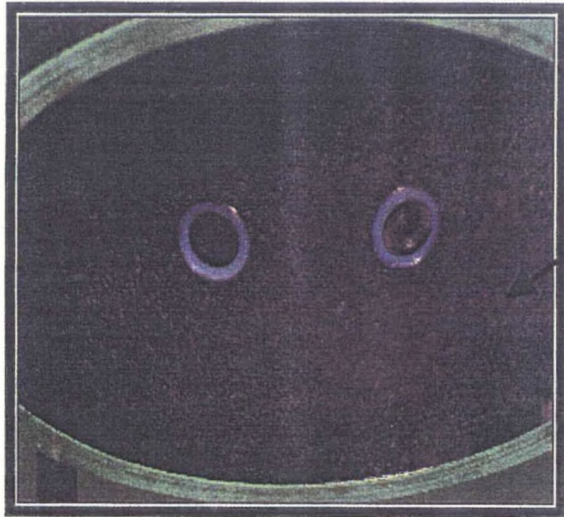


Figure 4.5 Biofilm Density Comparisons between Free Chlorine and Monochloramine



Reactor surface prior to experiment

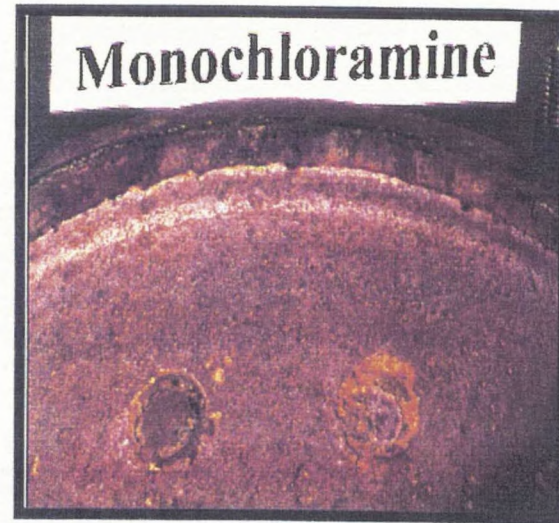
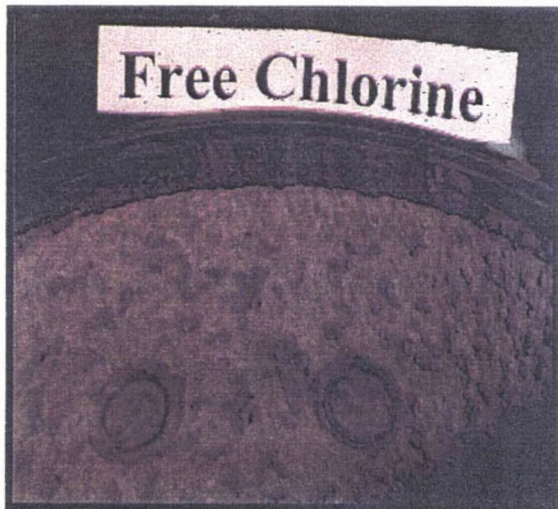


Figure 4.6 Photographs of Reactor Walls after Experiment using Free Chlorine and Monochloramine

chemical coating on the surface which minimized the formation of corrosion products on the pipe surface.

In view of Figure 4.6, several other significant observations can also be made. Observational comparisons can be made between the amount of corrosion products present on the pipe surfaces and biofilm densities on each reactor. For example, the chlorinated reactor usually had the most corrosion products and likewise had the highest biofilm density of all reactors. The reactor receiving the phosphorus buffered monochloramine had the lowest amount of corrosion products and the lowest biofilm density.

Another interesting observation from Figure 4.5 is the shape of the curve for the monochloramine-disinfected reactor. This graph indicates that there was a steady decrease in biofilm density after the 2nd week of operation, which is likely the result of the phosphorus passivation of the pipe surface. The steady decrease in biofilm density can be attributed to: (1) the reduction of disinfectant demand from the pipe surface, (2) reduction in habitat for microorganisms, and (3) changing the surface chemistry of the pipe surface which makes microbial attachment less likely.

4.3 Bench-scale Studies with Free Chlorine and Corrosion Inhibitors

As previously discussed in Chapter 2, the use of phosphorus based corrosion inhibitors is rapidly gaining popularity in the water industry as a method to control the leaching of lead and copper into the finished water. The use of

these inhibitors is of concern to water suppliers because phosphorus is an essential nutrient for microorganisms. It was therefore the purpose of this experiment to evaluate the impacts that two commonly used corrosion inhibitors (zinc orthophosphate and polyphosphate) have on distribution biofilms.

4.3.1 Experimental Design

To determine the effects of zinc orthophosphate and polyphosphate on distribution biofilms, four field type (unlined cast iron) reactors were used, each operating under the same nutrient and hydraulic conditions. Reactor 1 served as a non-chlorinated control without any type of corrosion control, while the remaining reactors each received the same disinfectant feed. In addition to nutrients and free chlorine, Reactors 3 and 4 also received zinc orthophosphate and polyphosphate respectively. Corrosion inhibitor influent feed dosages was determined based on water quality information using the OSCAR™ program by Calgon Chemical Corporation. Specific operating conditions associated with this experiment are presented in Table 4.6.

4.3.2 Results

During the course of this experiment, numerous biofilm and bulk fluid samples were taken to evaluate the efficacy of the corrosion control/disinfection treatment for each reactor. As illustrated in Figure 4.7, the use of corrosion inhibitors can have an influence on the amount of biofilm supported by a ductile iron pipe surface. Long-term effects of the corrosion control/disinfection systems

were analyzed using Fisher's Multiple Comparison with a 95% confidence level on the last four weeks of data. Results from this statistical analysis are presented in Table 4.7 and graphically in Figure 4.8.

Table 4.6 Operational Conditions of Bench-scale Study Comparing Free Chlorine with Zinc Orthophosphate and Polyphosphate

5 Parameter	Control Reactor	Free Cl ₂ Only Reactor	Free Cl ₂ and Polyphosphate Reactor	Free Cl ₂ and Zinc Orthophosphate Reactor
Residence Time, minutes	120	120	120	120
Carbon supplement, mg/L ^①	0.25	0.25	0.25	0.25
Influent Free Chlorine feed, mg/L	None	3.25	3.25	3.25
Influent Zinc Orthophosphate feed, mg/L ^②	0	0	0	10.0
Influent Polyphosphate feed, mg/L ^②	0	0	5.0	0

① In addition to background carbon present in dilution water

② Inhibitor dosages determined by OSCAR program

In review of Figure 4.7, Figure 4.8, and Table 4.7, it should be noted that the chlorinated control once again had the highest biofilm density and that the reactors utilizing corrosion inhibitors supported significantly less microorganisms than the chlorinated reactor. Another important observation is the reaction times of the two reactors that received corrosion inhibitors. As illustrated in Figure 4.7,

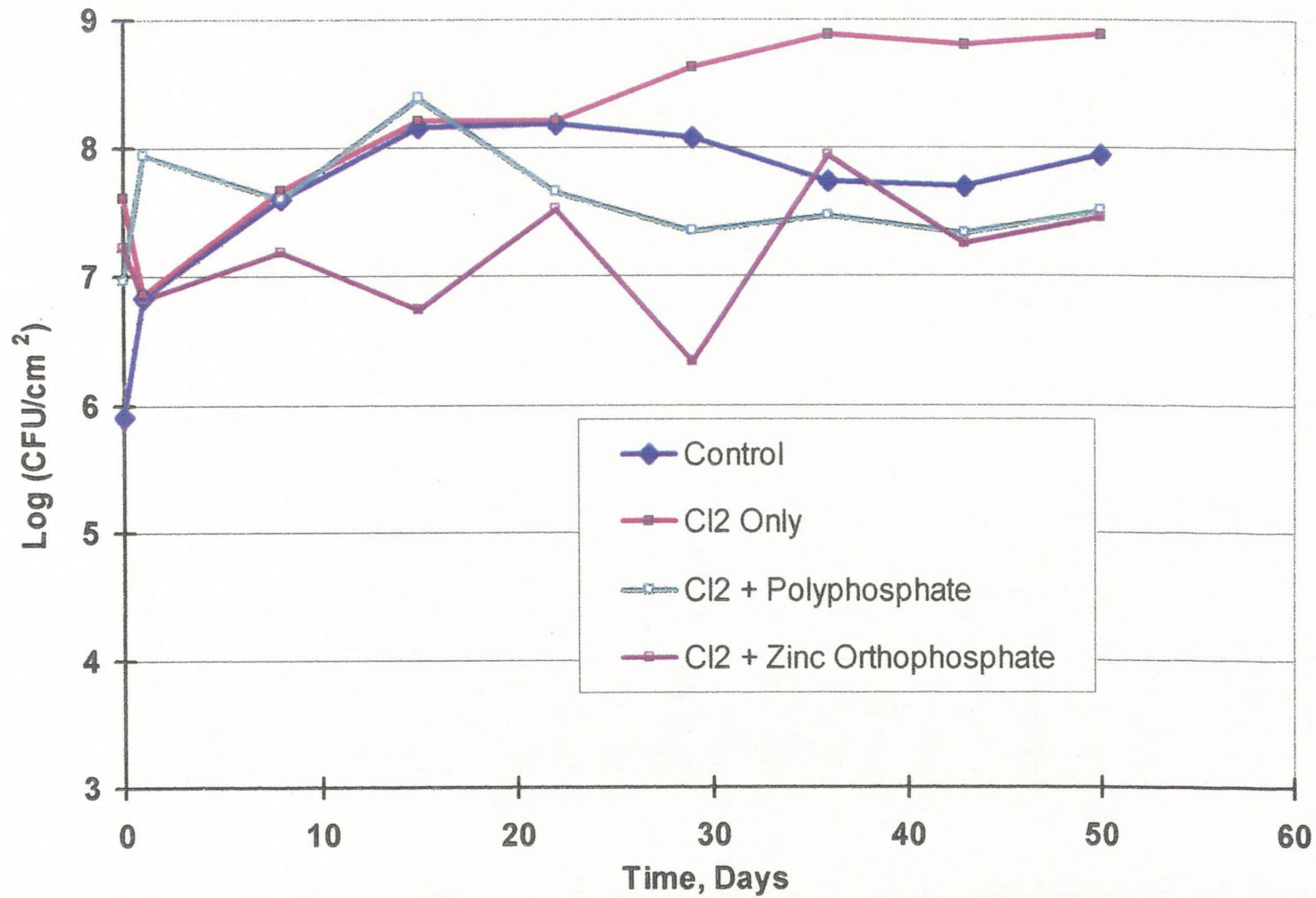


Figure 4.7 Biofilm Density Comparisons using Free Chlorine and Corrosion Inhibitors

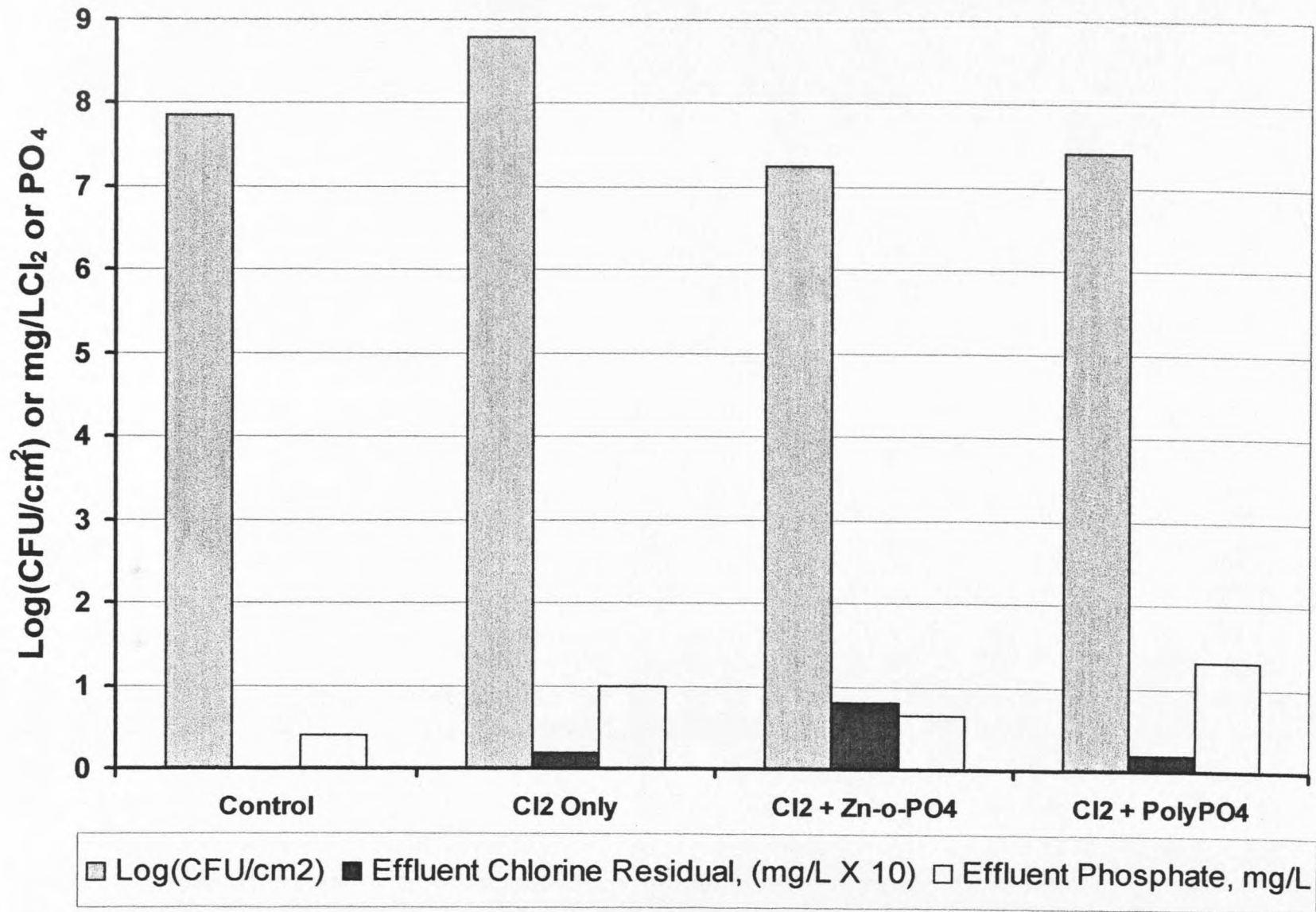


Figure 4.8 Summary Data from Bench-scale Experiment Using Free Chlorine and Corrosion Inhibitors

Table 4.7 Statistical Analysis of Biofilm Densities Using a 95% Confidence Level for Bench-scale Experiment Using Free Chlorine and Corrosion Inhibitors

Log Removal or Gain

Reactor ▼ As Compared to ▶	Control	Cl ₂ Only	Cl ₂ and Zinc Orthophosphate
Cl ₂ Only	1.06 Log		
Cl ₂ and Zinc Orthophosphate	-0.50 Log	-1.55 Log	
Cl ₂ and Polyphosphate	-0.08 Log Not Significant	-1.14 Log	0.41 Log Not Significant

Note: The Cl₂ Only Reactor had 1.06 Log more biofilm density than the Control Reactor. All values are statistically significant unless noted otherwise.

the zinc orthophosphate reactor had a rapid increase in disinfection efficacy while the polyphosphate reactor began to demonstrate increased disinfection efficacy and biofilm control after the 3rd week.

As with the previous experiment, a visual inspection of the pipe reactors at the conclusion of the experiment also provided some interesting observations. As illustrated in Figure 4.9, the chlorinated control reactor once again had the highest corrosion product mass and also the highest biofilm density. The non-chlorinated control and the polyphosphate had approximately the same quantity of corrosion product mass and likewise did not have any significant differences in biofilm density. The zinc orthophosphate reactor had the lowest corrosion product mass and the lowest biofilm density.

