OPTIMUM SCHEME FOR COMBINED REMOVAL OF IRON, MANGANESE, AND ORGANIC MATTER FROM POTABLE WATER

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TABLE OF CONTENTS

Chapter

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

The main objectives of this study were to provide baseline data on the water quality for the Guajataca Channel that flows from Guajataca Lake to Ramey Water Treatment Plant in Aguadilla; and to determine the effectivity of chlorine, potassium permanganate and their combination for the control and reduction of trihalomethanes(THMs) formation, iron and manganese.

The channel was sampled continuously each month at ten sampling points through out the entire channel in a period of six months (December 1993 - May 1994). Significant variation in pH between the lake and the plant, from 7.4 and 8.2 were found. On the other hand, turbidity was low through the entire channel. At each sampling point, the channel was very contaminated with fecal coliforms. Biological oxygen demand (BOD) concentration was low through all the channel. In the case of chemical oxygen demand (COD), there were significant variations at each point.

The other part of the project consisted of the use of chlorine, potassium permanganate and their combination for water treatment at Ramey's plant. Preliminary experiments were performed using a 24 hr prechlorination treatment. It was observed that THMs concentration was low and uniform in the mixing tank and clear well. An experiment was designed and carried out for evaluating at two levels of concentration the combined use of potassium permanganate solution as a substitute of prechlorination. It was concluded that the combination of low level of chlorine (0.4 - 0.8 mg/l, free chlorine) and a high level of potassium permanganate (0.8 mg/l, residual) is good for the oxidation of iron and the reduction of trihalomethane formation. For the reduction of manganese levels, the best combination was low levels of potassium permanganate solution (0.2 mg/l, residual) and high chlorine levels (2.5-3.0 mg/l, free chlorine).

A final experiment was performed by applying prechlorination with potassium permanganate solution with post-chlorination. In this case iron concentrations were lowered by 85 and 99%, while the concentrations of THMs remained under EPA limits.

According to an analysis of covariance there is no evidence that the THMs produced in each treatment depend on the initial concentration of carbon (TOC) content of the influent.

Fecal coliforms completely disappeared in all the experiments conducted at Ramey, which indicates full compliance with the concentration limit imposed by EPA on this parameter. A laboratory scale experiment conducted to study the disinfection capacity of potassium permanganate indicates that over 80% of the fecal coliforms always disappear in one hour. Therefore, potassium permanganate contributes significantly to the reduction of fecal coliforms, in addition to the low level of THMs produced and its contribution to the removal of iron. It is concluded that potassium permanganate is an excellent substitute to pre-chlorination in the potabilization of water.

CHAPTER 1

INTRODUCTION

Since the end of the nineteenth century surface water has been treated to make it safe for drinking (White,C. 1986). The normal treatment method is chlorination. Chlorine is used to disinfect and to attenuate microorganisms of sanitary significance; it is also used for the oxidation of organic matter. Around twenty years ago it was discovered that trihalomethanes (THMs) were formed after chlorination (Rook, 1974). The THMs are directly related to certain organic matter (precursors) present in raw waters. Since THMs are suspected carcinogens, their presence in drinking water has become an issue. The approval of the National Interim Primary Drinking Water Regulation limits the concentration of Total Trihalomethanes (THMs) in drinking water to 0.10 miligrams/liter (100 parts per billion) on an annual average. The common THMs identified in drinking water are: bromoform, chloroform, chlorodibromomethane, and bromodichloromethane.

Another important issue is the concentration of iron and manganese in potable water. These metal concentrations are regulated by the Environmental Protection Agency (EPA) and are included in the Secondary Drinking Water Standards. These concentrations limits were established to prevent staining of clothes during laundering. The EPA promotes and enforces these regulations through the corresponding agencies that handle water treatment facilities.

These are several methods to reduce the THMs, iron, and manganese content of drinking water. These methods include chlorination, ozonation, filtration through granular activated carbon, UV irradiation, and oxidation with potassium permanganate. The basis of our study was to optimize water purification systems related to the reduction of THMs formation, iron and manganese using different treatment methods. In our case, we evaluated the effectiveness of chlorine and potassium permanganate by their separate and combined application to raw water. It should be emphasized at this point that the scope of this work was limited to a qualitative assesment of these technologies for the stated purpose. It does not intend to model in any detail the many complex phenomena involved.

The water under study is from the Ramey Plant, a drinking water treatment facility of the Puerto Rico Aqueduct and Sewage Authority (PRASA) located at the Northwest side of Puerto Rico in the town of Aguadilla. This plant has a capacity of approximately 3 million galons per day. The surface water of this facility comes from Guajataca Lake, located south of the towns of Quebradillas and Camuy and north of the town of San Sebastian. This water flows through an open channel and travels 22 miles (35.2 km) by three towns: Quebradillas, Isabela, and Aguadilla. The channel was built in 1928 mostly for the development of a hydroelectric power generation, system water supply for agricultural purposes. The water supply under study was characterized for the following parameters: bacterial content, chemical oxygen demand (COD), turbidity, biological oxygen demand (BOD), and pH.

This project is an effort to solve problems in our community and is sponsored by the Water Resources Research Institute, United States Department of Interior, United States Geological Survey and the University of Puerto Rico at Mayagüez.

CHAPTER 2

PREVIOUS WORK

2.1 Trihalomethane Formation

A routine gas chromatographic analysis of the head space of a water treatment plant using chlorine revealed four new peaks (Rook, 1974). An investigation was initiated to identify the by-products and the cause of their formation. This investigation have shown that haloforms are produced during chlorination of humic substances in natural waters.

The humic substances are a product of plant decay and include macromolecules which are condensation products of quinones and polyhydroxybenzenes, with substituents of NH_2 groups. In Fig. 2.1 on page 3 a structure of a humic acid is illustrated.

At EPA's National Environmental Research Center Cincinnati, Ohio the first studies of the precursors and formation of THMs were effected (Bellar et al., 1974). Bellar and colleages suggested a possible mechanism for the formation of chloroform by the compounds detected in the tap water-ethanol solution and trihalogenated methanes. First the ethanol oxidizes to acetaldehyde. The acetaldehyde reacts with free chlorine to form chloral. The chloral reacts with water to form choral hydrate, and the choral hydrate decomposes to form chloroform. The study was based on different water sources such as municipal supplies and sewage treatment plants.

The formation of trihalomethanes occurs when the chlorine added to the water purification process interacts with the organic matter (humic and fulvic acids, which are precursors). A general equation of THMs formation is (Jolley et al., 1981):

Aqueous halogen species + Precursors --> THMs + By-product

Trihalomethane are molecules of methane which are formed when three of the hydrogen atoms have been substituted by atoms of the halogen family (chlorine,bromine,iodine or the combination of these).

The following are some examples of THMs:

$CHCl_3$ *(Chloroform)*, $CHBr_3$ *(Bromoform)*,

$CHCl_2Br$ *(Bromodichloromethane)*

$CHClBr_2$ *(Dibromochloromethane)*

Many water purification plants use chlorine gas at the entrance and exit. Chlorine ions interact with the humic and fulvic acids, which are substances that originate from vegetative decay and make up a significant portion of the total organic carbon content of natural waters (Babcock and Singer,1979). These acids together constitute over eighty percent by weight of all natural aquatic organic material (Black and Christman,1963).

Not all the THMs precursors are humic and fulvic acids. Hoehn et al., (1980) concluded that both green algae and blue-green algae produce extracellular products (ECP) which, upon chlorination, yield at least as much chloroform per unit organic carbon as has been reported from previous studies of humic and fulvic acids.

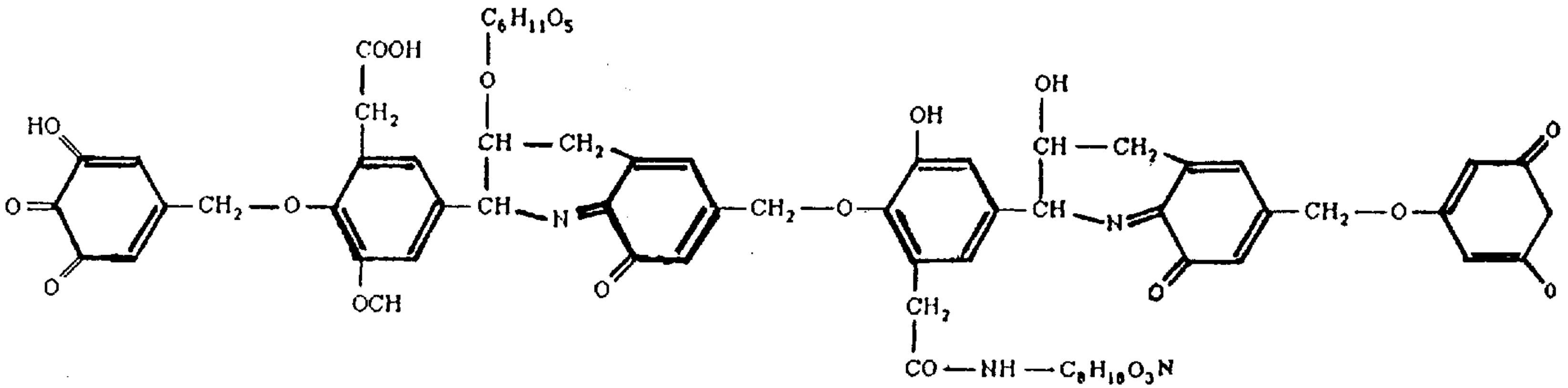

Figure 2.1
Structure of a Humic Acid according to Dragunov
Kononova, M.M. "Soil Organic Matter". 1982

Factors that affect the formation of trihalomethanes are specially: chlorine dosage at the water purification plant, pH, water temperature in pipelines, raw water origin, and treatment methodology (Glaze et al.,1982). In addition, precursors have been found in living and aquatic plants (Briley et al., 1985).

Recently at Ohio, an investigation conducted on THMs precursors was made by analyzing lake sediments (Martin et al., 1993). Samples were collected from littoral and profundal areas of two different lakes. They concluded that all sediments had significant THMs precursor releases relative to none-sediment controls. Anaerobic and aerobic conditions were studied. Anaerobic conditions produced less precursors than during an aerobic incubation.

The littoral sediment precursors release rate (μg/ THMs/m^2/day) was significantly greater than precursor release rates for lake and reservoir deep sediments.

2.2 Treatment for THMs precursor

In the past years, investigators have been working on different methods to eliminate and reduce THMs precursors. Strong base resins were used succesfully to remove most of the organic precursors to avoid the formation of chloroform caused by chlorination of natural waters (Rook, 1976). Also, a scavenging process was proved to be 75% effective in reducing the chloroform potential of Meuse River water (Rook and Evans, 1979). A scavenging process is where a column is loaded with a resin and water is passed through to remove organics. The resin is regenerated after a period of time which is called the elution process. Two commercial weak base resins were used.

Stevens et al. (1976) concluded from bench and pilot plant-scale studies, that the THMs production during chlorination process is probably a complex mixture of humic substances and simple low molecular weight compounds containing the acetyl moiety.. Granular activated carbon was used with limited success to remove precursor compounds because its effectiveness is limited to only few weeks. Harms (1977) has worked on chlorination adjustment to water plants to reduce THMs formation.

Singer (1980) worked on the use of potassium permanganate which oxidizes the precursors of THMs, thereby reducing subsequent haloform production. He concluded that the reactivity of permanganate in water is reflected by the rate and extent of permanganate consumption, and is a function of pH, permanganate dose, and raw water quality. López and Ortíz (1990), studied THMs production formation using potassium permanganate and chloramines. Some work has been done using ozone as a THMs precursor treatment. Glaze (1987) showed that the simultaneous application of ozone and ultraviolet radiation is appreciably more effective than ozone alone. The mechanism involves the destruction with ozone of the precursors initially present and the parallel formation and subsequent destruction (with UV radiation) of the secondary precursors resistant to oxidation with ozone. UV is more efficient in destroying the secondary precursors.

Ceinos (1992) evaluated the effectiveness of the combined use of UV irradiation and ozone in the reduction of THMs in local raw water. He developed a kinetic model which relates the rate of THMs formation to the residual ozone, UV irradiation intensity and time. Chapero (1994) is evaluating the degree of reduction of the THMs precursors in raw water through Ozone-UV irradiation as a function of the water source and season of the year. The raw water samples are taken from eight major water resources in Puerto Rico. Other studies conducted at the department of Chemical Engineering by Benítez (1990), Burgos (1990), and Guntín (1990) are related to THMs formation potential of chlorinated water (chlorination practices, mathematical model for THMs prediction, and THMs kinetics respectively).

In Italy (Agazzotti et al., 1986), a survey of volatile halogenated organics (THMs included) was made in the Emilia-Romagna Region where the following water samples were analyzed: drinking water, surface water, and swimming pools. Agazzoti and colleagues determined the maximum quantities; (41.8 µg/L) surface water, (263 µg/L) drinking water, (177 µg/L) swimming pool as a consequence of chlorination with sodium hypochlorite. Singer (1988) evaluated eight utilities were in two of them the extent of THMs formation was reduced succesfully (under maximum contaminant level MCL). In both of the utilities chloramination was adopted.

Myers (1990), after evaluating different disinfectants in small systems, suggested the use of chloramines instead of chlorine as the final disinfectant which is a relatively inexpensive method for THMs reduction. Granular activated carbon (GAC) was evaluated by McGuire and colleagues (1991). They concluded that this type of treatment is expensive for the control of trihalomethanes where the predominant postdisinfection by-products of GAC effluents were treated with chlorine and chloramines. Alawi et al. (1994), recently isolated definite amounts of humic acid from the Arzaq Oasis in Jordan, where concentrations of four THMs were reported.

2.3 Mathematical Models for Predicting THMs

Some models and equations for THMs formation have been developed in the past years. In Japan, (Urano et al., 1983) an empirical rate equation for THMs formation with chlorination of humic substances in water was developed. The equation is described as follows:

$$[THMs] = k(pH - a)\ [TOC]\ [Cl_2]_0^m t^n \qquad 2.3.1$$

where [THMs] is the concentration of total THMs after t hours, [TOC] and $[Cl_2]_o$ are the concentrations of Total Organic Carbon and chlorine dose, k is the rate constant and a, m, and n are parameters. The values of k,a,m and n for humic acid as reagent were obtained as 8.2×10^{-4} (l^m mg^{-m} h^{-n}), 2.8,0.25,0.36,respectively. It was shown that this equation could be applied to the rates of THMs formation from precursors in actual river and lake waters. Engerholm & Amy (1983) made a predictive model for chloroform formation from humic acid. This model was based on the following generalized reaction:

$$Precursor\ (as\ TOC) + Cl_2 \rightarrow CHCl_3 \qquad 2.3.2$$

Three submodels, ranging from simple to progresively more complex in character are described below.

$$CHCl_3 = k_c(t)^z \qquad 2.3.3$$

$$Cl_3 = k_b(Cl_2 / TOC)^y (t)^z \qquad 2.3.4$$

$$CHCl_3 = k_c(TOC)^x (t)^z \qquad 2.3.5$$

where $CHCl_3$ is the chloroform concentration (µg/l); t is the reaction time (hours); TOC is the initial TOC (mg/l); Cl_2/TOC is the initial chlorine-to-TOC ratio (dimensionless); x,y,z are empirically derived constants; and k_a,k_b,and k_c are reaction cosntants. Finally, the overall model was defined as

$$CHCl_3 = k(TOC)^x (Cl_2 / TOC)^y (t)^z \qquad 2.3.6$$

This equation can be transformed into natural log form and a multiple linear regression can be performed.

$$\ln CHCl_3 = \ln k + x \ln TOC + y \ln(Cl_2 / TOC) + z \ln t \qquad 2.3.7$$

This model showed that it is possible to model the chlorform formation reaction for a specific precursor with a significant degree of accuracy.

Morrow and Minear (1987) developed a nonlinear regression models for THMs formation using the laboratory chlorination data with respect to pH, temperature, chlorine dose, bromide, and non-volatile total organic carbon (NV-TOC) level. The actual values for these variables were substituted into regression models, using the field data. The resultant predictive THMs values were then compared with actual THMs values for the data sampled. In this study, a 74.1% of the predicted values were within ± 15.% of the measured values. Singer and Chang (1989) developed a correlation between THMs and (TOX) Total Organic Halides Formed, where surface water undergone conventional treatment were formed to contain a TOX to THMs ratio of aproximately 3.4 to 1.

Studies conducted by the U.S. Geological Survey, (Rathbun et al., 1992) presented a correlation of Trihalomethanes Formation Potential (THMFP) as function of pH and initial free chlorine, dissloved organic carbon, and bromide concentrations for a period of 21 months. The THMFP was determined for 17 samples water from the Kentucky river. The THMFP ranged from 59.7 to 731 µg/l and averaged 240 µg/l, compared with the EPA standard 100 µg/l. One of the equations developed is the following.

$$THMFP = 0.714 DOC^{1.19} pH^{2.12} Cl^{0.0969} \qquad 2.3.8$$

This equation predicted the THMFP with a standard error of estimate of 9.18 percent of the mean. Recently, Hutton and Chung (1994) developed a correlation which is an effective tool for estimating *simulated distribution system* THM (SDS-THM) species concentrations from source water precursor measurements such as THMFP. In this investigation, empirical relationships for SDS-THM formation are succesfully calibrated and verified with data collected over a 14 month period from six locations in California.

2.4 Iron and Manganese Oxidation

Iron and manganese removal has been done by different methods which use ozone and potassium permanganate acting as oxidants. Ozone and Permanganate act as oxidants of iron and manganese($Fe^{2+} \rightarrow Fe^{3+}$ and $Mn^{2+} \rightarrow Mn^{4+}$). At a higher oxidation state both are insoluble. The issue has been targeted by the USEPA (Lorenz et al., 1988) which has established secondary drinking water standards for iron at 0.3 mg/l and for manganese 0.05 mg/l. The standards were established to prevent staining of plumbing fixtures, encrustation of piping, clogging of home water softeners, and taste in the water supply.

Knocke (1987) tested various water treatment plants using ozone for iron and manganese oxidation, specifically, a water plant located in Hacksack, New Jersey which has a flow of 4.7 m^3/seg. Also, he showed that the results of his study allow for the formulation of general considerations regarding oxidant usage. Each treatment facility should test oxidant on-site to determine which promote manganese oxidation under the range of conditions (pH, TOC, and temperature) prevalent at the particular facility. Furthermore, Ficek (1978) says that in ground and surface water supplies, soluble iron generally exists as divalent ferrous salt. Soluble manganese, with few exceptions, also exists in the divalent manganous state. Iron and manganese appear in water as organic complexes. These complexes are formed by the combination of iron and manganese ions surrounded by negatively charged organic units called ligands.

Theoretically Ficek established that 1 mg/l of potassium permanganate oxidized 1.06 mg/l of ferrous iron, as described by this equation:

$$3Fe^{++} + MnO_4^- + 4H^+ \rightarrow MnO_2 + 3Fe^{+++} + 2H_2O$$

It required 1 mg/l of potassium permanganate ($KMnO_4$) to oxidize 0.52 mg/l of soluble manganese.

$$3Mn^{++} + 2MnO_4^- + 2H_2O \rightarrow 5MnO_2 + 4H^+$$

Wong (1984) describes three water treatment processes that are: (1) aeration filtration, (2) chlorination-filtration, (3) potassium permanganate-manganese-green sand filtration. At higher pH levels, the oxidative reaction should be rapid and complete.. This pilot study showed that the chlorination-filtration process can remove iron and manganese effectively from hard water if the pH is maintained at 8.5 or above. The aeration-filtration process is for water with high concentrations (75.0 mg/l) of iron to save chemical costs, and the potassium permanganate-manganese greensand filtration is recommended for the removal of low to moderate concentrations (0-5.0 mg/l).

2.5 Potassium Permanganate Background

In 1659, Glauber (German Chemist) was the first to use permanganate as a lab reagent. In 1859, H.B. Condy, a London industrialist, comissioned a prominent chemistry professor, A. W. Hoffman, to prepare an evaluation of the disinfecting power of potassium permanganate then known as the "chamaleon mineral" (Ficek 1992). Condy, in 1862, became the first industrial producer after Hoffman's evaluation. In 1873, $KMnO_4$ had become an all-purpose disinfectant, widely used in hospitals and househoulds across Europe (Cassebaum 1979, Reidies 1987). Investigations have been conducted for potassium permanganate disinfection effectiveness (Cleasby et al., 1964, Banerjea 1950). Cleasby determined that $KMnO_4$ is a good disinfecting agent against ***Escherichia Coli*** between 0° and 20°, slightly greater kill is obtained at high temperatures. Also, $KMnO_4$ has been utilized for manganese removal at low pH (6.5 to 7.0) and low hardness waters (Ficek, 1985). It was used for treatment of low level phenols in wastewater treatment (µg/l) (Viella et al., 1990). In this study two manufacturing sites were chosen. The two sites were industrial effluents from a thermoplastic resin manufacturer and from an aluminum casting plant. The results suggested that potassium permanganate would be effective in the oxidation of phenols. For example, it reduced the phenol concentration from 467 µg/l to 2 µg/l.

Yahya et al. (1989) had good results by inactivating a bacteria named ***Legionella pneumophila*** (bacterial pathogen for Legionares Disease and Pontiac Fever) with an exposure of 5.0 mg/l of $KMnO_4$. The bacterial number was reduced 99% in 10 minutes at a pH of 6.0. Potassium permanganate was used as an oxidant for the control of adult Zebra Mussels (Mollusk) which causes biofouling at a pump station for Toledo, Ohio.

The buildup of thick layers of zebra mussels which can cause a reduction in water transport capacity is a major problem at the water facilities near the great lakes (Klerks et al., 1991).

In a work performed at the Davenport water company plant, $KMnO_4$ has been used as a preoxidant (Blanck, 1983). The results at this plant showed a significant reduction in bacterial content of the Missisipi River water with treatment at low levels of Potassium Permanganate (0.51 to 0.68 mg/l). Also, it was noticed a decrease of \$1.15/MG in operating costs over the previously used prechlorination treatment. In Milwaukee, Wisconsin at Howard Purification Plant $KMnO_4$ is used for taste and odor treatment (Middlemas et al., 1986). Finally, in China pilot and full scale plant studies were conducted using potassium permanganate as an aid for coagulation (Ma et al., 1993). As a reult, positive effects of permanganate showed that the size of the flocs for the reaction tank became bigger if the water was preoxidized, lowering the polyaluminum chloride (PAC) consumption by about 36%.

2.6 THM Health Effects

In 1976, it was reported in a study for carcinogenesis bioassay of chloroform (by the U.S. National Cancer Institute) where $CHCl_3$ produces tumors in rats and mice when administered in large repeated doses (Page et al., 1976). Cantor et al. (1978) made a biostatistical study of cancer mortality associated with THMs. This study was a correlation between site and sex-specific county cancer mortality rates and levels of THMs. Bladder cancer mortality rates showed the strongest and most consistent association with a THMs exposure index, after control for differences in social class, ethnic group, urban vs. rural residence, region of the United States, and industralization. Also, (Reitz et al., 1982) studies were carried out in male B6C3F1 mice in order to investigate the potential of chloroform to induce genetic damage and/or toxicity. As a result, the studies revealed that carcinogenic doses of chloroform produced severe necrosis at the sites where tumors later developed.

Several counties of the state of Louisiana using the Missisipi River for this source of public drinking water have the highest mortality rates (1950-69) in United States for several cancers. Therefore, a case-control mortality study was made on cancer of the liver, brain, pancreas, bladder, kidney, prostate, rectum, colon, esophagus, stomach, and other diseases. As a result, in this study significantly increased risk for surface chlorinated water was noted for rectal cancer (Gottlieb et al., 1982). Also, (Morris et al., 1992) in a Meta-Analysis prepared by using individual epidmiological investigations found positive association between consumption of chlorination by products in drinking water and bladder and rectal cancer in humans.

Finally, a statistical study was developed from a population-based case control study of bladder cancer and drinking water disinfection methods during 1990-1991 in Colorado conducted by McGeehin and colleages (1993). A total of 327 histologically verified bladder cancer cases were frequency matched by age and sex to 261 other-cancer controls.

2.7 Previous Data

Table 2.7.1 illustrates the average of the THMs concentrations during the 1992 Fiscal Year. It can be noticed that all systems were violating the THMs Maximum Contaminant level (MCL) which is 100 ppb. The Department of Health makes inspections by sampling four times per year.

The water treatment has to meet a National Permit Discharge Elimination System (NPDES) for filter backwash discharges. This permit includes 22 parameters divided in 7 metals, temperature, turbidity, color, dissolved oxygen, BOD-5 day, pH, settleable solids, oil and grease, nitrite, chloride, flow in conduit, total solids, total chlorine, fecal coliform, and total coliform. Table 2.7.2 illustrates parameters that have exceeded the limits of NPDES for the period from June 1 to August 31, 1994.

Table 2.7.1
Total Trihalomethanes for Puerto Rico Aqueduct and Sewage Authority for 1992
(Data from Department of Health of Puerto Rico)

Municipality	System	Average Fiscal Year 1992 (ppb)
Trujillo Alto	Sergio Cuevas	131.03
Bayamón	La Plata	115.23
Canóvanas	Canóvanas	96.10
Rio Grande	Rio Grande	131.80
Guaynabo	Guaynabo	113. 67
Aguadilla	Ramey	104.97
Juncos	Quebrada	116.43

Table 2.7.2
NPDES Limits for the Ramey Plant
Data from the Puerto Rico Aqueduct & Sewer Authority (September 1994)

PARAMETER	LIMITS	LAB. RESULTS
BOD	5000 Ug/L	12,000 Ug/L
Copper	40 Ug/L	50 Ug/L
Iron	300 Ug/L	1500 Ug/L
Zinc	50 Ug/L	60 Ug/L
Settleable Solids	1 ml/L	40 ml/L
Residual Chlorine	500 Ug/L	600 Ug/L

CHAPTER 3

SITE DESCRIPTION

3.1 Channel Description

The Irrigation Law of 1908 made posible the creation of the first Irrigation System of Puerto Rico located in the south coast. In addition, the proclaim of the laws of 1924-25 (with the extension in 1927) gave the principal motivation for the hydroelectric development of Puerto Rico. By using this legislation, special funds were provided for research, construction, and operation of hydroelectric projects. The laws also gave initial support to a large hydrographic study which included plans for water control, electrical generation,and for water supply.

The Guajataca Diversion Channel and the Guajataca Lake were constructed in 1928. The channel is divided in four hydroelectrical plants which are: Isabela 1 (1928) 1200 KW, Isabela 2 (1938) 800 KW, Isabela 3 (1947) 1000 KW,and Isabela 4 (1947) 1300 KW. The channel is divided in two ; Moca Channel, and Aguadilla Channel. This division starts 10 miles down stream in the Gaujataca Diversion Channel. The Moca Channel has a length of 15.6 miles ending at the Aguadilla Water Treatment Plant (1968) (PRASA). The Aguadilla Channel flows 12 miles ending at the Ramey Water Treatment Plant (1939) (PRASA).

The first ten miles of the main channel flows by gravity through 23 tunnels, 5 pressure drops, and 7 flumes (Lizasoain, J. 1993). Also, this channel includes two PRASA water treatment plants which are Guajataca and Llanadas Plant. The channel divides in two at Forebay, the Aguadilla Channel covers a distance of 5 miles passing through road PR 112 and PR 2 finishing at the lake of Plant #2 (Isabela) which serves as water resource for PRASA Guerrero Water Treatment Plant. From this point the Aguadilla canal connects to Calero lake at Barrio Camaseyes and then it ends up at the Ramey Water Filtration Plant. The Moca Channel does not have any lake or water plant, before its end in Aguadilla. The irrigation system is operated today by the Mora Station Irrigation Services in Isabela which is administered by the Puerto Rico Electric and Power Authority (PREPA).

3.2 Plant Description

The Ramey Plant was built in 1938 by the Corps of Engineers of the United States to supply water for the Ramey Base(US Air Force). In 1970, the United States Air Force left its administration to the United States Coast Guard until 1974. Since that year the Puerto Rico Aqueduct and Sewage Authority (PRASA) is in charge of the Plant. PRASA has a 1 million gallon per day (MGD) contract with the Coast Guard. This plant is located at kilometer 0.1 of the Callejón Feliciano Road. , Barrio Camaseyes, Aguadilla, Puerto Rico. Today this plant treats from 2 to 3 MGD of water. The plant is composed of the following sections:

1) Raw Water Supply: Diversion Channel (3 ft deep x 8 ft wide)
2) Water Intakes: Water Intake #1 has two grids (two inlets) through a 14" OD galvanized pipe and Water Intake #2 with one grid through a 14" OD galvanized pipe.
3) Mixing Tank (rectangular tank 3' x 5' x 11'7" deep)

4) Chemical Feeders (Wallace & Tiernan Series 32-050) - one for Aluminum Sulfate(Carribbean Exporters Limited, Kingston, Jamaica) and the other for $CaCO_3$ (Calcium Carbonate).
5) Flocculator (Polymer) Feeder - has a pump connected to a 55 gallon drum. Three commercial polymers are used; (Floergger FL-16®, CAT-FLOC-FL®, Stern-Pac®)
6) Chlorine Room - It is localized in the first floor where a weight balance is located to weight the chlorine cylinders (0-150 lb) and two rotameters (Capitol Controls®) are connected for pre and post chlorination.
7) Clarifiers - This is a system of three clarifiers (octagonal form) which is fed from the mixing tank and has a motor for continous mixing (LIMA ELECTRIC Co.)(see Figure 3.4)
8) Flowmeter - this flow meter (1000 gal/min) is located between the clarifiers and the filters on a 20 inch pipe.
9) Filters - Water flows from the clarifiers to 6 filters (4 filters (constructed in1938) are in the building and the other two (1959) are out side of the building), whose dimensions are 17 feet long x 8 feet deep x 12 feet wide.
10) Clear Well - This storage, located in the first floor, is approximately 10 ft deep, 51 feet long,and 63 feet wide. Volume = 220,000 gallons. It has a level control alarm to indicate when it is empty or full.
11) Distribution Tanks - These are three storage tanks 500,000 gal each. The Tanks (26 feet high and 62.7 feet in diameter) are located on top of a hill at 360 feet above the sea level, a mile away from Ramey Airport.
12) Laboratory Room - The following measurements are made: pH, turbidity, Jar Test, and Free chlorine. There is a technician 24 hr a day (three shifts).

3.3 Theory of Water Treatment

The important terms to define in potable water treatment are: disinfection, coagulation, flocculation, mixing, sedimentation, and filtration. Disinfection is the most important step. Water disinfection is a process by which pathogenic microorganisms are destroyed. It provides essential public health protection. Disinfection is a unit process whose objective is the destruction or otherwise inactivation of pathogenic microorganisms, including bacteria, amoebic cysts, algae, spores, and viruses (Montgomery et al., 1985).

Coagulation comes from the Latin word *"coagulare"* , meaning to drive together. This process describes the effect produced by the addition of a chemical to colloidal dispersion by a reduction of the forces tending the particles apart.

Flocculation is the second stage in the formation of settleable particles from destabilized colloidal-sized particles. This term comes from the latin word *"flocculare"* , meaning to form a floc, which visually resembles a thrift of wool or highly fibrous structure. In contrast to coagulation where the primary force is electrostatic or interionic, flocculation occurs by a chemical bridging or physical enmeshment mechanism.

Filtration is defined as the passage of a fluid through porous medium to remove matter held in suspension. The matter which is removed in water purification includes suspended silt, clay, colloids, and microorganisms, including algae, bacteria and viruses. A filter consists of thin porous layer of filter sand deposited by flow on a bed of granular nonporous material held in place by the force of gravity or by the direction of flow.

CHAPTER 4

EXPERIMENTAL PROCEDURE

4.1 Experimental Procedure for Channel Study

Raw water was obtained from ten sampling points, from the beginning to the end of the diversion channel from lake Guajataca to the city of Aguadilla. The following parameters were measured in each sample: chemical oxygen demand (COD), concentration of iron and manganese, pH, water temperature, and turbidity. These measurements were made from December 1993 to May 1994. The ten sampling points used, include the two channels, which the Moca Channel and the Aguadilla Channel. Sampling points 1 to 3 are located in the Guajataca Channel, points 4,5,6, and 7 cover the Aguadilla Channel, and sampling points 8,9,and 10 are located in the Moca Channel. Table 4.1 illustrates the sampling points addressed and Figure 5.1 illustrates them on the map.

Table 4.1
Channel Sampling Points

#1	At the begining of the channel at Guajataca Lake.
#2	Bo. Llanadas, Isabela 2 km away from point #1
#3	Bo. Pueblito of Ponce, Isabela Road # 475
#4	Road # 112 South of Road #2, Bo. La Curva,Isabela
#5	Road # 110 Km 3 Hm 2, Aguadilla
#6	Calero Lake, Aguadilla
#7	Ramey Filter Plant
#8*	Road #112 South 500 m away from point #4
#9*	Villa Estela Urbanization, Aguadilla Road #2 km 122.3
#10*	Intersection of Street #16 with Tunnel Road Vista Verde Urbanization

* Moca Channel

4.2 Experimental Design and Procedure for Ramey Water Treatmant Plant

Water samples were obtained from seven points at the Ramey Water Treatment Plant where two experiments were conducted: pre and post chlorination (original treatment), and post chlorination. These samples were analyzed for trihahalomethanes concentration to follow formation behavior. In these experiments surrogate parameters were analyzed which included (pH, turbidity, free chlorine, COD, THMs, and Fecal Coliforms).

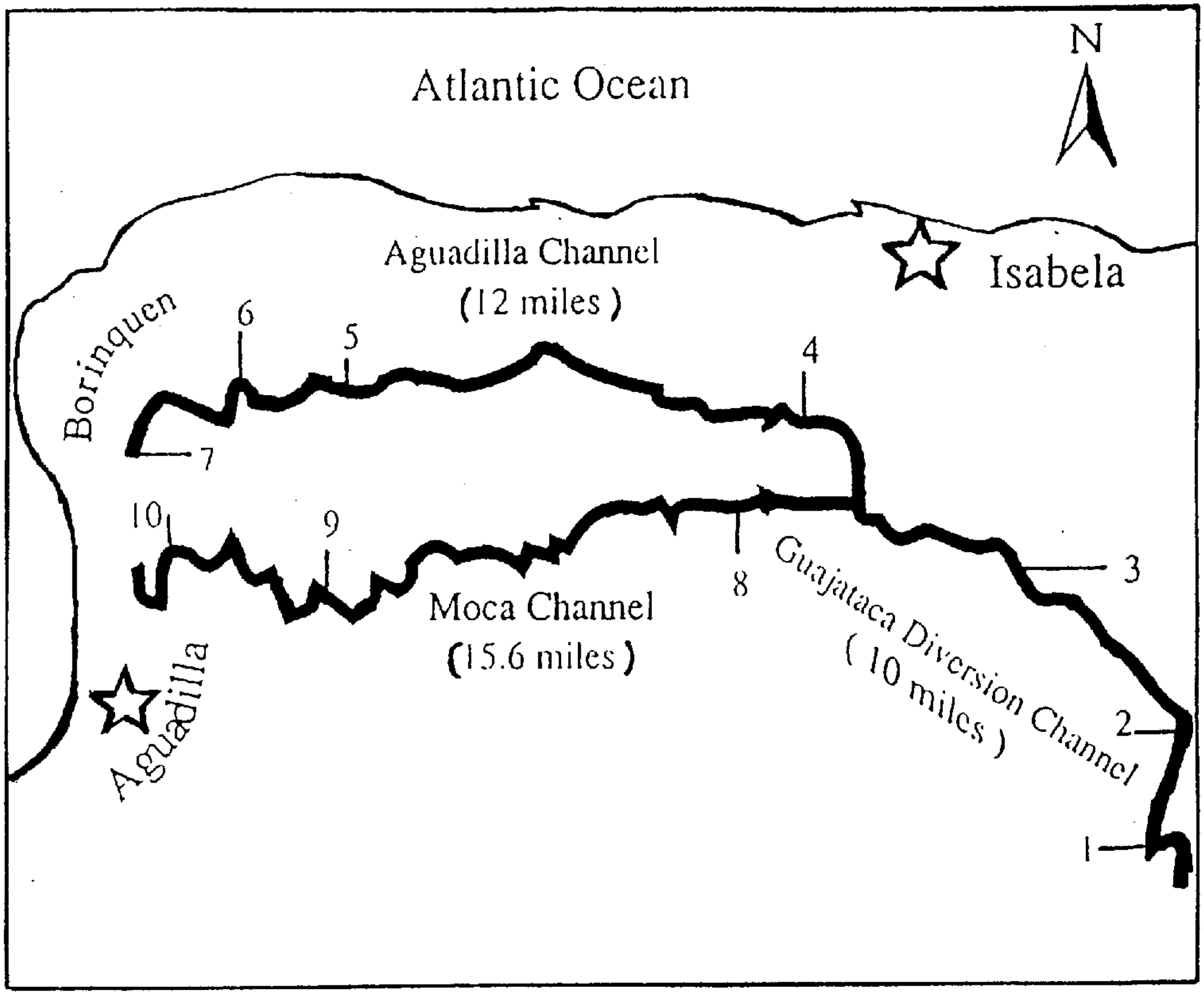

Figure 4.1 Sampling Points Through Guajataca, Moca, and Aguadilla Channels

Two preliminary experiments were done by using two different treatments. One treament was made by feeding potassium permanganate solution during twelve hours, collecting samples every four hours. The other treatment was using exclusively pre-chlorination during 24 hours. Each of these experiments had one replicate. The experiment of potassium permanganate was made to see when steady state was reached to later apply it to the experimental design. The pre-chlorination experiment was to see the behavior of THMs formation, and the iron and manganese removal. In these experiments, the parameters measured were COD, TOC, pH, Turbidity, plant flow (GPM), $KMnO_4$ residual,and chlorine residual.

Following these preliminary experiments a factorial design was proposed. A 2^n design was selected, where the exponential n is the number of indepedent variables (potassium permanganate, and chlorine). Table 4.2.1 illustrates the experimental arrangement. SEE APPENDIX D for more details of plant operation proceedings and potassium permanganate application.

K= Potassium Permanganate level
$KMnO_4$ (-): 0.2 mg/l residual
$KMnO_4$ (+): 0.8 mg/l residual

Cl=Chlorine Concentration level
Post-Chlorine(-): 20 lb/24 hr
Post-chlorine(+): 80 lb/24 hr

Table 4.2.1 Factorial Experiment Design for Ramey Water Treatment Plant using combination of Chlorine and Potassium Permanganate

EXPERIMENT	COMBINATION
1	K(-) Cl(+)
2	K(-) Cl(-)
3	K(+) Cl(+)
4	K(+) Cl(-)

A final experiment was performed by using pre-chlorine and potassium permanganate solution at the entrance of the plant and post-chlorine at the clear well. Two runs were made to analyze THMs, iron and manganese concentrations.

4.3 Equipment and Materials

The Chemical Oxygen Demand (COD) was measured with a HACH DR/2000 spectrophotometer. To verify the performance of alumina at the Ramey Water Treatment Plant the Jar Test method was used with stirring (Model: Phipps & Bird 7790-400). The trihalomethanes were analyzed with a Perkin Elmer gas chromatograph GC-MS coupled to a purge & trap unit, and a Hall Detector. The concentrations of iron and manganese were measured with two different kinds of Atomic Absorption Equipment: a Perkin Elmer 3030b (aspiration), and a Perkin Elmer 4000 (graphite) (Dept. of Health). At Analytical Technologies Inc. (ATI), the concentrations of THMs and iron and manganese were performed by using the correspondent EPA methods (EPA 624 for THMs and EPA 200.7 for metals). At ATI, the concentrations of iron and manganese were measured with an inductively coupled argon plasma emission spectrometer (ICAP-

61 Thomas Jarrel®). The pH was measured with a HACH pH meter. The turbidity was obtained with a HACH 2100 turbidimeter.

Reagents

BOD (Azide modification) Standard Methods

A manganese sulfate solution was prepared by dissolving 400 g $MnSO_4 \cdot 2H_2O$ in distilled water, filtered and diluted to 1 L. An alkali-iodide-azide reagent was prepared by dissolving 500 g of NaOH and 135 g NaI in distilled water to 1 L. Ten grams sodium azide (NaN_3) were added and dissolved in 40 ml distilled water. Potassium and sodium salts may be used interchangeably. This reagent should not give a color with starch solution when diluted and acidified. Concentrated sulfuric acid was used as a alkali iodide-azide reagent by the addition of one milliliter. A stock solution of sodium thiosulfate 0.10 N was prepared by dissolving 24.82 g of $Na_2S_2O_3 \cdot 5H_2O$ in distilled water and diluting to 1 L. It was preserved by adding 5 ml chloroform or 1 g NaOH/L. Finally, a standard sodium thiosulfate titrant (0.0250 N) was prepared either by diluting 250.0 ml sodium thiosulfate stock solution to 1000 ml or by dissolving 6.205 g $Na_2S_2O_3 \cdot 5H_2O$ in freshly boiled and cooled distilled water and diluting to 1000 ml. It was preserved by adding 5 ml chloroform, or 0.4 g NaOH/L, or 4 g of borax and 5 to 10 mg HgI2/l (1.00ml = 200µg DO).

COD Reagents

Vials are supplied by Hach Co. which range from (0-150 mg/l) & (0-1500 mg/l). The chemical oxygen demand reaction was performed in a COD reactor of Hach Co.

Potassium Permanganate

The principal reagent that was used was potassium permanganate which is a crystalline solid with a bulk density of 90 lb/ft^3. There are three suppliers: Carus Chemical Co., United Material & Chemical Corporation,and Mallinckrodt®.

TOC Analysis

The TOC analysis were performed on a Shimadzu TOC-5000® which uses air (ultrahigh purity) as a carrier gas. The samples were also preserved with a solution of 2N hydrochloric acid that lowers the pH between 2 to 3. For the calibration of the Shimadzu TOC-5000®, a dried reagent potassium hydrogen phtalate was used for the preparation of the stock solution for Total Carbon. A mixture of reagent grade sodium hydrogen carbonate and sodium carbonate was used for a stock solution of Inorganic carbon.

Fecal Coliforms

The fecal coliforms parameter was measured by using a Millipore® Glass Filter Holder (47 mm) and filtration equipment. This equipment included filtration paper, two ml plastic ampoules media solution packs, and disposable petri dishes. The incubation time was 24 hr and the temperature 44.5ºC.

Trihalomethanes

The sample for trihalomethane was collected in a 40 ml sample vial with no gas headspace. When free chlorine is present in the water a reducing agent is added, ranging from 2.5 to 3.0 mg of sodium thiosulfate.The sample was stored at 4ºC for 14 days.

Iron and Manganese

The sample for the analysis of metals was collected in a glass amber bottle of 250 ml (as suggested by Analytical Technologies, Inc.) and was preserved with 1 ml of concentrated Nitric Acid.

CHAPTER 5

RESULTS

5.1 Channel Study Results

Experiments were carried out in the Guajataca Diversion Channel for a period of 6 months (December 1993 - May 1994). Representative data from the month of December 1993 and January 1994, respectively are illustrated in Table 5.1.1 and Table 5.1.2. Table 5.1.1 contains surrogate parameters such as pH, Turbidity, COD_{av}, and BOD_5 . Table 5.1.2 illustrates the Fecal coliforms at each sampling point. The rest of the data can be found in detail on Appendix A and Appendix B respectively.

Table 5.1.1

Reported Data of Surrogate Parameters for the Guajataca Diversion Channel

Month: December 1993

Lake Level: 195.00 m Area: 26,600 acres-ft

Points	pH	Turbidity	COD_{av}(mg/L)	BOD_5(mg/L)
#1	7.4	1.0	25	2.6
#2	7.5	0.6	24	1.8
#3	7.9	0.5	17	0.9
#4	8.1	0.5	10.5	1.0
#5	8.1	1.4	5.5	0.4
#6	8.1	2.8	11	1.3
#7	8.2	2.0	25	1.6
#8	7.9	0.4	18	1.2
#9	8.3	1.9	5.5	0.4
#10	8.3	2.0	15.5	1.3

It is clearly noticed from Table 5.1.1 that the pH increases from the beginning to the end of the canal. The turbidity parameter does not increase that much. The COD_{av} is different at each sampling point.The BOD_5 is very low through the entire channel.

Table 5.1.2

Reported Data of Fecal Coliforms (# Colonies) for the Guajataca Diversion Channel for January 1994

Sampling Points	Fecal Coliforms 1ml	Fecal Coliforms 1ml	Fecal Coliforms 10ml	Fecal Coliforms 10ml
#1	TNTC	TNTC	TNTC	TNTC
#2	88	49	TNTC	TNTC
#3	TNTC	TNTC	TNTC	TNTC
#4	TNTC	TNTC	TNTC	TNTC
#5	140	190	TNTC	TNTC
#6	105	110	TNTC	TNTC
#7	TNTC	200	TNTC	TNTC
#8	TNTC	200	TNTC	TNTC
#9	105	120	TNTC	TNTC
#10	190	200	TNTC	TNTC

TNTC = To numerous to count which include 200 colonies or more.

From Table 5.1.2 it can be concluded that the channel is polluted at each sampling point by fecal coliforms.

5.2 Experimental Results at Ramey Water Treatment Plant

The different sampling points used in this section are presented in Figure 5.2.1,page 43.. Table 5.2.1 shows surrogate parameters at different sampling points of the Ramey Water Treatment Plant.

Table 5.2.1
Trihalomethane Formation by using Pre and Post Chlorination at Sampling Points
February 1994

Sampling Points	pH	Turbidity NTU	Cl free (mg/l)	COD_{av} (mg/l)	TTHM ppb
1	8.35	0.45	0	3	0.0
2	7.83	1.7	1.0	5	60.2
3	7.87	1.3	0.3	5	51.4
4	7.81	1.6	0.1	2.5	50.7
5	7.83	1.5	0.05	4.5	43.8
6	7.54	0.7	2.6	1	104.2
7	7.73	0.5	0.6	1	90.2

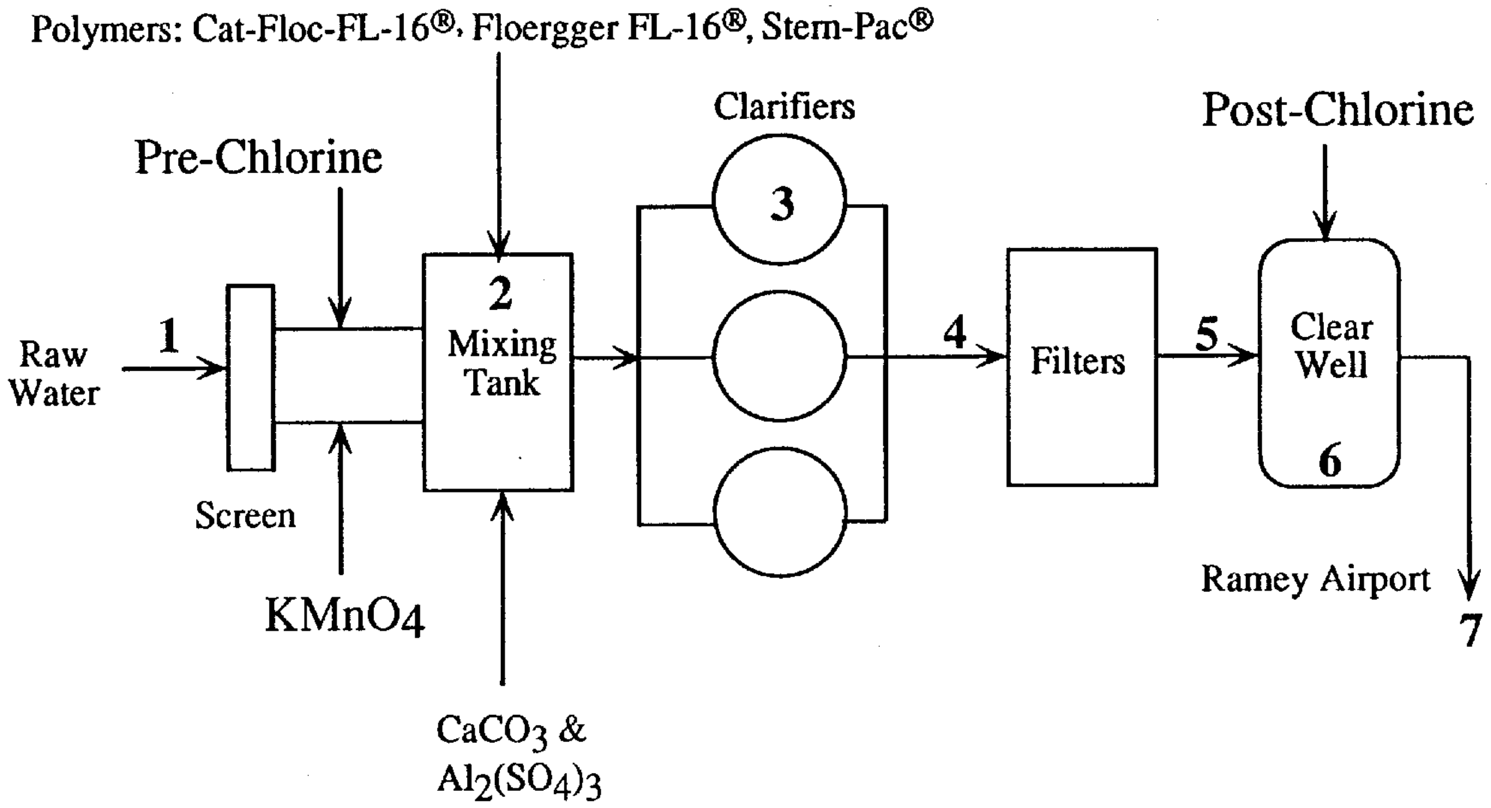

Figure 5.2.1 Schematic Diagram of Ramey Water Treatment Plant
(showing the sampling points)

The distribution of each trihalomethane by species and sampling point is included on Table 5.2.2. The raw water does not contain any concentration of Trihalomethanes. It is evident that the major percentage of trihalomethane produced is chloroform. The THM's in less quantity are the bromoform and dichlorodibromomethane.

Table 5.2.2

Distribution of Trihalomethanes by specie using pre and post chlorination

Sampling Point	$CHCl_3$ ppb	$CHBrCl_2$ ppb	$CHClBr_2$ ppb	$CHBr_3$ ppb	TTHMs ppb
1	----	-----	------	------	------
2	45.4	11.6	1.3	1.9	60.2
3	35.7	9.9	2.1	3.7	51.4
4	35.6	9.7	1.9	3.4	50.7
5	30.8	8.6	1.7	2.7	43.8
6	82.1	16.5	2.7	2.9	104.2
7	69.0	15.6	2.7	2.9	90.2

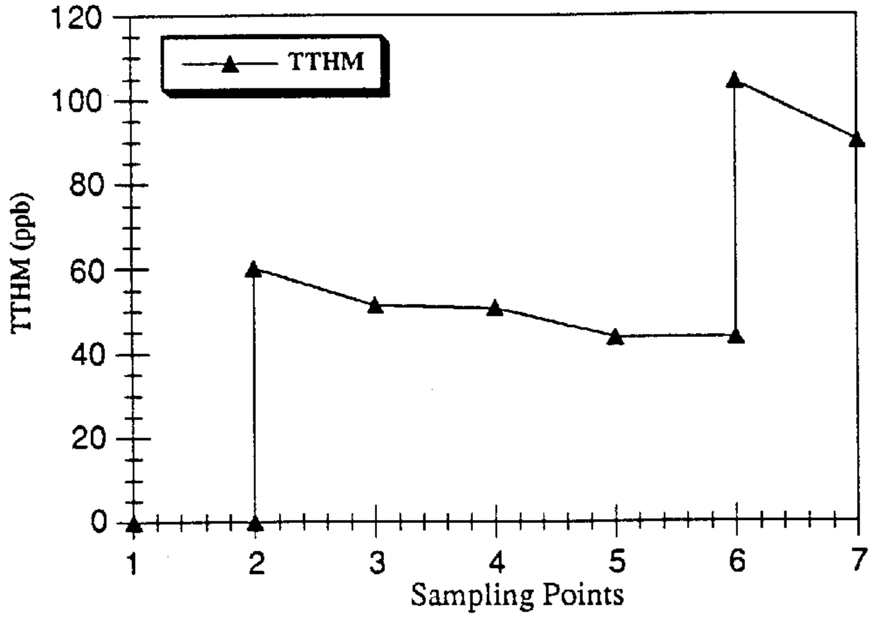

Figure 5.2.2 Total Trihalomethane Formation versus Sampling Points through out the Ramey Water Treatment Plant (Using Pre and Post Chlorination, February 1994)

Table 5.2.3
Trihalomethane Formation by using Post Chlorination
June 1994

Sampling Points	pH	Turbidity NTU	Cl free (mg/l)	COD_{av} (mg/l)	TTHM ppb
1	8.2	1.7	<LDL	4.0	-----
2	7.8	2.0	<LDL	5.0	-----
3	7.7	1.8	<LDL	3.7	1.0
4	7.7	1.6	<LDL	7.7	0.6
5	7.7	0.3	<LDL	3.7	0.8
6	7.4	0.6	<LDL	1.3	96.0
7	7.5	0.6	2.0	2.0	136.2

LDL = Lowest Detection Limit

Figure 5.2.1 illustrates an experimental run at the Ramey plant using pre and post chlorination. The increase in THMs concentration of from point #1 to point #2 from 0 to 60 ppb is due to the addition of pre-chlorine. From point 2 to point 5 the decrease in THMs concentration is probably due to the processes used for the removal of organic matter. The THMs concentration may also decrease due to the volatilization of the individual components. Table 5.2.3 illustrates the post-chlorination experiment. The THMs has a significant concentration at sampling point #6 (96 ppb) due to the addition of chlorine.

5.3 Preliminary Experiments

A set of experiments was performed at Ramey Water Treatment Plant using pre-chlorination for 24 hours at each run. Another set of preliminar experiments were conducted to study the response of an application of potassium permanganate solution at the entrance of the plant.

Table 5.3.1
Iron and Manganese Concentration with 24-hour prechlorination treatment
(Run #1)

Parameter	Raw Water	Clear Well	Ramey Airport *
Iron (mg/l)	0.016	0.005	0.006
Manganese (mg/l)	0.008	0.001	0.002

Table 5.3.2
Trihalomethane concentration with 24-hour prechlorination treatment
(Run #1)

Parameter	Mixing Point	Clear Well	Ramey Airport *
TTHM (ppb)	45	43	44

Table 5.3.3
Iron and Manganese concentration with 24-hour prechlorination treatment
(Run #2)

Parameter	Raw Water	Clear Well	Ramey Airport *
Iron (mg/l)	0.013	0.005	0.009
Manganese (mg/l)	0.008	0.001	0.016

Table 5.3.4
Trihalomethane concentration with 24-hour prechlorination treatment
(Run #2)

Parameter	Mixing Point	Clear Well	Ramey Airport *
TTHM (ppb)	53	50	53

* The Ramey Airport sampling point is isolated from the treatment,
it is used for comparison to clear well samples

Discussion of Results

Table 5.3.1 illustrates the iron and manganese concentrations for the prechlorination runs. In the case of iron, the reduction was from 0.016 to 0.005 mg/l. For the case of manganese, the reduction was from 0.008 to 0.001. The reduction of iron and manganese is not affected by the prechlorination treatment, it is affected by the flocculant polymer (Stern-Pac®) which reacts at the clarifier and helps to coagulate iron, manganese, and some other organic and inorganic matter which are in the filters. The THMs illustrated on Table 5.3.2 and Table 5.3.4 appear to be constant from the mixing tank to the clear well (for Run #1 45 and 43 ppb, respectively, and 53 and 50 ppb, respectively for Run #2).

The samples for THMs taken at the Ramey Airport appeared approximately constant at both times. They are also in compliance with the Primary Drinking Water Standard (100ppb maximum). Using postchlorination treatment instead of postchlorination shows that an addition of chlorine to the clear well elevated the concentration of THMs produced when compared to the prechlorination treatment. This 24-hour prechlorination treatment proved to be efficient for iron and manganese removal and for a decrease in the THMs concentration produced. The removal efficiency of iron and manganese depends on the filter operation, the concentrations of the metals present, the amount of polymer used, and the amount of oxygen present.

Table 5.3.5
Iron concentrations with $KMnO_4$ and post-chlorination treatment
Treatment Period: 12 hours

Time (hours)	Raw Water (mg/l)	Clarifier (mg/l)	Clear Well (mg/l)	Ramey Airport (mg/l)*
4	0.022	0.014	0.005	0.005
8	0.028	0.008	0.005	0.015
12	0.026	0.014	0.005	0.013

* The Ramey Airport sampling point is isolated from the treatment, it is used for comparison to clear well samples

Table 5.3.6
Manganese concentrations with $KMnO_4$ and post-chlorination treatment
Treatment Period: 12 hours

Time (hours)	Raw Water (mg/l)	Clarifier (mg/l)	Clear Well (mg/l)	Ramey Airport (mg/l)*
4	0.022	0.199	0.006	0.013
8	0.028	0.175	0.017	0.005
12	0.026	0.150	0.014	0.011

* The Ramey Airport sampling point is isolated from the treatment, it is used for comparison to clear well samples

Table 5.3.7
THMs concentrations with $KMnO_4$ and post -chlorination treatment
Treatment Period: 12 hours

Time (hours)	Clear Well (ppb)	Ramey Airport (ppb) *
4	43	50
8	49	61
12	53	52

* The Ramey Airport sampling point is isolated from the treatment, it is used for comparison to clear well samples

A preliminary experiment was conducted using $KMnO_4$ and postchlorination. The results are tabulated in Tables 5.3.5, 5.3.6, and 5.3.7. The objective pursued in this experiment was, to sample every four hours, to see if steady state was reached for a 12-hour treatment period. Table 5.3.7 shows that steady state is reached for THMs formation having a mean value of 48.3 ppb. Therefore, this experiment showed that at constant postchlorination the THMs formation is fairly constant.

5.4 Factorial Experimental Design Results

In this section the results of the factorial experiment arrangement for potassium permanganate at the entrance and chlorine at the clear well will be presented. Four experiments were made with one repetition each.

Table 5.4.1
THMs concentrations (ppb)

Run Number	KMnO4 residual (mg/l)	Chlorine residual (mg/l)	TTHMs (ClearWell) (ppb)
1 K(-)Cl(+)	0.2	2.5	48
1 A	0.2	2.5	44
2 K(-)Cl(-)	0.2	0.5	35
2A	0.2	0.4	20
3 K(+)Cl(+)	0.8	2.2	24
3A	0.8	3.0	50
4 K(+)Cl(-)	0.8	0.8	28
4A	0.8	0.6	28

Table 5.4.1 illustrates the THMs concentration for the clear well at each run, with the indicated KMnO4 and Chlorine residual. These runs showed a mean value of 34.6 ppb which is in compliance with respect to the primary drinking water standards of 100 ppb. Also, the concentration of THMs illustrated in runs 1, 1A [K(-)Cl(+)] and 3,3A [K(+)Cl(+)], where post-chlorination is high, the mean values for each run were 46 and 37 ppb, respectively. Otherwise, for runs 2,2A [K(-) Cl(-)] and 4,4A [K(+),Cl(-)], the mean values were 27.5 and 28 ppb, respectively. As a result, the influence of high levels of chlorine in the THMs formation is clearly evidenced when it s compared to the lower levels.

Table 5.4.2
TOC concentrations (ppm)

t = time of sampling

Run Number	Raw Water t = 0 hr	Clarifier t = 2 hr	Clear Well t = 3 hr	Ramey Airport *
1	3.430 ©	3.023	2.589	2.522
1 A	2.854	3.335	2.862	2.683
2	2.973	2.446	2.061	2.503
2A	2.838	1.979	1.931	25.120
3	2.932	1.731	1.517	1.523
3A	1.955	< LDL	1.649	1.497
4	0.041	0.372	0.037	0.006
4A	< LDL ‡	2.444	1.341	1.716

* The Ramey Airport sampling ponit is isolated from the treatment, it is used for comparison to clear well samples
© This analysis result is an average of 3 runs.

‡ LDL = Lowest Detection Limit

The variation in TOC concentration through all the runs were different and inconsistent. In some runs it decreased and in other runs it increased. For example, Run #1 had a decrease in concentrations 3.430, 3.023,and 2.589 ppm from the raw water,clarifier,and clear well respectively. On the other hand, Run #4A had an increase (< LDL, 2.444, 1.341) mg/l from raw water, clarifier, and clear well, respectively. This phenomena is due to the nature of the organic matter, which forms clusters or aggregates of organic matter and at the time of sampling the solution is not homogeneous. The formation of clusters of organic matter is also possible due to the residuals accumulated through the pipe walls, clarifier, filter, and clear well walls. These samples were analyzed in a TOC analyzer where it had a coeficient of variation lower than 10%, which reflects a low deviation from the average. At Ramey Airport the variation in TOC concentration were not that much but in Run #2A and #4 where the concentrations are 25.120 and 0.006 ppm. At Ramey Airport the samples were taken to compare these values to those at the clear well. It can be concluded that the organic matter carried by the water is unpredictable since it may deposited at the pipe walls or washed away by the flow.

Table 5.4.3
Iron concentrations † (mg/l)

t = time of sampling

Run Number	Raw Water t = 0 hr	Clarifier t = 2 hr	Clear Well t = 3 hr	Ramey Airport *
1	0.010	0.010	0.010	0.010
1 A	0.010	0.010	0.010	0.010
2	0.005	0.005	0.005	0.005
2A	0.005	0.005	0.005	0.005
3	0.005	0.005	0.005	0.005
3A	0.054	0.046	0.462	0.015
4	0.130	0.166	0.014	0.014
4A	0.142	0.108	0.016	0.016

* The Ramey Airport sampling point is isolated from the treatment, it is used for comparison to clear well samples

† The detection limit for iron concentration is ± 0.001 mg/l.

It can be noticed that the concentration of iron is in compliance with the EPA secondary drinking water standard of 0.3 mg/l. The first three runs where the concentration of potassium permanganate is low, the increase of iron concentration from raw water to clear well was zero. Run 3A does not appear to be a good one because there is no logical reason for an increase in the iron concentration from 0.054 to 0.462 ppm in its path through the plant. In experiment 4 and 4A, the iron concentration was reduced notably from 0.130 to 0.014, and from 0.142 to 0.016, respectively. At Ramey Airport, the concentration of iron is in compliance with the EPA standard of 0.3 mg/l.

Table 5.4.4
Manganese concentrations (mg/l) †

t = time of sampling

Run Number	Raw Water t = 0	Clarifier t = 2 hr	Clear Well t =3 hr	Ramey Airport *
1	0.008	0.084	0.020	0.005
1 A	0.010	0.098	0.020	0.007
2	0.011	0.107	0.018	0.003
2A	0.011	0.115	0.029	0.001
3	0.010	0.305	0.011	0.003
3A	0.012	0.369	0.048	0.002
4	0.041	0.372	0.037	0.006
4A	0.015	0.345	0.026	0.001

* The Ramey Airport sampling point is isolated from the treatment, it is used for comparison to clear well samples

† The detection limit for manganese concentration is ± 0.001 mg/l.

The concentration of manganese illustrated in Table 5.4.4 is in compliance with the secondary drinking water standard at the clear well (0.05 mg/l). In the first two runs where the concentration of potassium permanganate is low, the increase of manganese concentration from raw water to the clear well ranges from 0.009 to 0.018 mg/l. At Ramey Airport, the concentration of manganese is in compliance with the standard of 0.05 mg/l.

Therefore the use of potassium permanganate as an oxidizer produces lower concentrations of THMs without violating the manganese concentration in the water leaving the plant.

5.5 Final Experiment

In this section the results of the combination of pre-chlorination and potassium permanganate applied to raw water and the use of post-chlorination are presented. This experiment was conducted with one replicate.

Table 5.5.1
Iron concentrations (mg/l)

Run Number	Raw Water t = 0 hr	Clarifier t = 2 hr	Clear Well t = 3 hr	Ramey Airport *
1	0.091	0.093	0.014	0.064
1 A	1.194	0.074	0.013	0.020

* The Ramey Airport sampling point is isolated from the treatment, it is used for comparison to clear well samples

Table 5.5.2
Manganese concentrations (mg/l)

Run Number	Raw Water t = 0 hr	Clarifier t = 2 hr	Clear Well t = 3 hr	Ramey Airport *
1	0.011	0.191	0.011	0.003
1 A	0.015	0.203	0.027	0.006

* The Ramey Airport sampling point is isolated from the treatment, it is used for comparison to clear well samples

Table 5.5.3
TOC concentrations (ppm)©

Run Number	Raw Water t = 0 hr	Clarifier t = 2 hr	Clear Well t = 3 hr	Ramey Airport *
1	1.868	1.565	1.606	< LDL ‡
1 A	< LDL	< LDL	1.238	< LDL

* The Ramey Airport sampling point is isolated from the treatment, it is used for comparison to clear well samples

‡ LDL = Lowest Detection Limit

© This TOC result is an average of 3 runs.

Table 5.5.4
Total Trihalomethane concentration (ppb)

Run Number	Mixing Point t = 1 hr	Clear Well t = 3 hr	Ramey Airport *
1	21	31	46
1A	24	48	44

* The Ramey Airport sampling point is isolated from the treatment, it is used for comparison to clear well samples

With respect to the iron concentration illustrated on Table 5.5.1, the oxidation was very good for Runs 1 and 1A (0.091 to 0.014)mg/l and (1.194 to 0.013)mg/l, respectively. These oxidations represent an 85 % and 99% reduction of iron respectively. The manganese concentrations did not increase much for Runs 1 and 1A, from 0.011 to 0.011 and 0.015 to 0.027mg/l, respectively. Table 5.5.3 illustrates the Total Organic Carbon changes in concentration through the plant which are interesting because at Run 1 there was a decrease in TOC from 1.868 to 1.606 ppm. On the other hand, in Run 1A the TOC concentrations increased from raw water to the clear well, from 0.000 to 1.238 ppm. The total trihalomethanes concentrations (ppb) at the clear well are under 100 ppb, (31 and 48 ppb, respectively). The percentage increase of THMs from the mixing tank to the clear well was 48%. At Ramey airport the THMs were under the EPA limit, 44 and 46 ppb, respectively.

5.6 Statistical Analysis

The results of the factorial experimental design (2^2) are discussed in this section. For each of the parameters analyzed such as iron, manganese, and trihalomethanes concentration a statistical approach was made to interpret the validity of the experimental results. In our case, we prepared an ANOVA(analysis of variance) analysis for the iron and manganese cases, and for the trihalomethanes formation. An analysis of covariance was made to see the effect of total organic carbon in the THMs production. ANOVA is a useful tool in engineering evaluations, where is a need for comparisons (Montgomery, 1991).

The sum of the squares for each of the sources of variation(treatments, repetitions, and error) is calculated. The mean squares are obtained dividing the sum of squares by their respectives degrees of freedom. The statistical parameter F (is a function that describes the ratio of two independent random variables) is used for comparison and is computed dividing the regression mean squares by the residual mean squares. The calculated value F is compared to a value of F (Fcrit.) that corresponds to an upper-tail area of 1%. If the calculated F is greater than the value of F (obtained value from the percentage points of the F distribution tables) at a (confidence interval) = 0.05 then the comparison will indicate a significant variation between each treatment. The other important statistical parameter is the coeficient of variation which shows the deviation from the average of the experiemental results.

Also, interaction plots were prepared to help understand the effects of high and low level concentrations of chlorine and potassium permanganate on iron oxidation, manganese increment, and THMs formation. Residual plots were made by comparing Residuals versus Estimated Values (for iron and manganese). Probabilty plots were made by comparing Probabilty versus residuals (for iron and manganese). See Appendix C for the tabulated values of the Statistical analysis.

5.6.1 Analysis of Variance for Iron (Fe)

Levels of Concentration

K(-) = 0.2 mg/l of $KMnO_4$ residual, K(+) = 0.8 mg/l of $KMnO_4$ residual

Cl(-) = 0.4 mg/l of Post-Chlorine residual, Cl(+) = 3.0 mg/l of Post-Chlorine residual

Table 5.6.1

Data of Iron Concentrations (mg/l)

Treatment Combination	Raw Water		Clear Well		Removal	
	Trial 1 (mg/l)	Trial 2 (mg/l)	Trial 1 (mg/l)	Trial 2 (mg/l)	Trial 1 (mg/l)	Trial 2 (mg/l)
K(-) Cl(-)	0.005	0.005	0.005	0.005	0.000	0.000
K(+) Cl(-)	0.130	0.142	0.014	0.016	0.116	0.126
K(-) Cl(+)	0.010	0.010	0.010	0.010	0.000	0.000
K(+) Cl(+)	0.005	0.054	0.005	0.462	0.000	0.003*

*Estimated Value

An inspection of Table 5.6.1 reveals that a non-logic value concentration of iron appears for the second trial of the experiment represented as K(+) Cl(+) because it increases instead of decreasing. When a non-logic value appears in a randomized experimental design, the suggested procedure is to substitute the value by an estimated one. Then the usual analysis of variance is performed proceeding just as if the estimated observation were real data, with the error degrees of freedom reduced by one.

The estimated value is obtained from the following equation :

: $x = (a\,y'_{i.} + b y'_{.j} - y'_{..}) / (a-1)(b-1)$

(Eq. 5-17, From the book *Design and Analysis of Experiments,* by Montgomery, Douglas,1991)

definition of variables:

a= # of treatments, corresponds to the different experimental combinations (a = 4 in our case)

b = # of repetions of each treatment (b = 2 in our case)

$y'_{i.}$ = sum of values (a) of treatments, in our case corresponds to the addition of the concentrations of iron at a sampling point for a single experiment

$y'_{.j}$ = sum of the values (b) of the repetitions, in this case the sum of the concentrations of iron at a sampling point in all for a single repetition

$y'_{..}$ = Total Sum of Values of (a) and (b) $y'_{i.} + y'_{.j}$

See Appendix C for the calculation of the missing value.

Table 5.6.1-A

ANOVA for Iron

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Fo	F critic	CV (%)
A	0.007523	1	0.007523	677.237	6.61	10.87
B	0.00712	1	0.00712	640.966	6.61	
AB	0.00712	0	-	-		
Error	5.55E-05	5	1.11E-05			
Total	0.02182	7				

Discussion of Statistical Results

1) The comparison between Fcrit and Fo for each treatment of A($KMnO_4$) and B(Chlorine) describes that there is a significant variation between each treatment because the values of Fo (677.24, and 640.97 respectively) are larger than Fcrit, 6.61. This shows that all the treatments had a significant effect on the concentration of iron.
2) The coeficient of variation describes quantitatively that the variation of the experimental data is a low percentage (10.87%). This implies that there was a uniform sampling data.

Discussion of Interaction Plot for Iron

The difference in oxidation of iron from raw water to the clear well versus the chlorine level is described in the interaction plot figure for iron (Figure 5.6.1). This experiment involves a study of the effects of two factors, which are potassium permanganate and chlorine, on the removal of iron. In general, it can be shown that factorial designs are more efficient to analyze the results of this type of experiment. By a factorial design we mean that in each complete trial or replication of the experiment, the levels of all posible combinations are investigated. The effect of a factor is defined to be the change in response produced by a change in the level of the factor. This is frequently called a main effect because it refers to the primary factors of interest in the experiment. A way to describe these effects is by showing an interaction plot of response.

It is clearly noticed that using a treatment of K(+) Cl(-) is the best combination for oxidation difference of iron (0.12 mg/l),since for this case the removal of iron was the highest for all experiments. For the treatment of K(-)Cl(+) and K(-)Cl(-) the effect on the removal of iron was small but equally low was the concentration of iron at the influent. Therefore, the use of $KMnO_4$ will be more effective for higher concentrations of iron at the entrance to the plant.

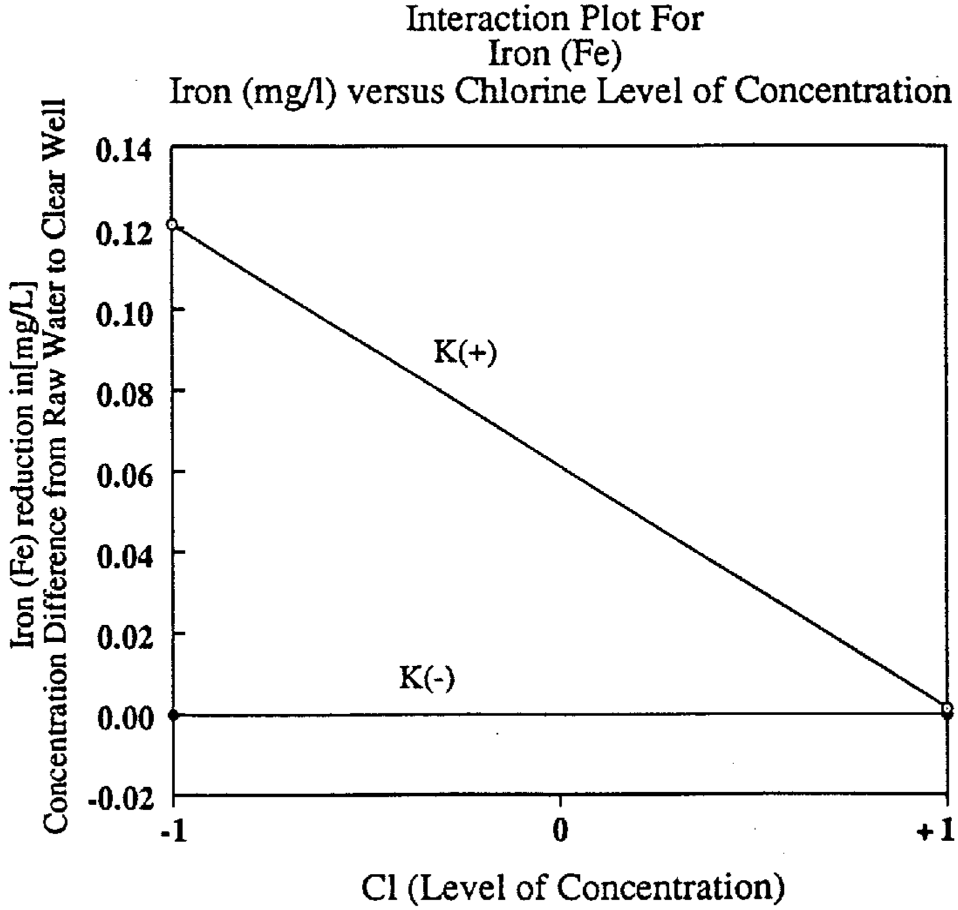

Figure 5.6.1 Interaction Plot for Iron

5.6.2 Analysis of Variance for Manganese (Mn)

Discussion of Statistical Results (See Appendix C)

1) The comparison between Fcrit and Fo for the treatment with B (Chlorine) describes that there is no significant variation because 0.57 is less than 6.61. As a result, the concentration of manganese was not affected by this treatment.
2) The comparison between Fcrit and Fo for the treatment with AB combination describes that there is no significant variation because 0.85 is less than 6.61. As a result, the concentration of manganese was not affected by the combination of treatment AB.
3) The coeficient of variation describes quantitatively that the variation of the experimental data is high percentage, 109.6%. This represents a high deviation from the average.

Discussion of Interaction Plot for Manganese

The interaction plot figure for managanese descibes the manganese concentration from raw water to the clear well (on the y axis) versus the chlorine level. It is clearly noticed that using the combination of K(+) Cl(-) is the best of all treatments because it has the smallest increase in manganese concentration.

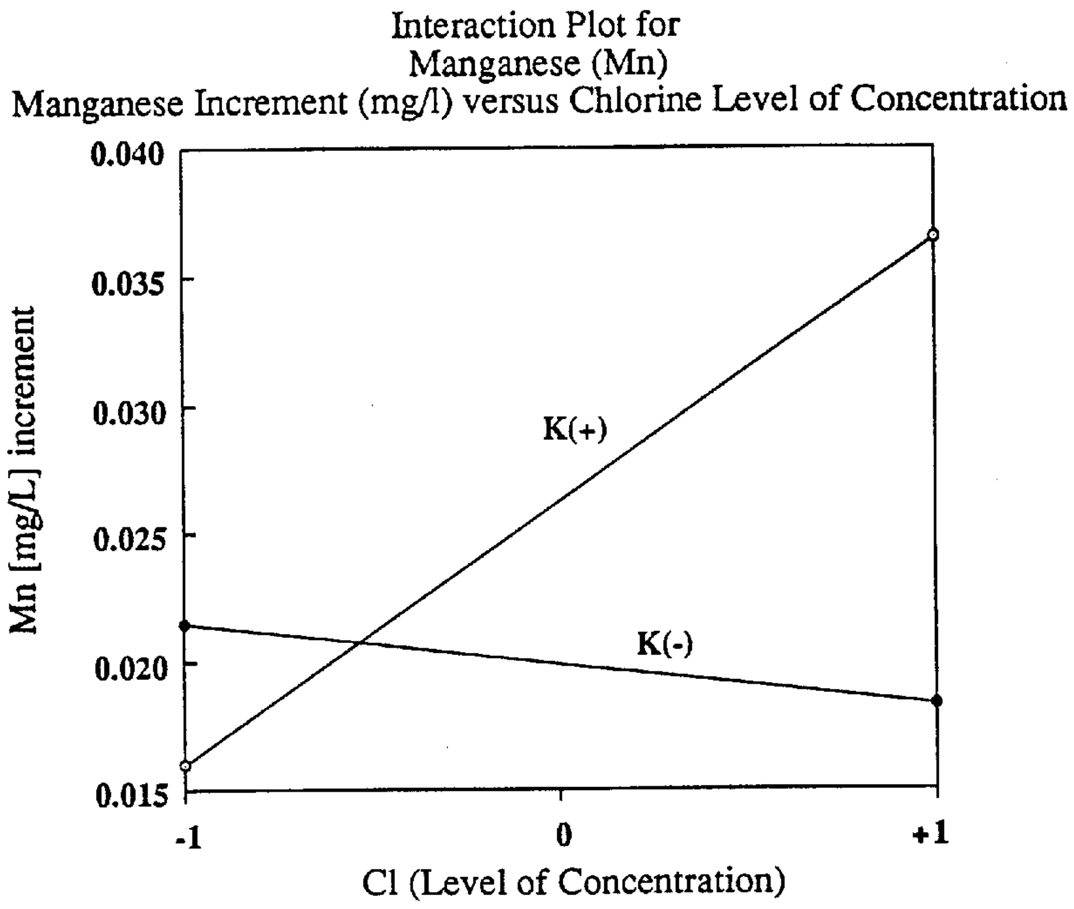

Figure 5.6.2 Interaction Plot for Manganese

5.6.3 Analysis of Covariance for Total Trihalomethane with TOC as a Covariable

The purpose here is to see how the quantity of organic matter at the the entrance of the plant is related to the Total Trihalomethane formation with an analysis of covariance. Douglas Montgomery (1991) established that the analysis of covariance is another technique occasionally useful for improving the precision of an experiment. For example in an experiment with response variable y (THMs), there is another variable, such as x (TOC), and y is linearly related to it.

Furthermore, suppose that x cannot be controlled by the experimenter but can be observed along with y. The variable x (TOC) is called a *covariate or concomitant variable*. The analysis of covariance involves adjusting the observed response variable for the effect of the concomitant variable. If such an adjustment is not performed, the concomitant variable could inflate the error mean square and make true differences in the response due to treatments harder to detect. Thus, analysis of covariance is a method of adjusting for the effects of an uncontrollable nuisance variable.

Table 5.6.3
Concentrations of Trihalomethanes and Total Organic Carbon
for each experimental combination

Comb.	(-) (-)		(+) (-)		(-) (+)		(+) (+)	
Trial	THMs (ppb)	TOC (ppm)	THMs (ppb)	TOC (ppm)	THMs (ppb)	TOC (ppm)	THMs (ppb)	TOC (ppm)
1	35	2.97	28	0.04	48	3.43	24	2.93
2	20	2.84	28	0.00	44	2.85	50	1.96

Table 5.6.3-A
Analysis of Covariance

Source of Variation	DF	Sum of Squares and Products			Adjusted for Regression			Fo	Fcrit.
		x	xy	y	y	DF	Mean Square		
Treat.	3	12.35	41.41	459.37					
Error	4	0.65	10.54	458.50	288.51	3	96.17	1.92	9.28[a]
Total	7	13.00	30.86	917.87	844.55	6			
Adjusted treatments					556.03	3	185.34		

Discussion of Statistical Results

The conclusion of the analysis of covariance between THMs and TOC (covariable) is that, there is no evidence that the THMs produced in each treatment differ by the initial concentration of carbon (TOC) at the intake. This is clearly demostrated because Fo is much less than Fcrit. It is due to the influence of each treatment and not to the concentration of the initial quantity of TOC.

Discussion of Interaction Plot

The interaction plot figure for THMs represents its production from the raw water to the clear well versus the chlorine level. It is clearly noticed that the production or formation of trihalomethanes was lower during treatment K(+) Cl(+) compared to K(-)Cl(+). It is evident that during the treatment with K(+) Cl(-) or K(-) Cl(-) the formation of trihalomethanes is lower than 30 ppb. As a result, it is demonstrated that the chlorine dosage affects the production of THMs.

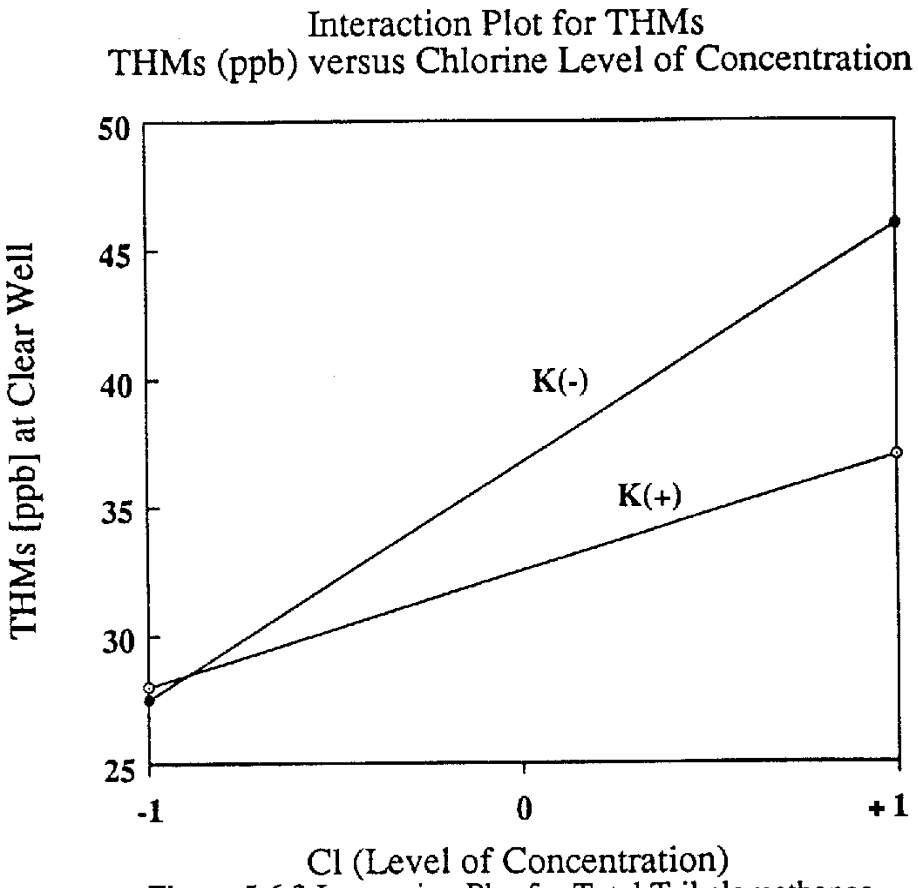

Figure 5.6.3 Interaction Plot for Total Trihalomethanes

5.7 Aspects of Disinfection

The disinfection performance of Ramey Water Treatment Plant in terms of fecal coliforms is presented in this section using chlorine as disinfection agent. Also, the disinfection properties of potassium permanganate are shown.

The average percentage reduction in fecal coliforms from raw water to the mixing point was 88.5 %, a reduction from 191 to 22 colonies of fecal coliforms in 1ml. The percentage reduction in fecal coliforms from raw water to clear well was 100%, a reduction from 191 to 0. The first result shows the effect of prechlorination and the second result shows the effect of post-chlorination on fecal coliforms reduction. The disinfection effectiveness of Ramey Water Treatment Plant is excellent since the water was completely disinfected. The number of colonies found at sampling point #6 (clear well) and #7 (Ramey Airport) was none which is in compliance with the Primary Drinking Water Standards and the Department of Health.

Table 5.7.1
Disinfection Performance at Ramey Water Treatment Plant
(July 1994)

	Fecal Coliform (1 ml)		Fecal Coliform (10 ml)	
Sampling Point	Sample 1	Sample 2	Sample 1	Sample 2
#1	181	200	350	230
#2	40	3	100	87
#3	1	2	4	22
#4	none*	none	3	3
#5	none	1	2	none
#6	none	none	none	none
#7	none	none	none	none

*** none = Below Lowest Detection Limit**

Table 5.7.2
Disinfection Effectiveness of Potassium PermanganateJar Test
Performed @ 60 RPM

	Fecal Coliforms (1 ml)	Fecal Coliforms (10 ml)	% of Reduction of (1ml)	% of Reduction of (10 ml)
Raw Water	190	400		
KMnO4 Concentrations				
1.75	24	46	87.4	88.5
2.00	9	15	95.3	96.3
2.25	9	15	95.3	96.3
2.50	1	15	99.5	99.5
2.75	1	6	99.5	98.5
3.00	30	7	84.2	98.3

Table 5.7.2 illustrates the disinfection effectiveness of $KMnO_4$, performed at the Pollution Control Laboratory (Chemical Engineering Department, University of Puerto Rico) using a six beaker Jar Test at 60 RPM for one hour. Each beaker had a volume of 1000ml. The percentage reduction of coliforms using $KMnO_4$ was high, being over 84% in each run. The purpose of this experiment was to compare the effectiveness of potassium permanganate versus pre-chlorination.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

This work is divided in two areas: the study of the water distribution channel (Guajataca, Aguadilla, and Moca channels) and the study of the Ramey Water Filtration Plant.

The channel is polluted with fecal coliforms from the Guajataca Lake to its end in Aguadilla. There is no clear indication of an increase in pollution through the channel. This observation may have been improved if the samples analyzed for fecal coliforms were further diluted. Turbidity remains approximately constant through the entire channel. The Biological Oxygen Demand was very low in all the sampling points. There was a clear trend of pH increase as water flows through the channel. This pH trend is affected by the human and agricultural activity that detergent, fertilizers and other effluents from households.

Experiments conducted at Ramey Water Treatment Plant indicated that the application of gaseous chlorine at the entrance to the plant affects the production of THMs at each sampling point. The analysis also indicated that the THM concentration is less than Lowest Detection Limit (LDL) in the raw water. The 24 hour pre-chlorination experiments generated a uniform production of THMs at the mixing tank and at the clear well. In all these cases the production of THMs concentration is less than 50.0% of the maximum permitted by EPA. Results show that the best treatment for a reduction of the THMs formation potential and a reduction of iron and manganese was an application of a high level of potassium permanganate and a low level of chlorine at the entrance to the treatment plant.

Experiments indicate that the best treatment for the removal of iron is an application of a high concentration of potassium permanganate (0.8 mg/l) and a low concentration of chlorine (0.6 to 0.8 mg/l), both applied to the raw water. Results show that at higher concentrations of iron in the raw water entering the plant, its oxidation improves as the level of potassium permanganate applied is increased.

As the level of potassium permanganate applied to the raw water was increased, the level of manganese at the clear well also increased. This was no real problem because the manganese concentration was always below the compliance limit of 0.05 mg/l.

In order to study the effect of TOC on the THMs formation for different levels of chlorine and potassium permanganate applied to the raw water, an analysis of covariance was developed in section 5.6.3. No evidence was found that the amount of THMs produced depend on the concentration of TOC entering the plant in the raw water. The experiments indicated above reveal an effect over the THMs formation and the iron and manganese removal.

It is concluded that the best treatment to reduce the concentration of trihalomethanes and iron simultaneously is the application of a high level of potassium permanganate (0.8 mg/l residual) and a low level of chlorine (0.4 mg/l of free chlorine)(See Figures 5.6.1 and 5.6.3). According to Singer et. al 1980, he concluded that permanganate can reduce chloroform formation is proportional to the amount of permanganate consumed after the initial oxidant demand. By comparing our results with Singer's study we can conclude that potassium helped as a preoxidant of organic matter as well as a reduction in chloroform (THM). Also, it is concluded that the best combinations to control the manganese concentration at the plant were two, K(-)Cl(+) and K(-) Cl(-)(see figure 5.6.2). Although the concentration of manganese increased, this does not discard the application of K(+)Cl(-) and K(+)Cl(+) as good because at these levels of treatment the water was in compliance with the maximum limit of manganese permitted (0.05 mg/l).

It is concluded that the oxidation of iron concentration was effective. The manganese concentrations did not increase that much. From the parameter of total organic carbon, it is concluded that organic matter is present at the clear well, which implies that the process does not oxidize all the organic matter present. Part of this matter reacts with the post-chlorination to form more trihalomethanes. The concentrations of trihalomethanes generated were similar in magnitud to those produced in the other treatments presented before.

Fecal Coliforms disappear in all the experiments conducted at Ramey which indicates a full compliance with the concentration limit imposed by EPA on this parameter. A laboratory scale experiment conducted to study the disinfection capacity of potassium permanganate indicates that over 80% of the fecal coliforms always disappear in one hour. A study of Cleasby et. al 1964 demonstrated the effectiveness of potassium permanganate(at different contact times killing the coliform population). His results for a contact of 60 minutes is very similar to our results. Therefore, potassium permanganate has a significant contribution to the reduction of fecal coliforms, in addition to the low level of THMs produced and its contribution to the removal of iron. It is concluded that potassium permanganate is an excellent substitute to pre-chlorination.

For further investigations the following is suggested:

1) Construction of a pilot-plant is suggested to determine kinetic parameters of tropical (Puerto Rico) surface waters when potassium permanganate and chlorine are applied simultaneously.

2) From the point of view of this study, it is suggested to the correspondent agencies (Department of Health and PRASA) to substitute the chlorine for potassium permanganate as a preoxidant for the reduction of THMs formation in this tropical climate. Therefore, Philip C. Singer (1988) made a study of "Alternative Oxidant and Disinfectant Treatment Strategies for Controlling Trihalomethane Formation" where he showed the use of potassium permanganate as a substitute of prechlorination at two water treatment facilities; Monroe, North Carolina and Lancaster, South Carolina.

3) Several pilot plant experiments should be conducted using a synthetic raw water with the following surrogate parameters constant such as; pH, turbidity, TOC,COD, and BOD. This will permit a better understanding of the reactions involved and the effect of each parameter.

CHAPTER 7

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APPENDIX A

Monthly Reported Data from the Guajataca Diversion Channel

TABLE A-1

Reported Data of Surrogate Parameters for the Guajataca Diversion Channel for for December 1993

Lake Level: 195.00 m Area: 26,600 acres-ft

Points	pH	Turbidity	COD_{av}(mg/L)	BOD_5(mg/L)
#1	7.4	1.0	25	2.6
#2	7.5	0.6	24	1.8
#3	7.9	0.5	17	0.9
#4	8.1	0.5	10.5	1.0
#5	7.9	0.4	18	1.2
#6	8.1	1.4	5.5	0.4
#7	8.1	2.8	11	1.3
#8	8.3	1.9	5.5	0.4
#9	8.3	2.0	15.5	1.3
#10	8.2	2.0	25	1.6

TABLE A-2

Reported Data of Surrogate Parameters for the Guajataca Diversion Channel for for January 1994

Lake Level: 193.8m Area: 23,400 acres-ft

Points	pH	Turbidity	COD_{av}(mg/L)	BOD_5(mg/L)
#1	7.3	1.9	15.5	1.3
#2	7.3	1.3	19.5	1.5
#3	7.8	1.4	12.0	1.3
#4	8.0	1.7	10.5	1.1
#5	7.9	0.8	6.0	0.9
#6	8.2	2.7	3.0	0.6
#7	8.1	1.5	6.0	0.4
#8	8.1	1.3	5.5	1.0
#9	8.2	3.9	9.5	0.3
#10	8.2	2.1	7.5	0.4

TABLE A-3
Reported Data of Surrogate Parameters for the Guajataca Diversion Channel for for February 1994
Lake Level: 193.0m Area: 20,600 acres-ft

Points	pH	Turbidity	COD_{av}(mg/L)	BOD_5(mg/L)
#1	7.5	1.2	18.0	0.9
#2	7.8	1.1	10.3	----
#3	8.2	1.7	10.1	0.8
#4	8.1	0.8	9.7	0.5
#5	8.2	1.3	9.9	0.7
#6	8.2	1.5	10.1	0.6
#7	8.1	1.9	11.0	0.5
#8	8.2	1.3	11.5	0.7
#9	8.2	1.2	7.1	0.6
#10	8.2	2.1	9.6	0.7

TABLE A-4
Reported Data of Surrogate Parameters for the Guajataca Diversion Channel for for March 1994
Lake Level: 192.30m Area: 19,100 acres-ft

Points	pH	Turbidity	COD_{av}(mg/L)	BOD_5(mg/L)
#1	8.2	0.6	19.5	1.0
#2	8.2	0.6	11.5	0.5
#3	8.2	0.4	10.0	0.8
#4	8.2	0.8	11.5	1.1
#5	8.2	0.4	11.5	1.0
#6	8.0	1.1	10.5	1.1
#7	7.9	2.9	12.5	1.2
#8	8.0	1.1	12.0	---
#9	8.0	1.3	4.5	---
#10	8.2	1.8	12.0	1.2

TABLE A-5

Reported Data of Surrogate Parameters for the Guajataca Diversion Channel for for April 1994

Lake Level: 191.00 m Area: 14,600 acres-ft

Points	pH	Turbidity	COD_{av}(mg/L)	BOD_5(mg/L)
#1	7.3	1.9	34.7	0.2
#2	7.3	1.3	22.0	----
#3	7.8	1.4	4.3	----
#4	8.0	1.7	19.7	1.1
#5	7.9	0.8	0.3	0.6
#6	8.2	2.7	1.0	0.1
#7	8.1	1.5	4.7	1.0
#8	8.1	1.3	1.7	0.7
#9	8.2	3.9	12.7	1.3
#10	8.2	2.1	31.0	1.4

TABLE A-6

Reported Data of Surrogate Parameters for the Guajataca Diversion Channel for for May 1994

Lake Level: 192.00 m Area: 17,600 acres-ft

Points	pH	Turbidity	COD_{av}(mg/L)	BOD_5(mg/L)
#1	7.3	0.6	5.3	4.0
#2	7.5	0.9	4.7	3.2
#3	7.8	0.9	4.0	----
#4	8.2	0.6	5.3	----
#5	8.3	0.4	4.0	1.0
#6	8.3	1.2	4.7	----
#7	8.2	1.5	2.7	1.9
#8	8.3	1.2	8.7	1.2
#9	8.3	3.5	1.7	2.4
#10	8.0	2.0	5.7	4.0

APPENDIX B

Monthly Reported Data of Fecal Coliforms from the Guajataca Diversion Channel

Table B-1
Reported Data of
of Fecal Coliforms (# Colonies) for the Guajataca Diversion Channel
for December 1993

Sampling Points	Fecal Coli. 1ml	Fecal Coli. 1ml	Fecal Coli. 10ml	Fecal Coli 10ml
#1	70	68	TNTC	TNTC
#2	0	6	3	7
#3	TNTC	TNTC	TNTC	TNTC
#4	30	TNTC	130	TNTC
#5	0	2	2	4
#6	15	35	TNTC	120
#7	45	22	TNTC	TNTC
#8	1	2	1	2
#9	35	30	TNTC	TNTC
#10	23	62	TNTC	TNTC

TNTC = Too Numerous to Count over 200 colonies

Table B-2
Reported Data of
of Fecal Coliforms (# Colonies) for the Guajataca Diversion Channel
for January 1994

Sampling Points	Fecal Coli. 1ml	Fecal Coli. 1ml	Fecal Coli. 10ml	Fecal Coli 10ml
#1	TNTC	TNTC	TNTC	TNTC
#2	88	49	TNTC	TNTC
#3	TNTC	TNTC	TNTC	TNTC
#4	TNTC	TNTC	TNTC	TNTC
#5	TNTC	200	TNTC	TNTC
#6	140	190	TNTC	TNTC
#7	105	110	TNTC	TNTC
#8	105	120	TNTC	TNTC
#9	190	200	TNTC	TNTC
#10	TNTC	200	TNTC	TNTC

Table B-3
Reported Data of
of Fecal Coliforms (# Colonies) for the Guajataca Diversion Channel
for February 1994

Sampling Points	Fecal Coli. 1ml	Fecal Coli. 1ml	Fecal Coli. 10ml	Fecal Coli 10ml
#1	191	TNTC	TNTC	TNTC
#2	145	139	TNTC	TNTC
#3	167	156	TNTC	TNTC
#4	140	138	TNTC	TNTC
#5	87	81	TNTC	TNTC
#6	47	58	TNTC	TNTC
#7	76	83	TNTC	TNTC
#8	50	47	TNTC	TNTC
#9	105	124	TNTC	TNTC
#10	TNTC	TNTC	TNTC	TNTC

Table B-4
Reported Data of
of Fecal Coliforms (# Colonies) for the Guajataca Diversion Channel
for March 1994

Sampling Points	Fecal Coli. 1ml	Fecal Coli. 1ml	Fecal Coli. 10ml	Fecal Coli 10ml
#1	140	132	TNTC	TNTC
#2	40	32	130	167
#3	TNTC	TNTC	TNTC	TNTC
#4	30	TNTC	TNTC	TNTC
#5	120	132	122	114
#6	15	35	TNTC	TNTC
#7	45	22	TNTC	TNTC
#8	34	22	TNTC	172
#9	TNTC	TNTC	TNTC	TNTC
#10	58	82	TNTC	TNTC

Table B-5
Reported Data of
of Fecal Coliforms (# Colonies) for the Guajataca Diversion Channel
for April 1994

Sampling Points	Fecal Coli. 1ml	Fecal Coli. 1ml	Fecal Coli. 10ml	Fecal Coli 10ml
#1	140	132	TNTC	TNTC
#2	40	32	130	167
#3	TNTC	TNTC	TNTC	TNTC
#4	30	TNTC	TNTC	TNTC
#5	120	152	122	114
#6	15	35	TNTC	TNTC
#7	45	22	TNTC	TNTC
#8	34	22	TNTC	172
#9	TNTC	TNTC	TNTC	TNTC
#10	TNTC	TNTC	TNTC	TNTC

Table B-6
Reported Data of
of Fecal Coliforms (# Colonies) for the Guajataca Diversion Channel
for May 1994

Sampling Points	Fecal Coli. 1ml	Fecal Coli. 1ml	Fecal Coli. 10ml	Fecal Coli 10ml
#1	TNTC	TNTC	TNTC	TNTC
#2	TNTC	TNTC	TNTC	TNTC
#3	80	150	TNTC	TNTC
#4	140	150	TNTC	TNTC
#5	75	55	140	70
#6	70	140	130	100
#7	65	80	100	125
#8	60	75	90	TNTC
#9	65	95	100	TNTC
#10	60	70	65	TNTC

APPENDIX C

STATISTICAL ANALYSIS

a) Iron Case

Table C-1
Data of Iron Concentrations

Treatment Combination	Raw Water		Clear Well		Removal	
	Trial 1 (mg/l)	Trial 2 (mg/l)	Trial 1 (mg/l)	Trial 2 (mg/l)	Trial 1 (mg/l)	Trial 2 (mg/l)
K(-) Cl(-)	0.005	0.005	0.005	0.005	0.000	0.000
K(+) Cl(-)	0.130	0.142	0.014	0.016	0.116	0.126
K(-) Cl(+)	0.010	0.010	0.010	0.010	0.00	0.00
K(+) Cl(+)	0.005	0.054	0.005	0.462	0.00	0.003*

* Estimated Value

			Response	
A	B	Treatment Combination	Trial 1	Trial 2
-	+	b	0	0
-	-	(1)	0	0
+	+	ab	0	0.00333
+	-	a	0.116	0.126

Table C-2
Yates Algorithm Table
n = 2 A = K
k = 2 B = Cl

Treatment Combination	Response	(1)	(2)	Estimate of Effect	Mean Square
(1)	0	0.242	0.24533	-	-
a	0.242	0.00333	0.24533	0.061333	0.007523
b	0	0.242	-0.23867	-0.05967	0.00712
ab	0.00333	0.00333	-0.23867	-0.05967	0.00712

Table C-3
ANOVA Table
for Iron Concentration

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Fo	F critic	CV (%)
A	0.007523	1	0.007523	677.237	6.61	10.87
B	0.00712	1	0.00712	640.966	6.61	
AB	0.00712	0	-	-		
Error	5.55E-05	5	1.39E-05			
Total	0.02182	7				

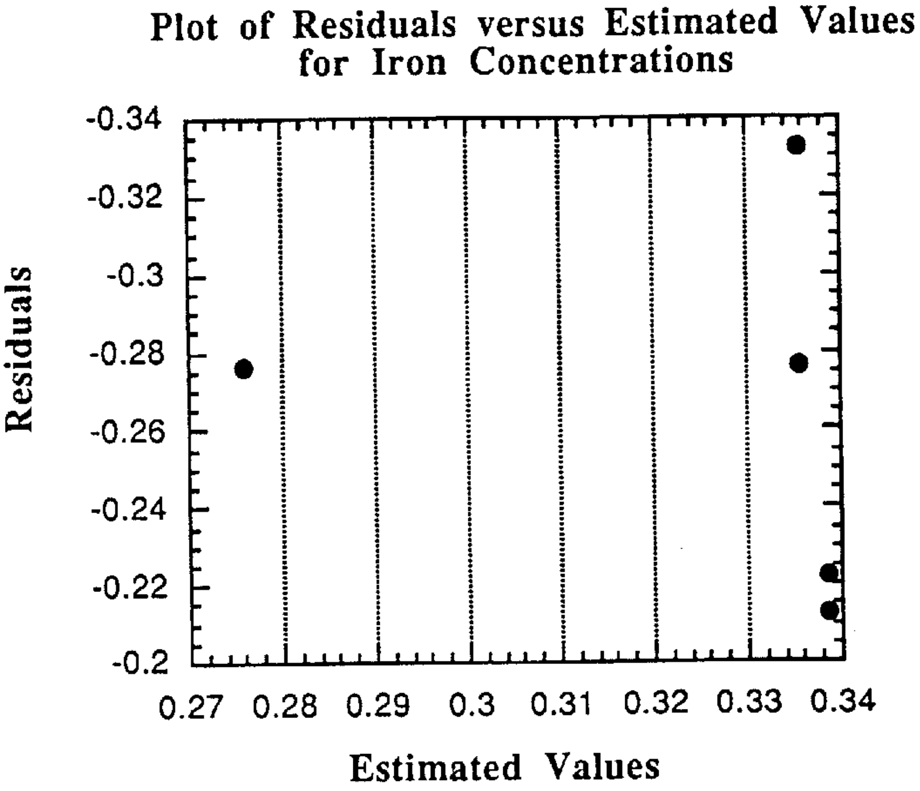

Figure C-1
Plot of Residuals versus Estimated Values for Iron

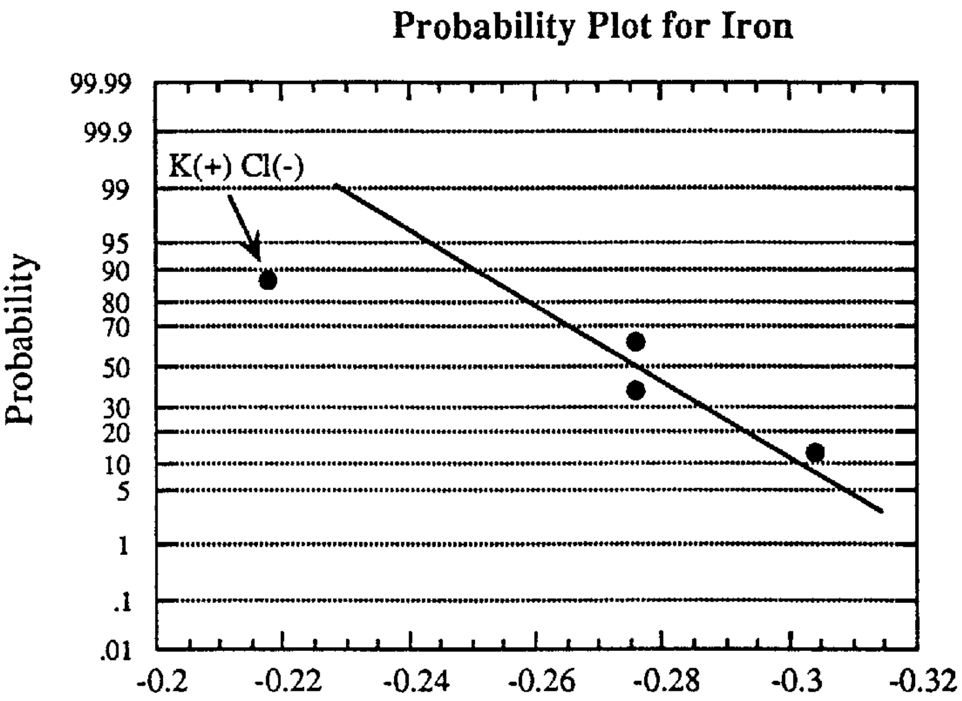

Figure C-2
Probability Plot for Iron Residuals

b. Manganese Case

Table C-4
Data of Manganese Concentrations (mg/l)

Treatment Combination	Raw Water		Clear Well		Increment	
	Trial 1 (mg/l)	Trial 2 (mg/l)	Trial 1 (mg/l)	Trial 2 (mg/l)	Trial 1 (mg/l)	Trial 2 (mg/l)
K(-) Cl(-)	0.011	0.011	0.018	0.029	0.007	0.018
K(+) Cl(-)	0.041	0.015	0.037	0.026	-0.004*	0.011
K(-) Cl(+)	0.008	0.010	0.020	0.020	0.012	0.010
K(+) Cl(+)	0.010	0.012	0.011	0.048	0.011	0.036

*** Estimated Value**

From the book (*Design of Experiments*, by Montgomery, Douglas) the equation

$x = (a\, y'_{i\bullet} + b y'_{\bullet j} - y'_{\bullet\bullet}) / (a-1)(b-1)$

A	B	Treatment Combination	Repitions I	II
-	+	b	0.012	0.010
-	-	(1)	0.007	0.018
+	+	ab	0.001	0.036
+	-	a	-0.004	0.011

Table C-5
Yates Algorithm Table

n = 2 A = K
k = 2 B = Cl

Treatment Combination	Response	(1)	(2)	Estimate of Effect	Mean Square
(1)	0.025	0.03233	0.09133	-	-
a	0.00733	0.059	-0.00267	-0.00067	8.91E-07
b	0.022	-0.01767	0.02667	0.006668	8.89 E-05
ab	0.037	0.041	0.03267	0.008168	0.000133

Table C-6
ANOVA Table
for Iron Concentrations

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Fo	a=.05 F critic	CV (%)
A	8.91E-07	0	-			109.59
B	8.89E-05	1	8.89E-05	0.568046	6.61	
AB	1.33E-04	1	0.000133	0.85239	6.61	
Error	7.83E-04	5	0.000157			
Total	1.006E-03	7				

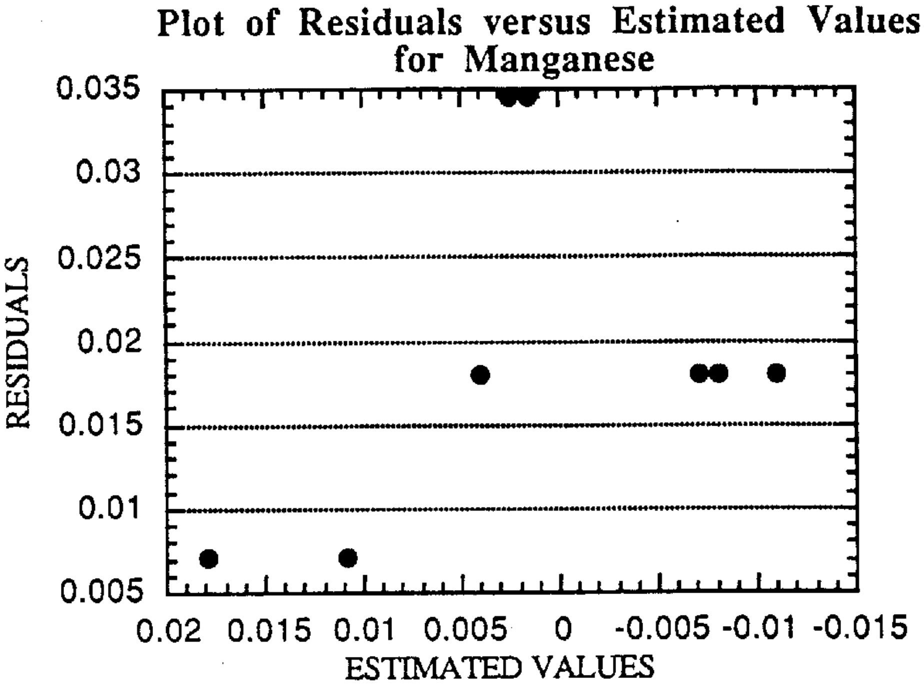

Figure C-3
Plot of Residuals versus Estimated Values for Manganese

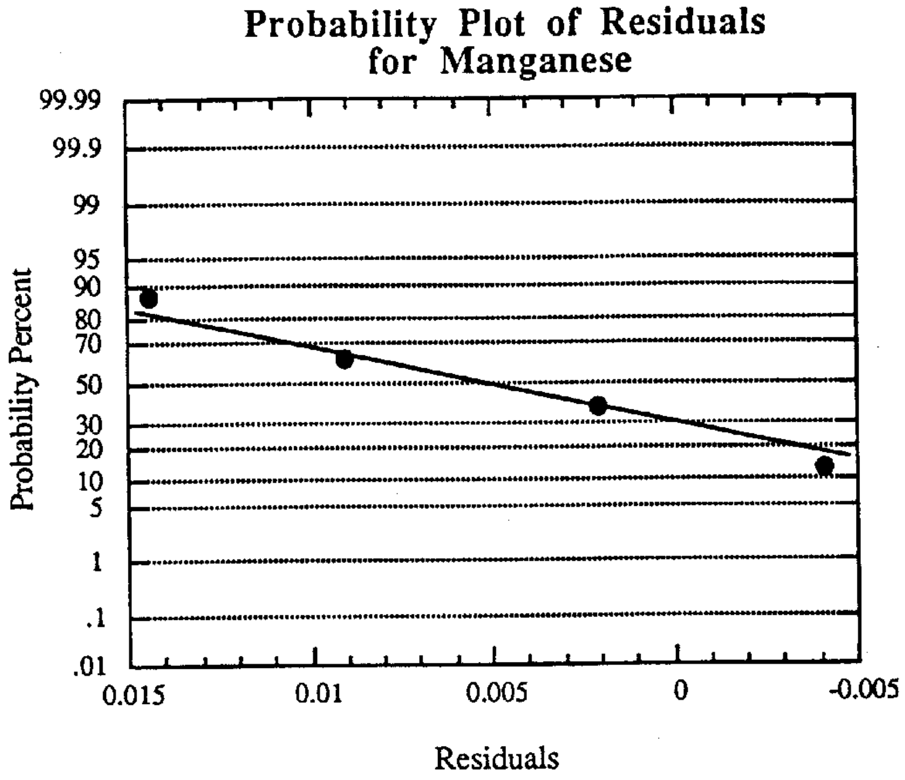

Figure C-4
Probabilty Plot for Manganese Residuals

c) Trihalomethane Case

The assumption here is to see how the quantity of organic matter at the entrance of the plant is related to the Total Trihalomethanes formation, assuming there is a linear relationship between the response and the covariate.

TABLE C-7
Triahlomethanes Concentration (ppb) and Total Organic Carbon (ppm)

Comb.	(-) (-)		(+) (-)		(-) (+)		(+) (+)	
Trial	THM (ppb)	TOC (ppm)	THM (ppb)	TOC (ppm)	THM (ppb)	TOC (ppm)	THM (ppb)	TOC (ppm)
1	35	2.973	28	0.041	48	3.431	24	2.932
2	20	2.838	28	< LDL	44	2.854	50	1.955

LDL = Lowest Detection Limit

Source of Variation	DF	Sum of Squares and Products			Adjusted for Regression			Fo	Fcrit.
		x	xy	y	y	DF	Mean Square		
Treat.	3	12.347	41.412	459.37					
Error	4	0.653	10.537	458.50	288.51	3	96.1718	1.93	9.28[a]
Total	7	13.000	30.875	917.87	844.55	6			
Adjusted treatments					556.03	3	185.344		

APPENDIX D

DETAILED PROCEDURE
FOR EXPERIMENTAL RUNS AT RAMEY WATER TREATMENT PLANT

D-1) Estimation of Residence Time of the Plant

A) Time of Treatment

1) Volume of Pipes =	1343.86	gallons
2) Filters Volume =	41,000	gallons
3) Clarifier Volume =	105,000	gallons
4) Clear Well Volume =	220,000	gallons
5) Mixing Tank Volume =	1234	gallons
Total Volume =	368,577	gallons

Volumetric Flow = 2100 gallons / minute

Residence treatment overall time = Plant Volume / Volumetric Flow

= 368,577 gallons/ (2100 gallons/minute)

= 175.51 minutes = 2.92 hours

B) Time of Reaction of Potassium Permanganate or Chlorine

Volume of Reactor = Volume of Pipe + Volume mixing tank + Volume Clarifier

= 1343.86 + 1234 + 105,000

= 107,577 gallons

Time reaction = Volume/Volumetric Flow

= 107,577 gallons/(2100 gallons/minute)
= 0.85 hour

D-2) Plant Operation Proceeding

1) Check the clear well level.
2) Check the number of Filters that are operating.
3) Check the chlorine tanks and the in flowmeters.
4) Check the level of the channel.
5) Check the polymer feeders.
6) Laboratory Check Out; Check the parameters of turbidity, pH, free chlorine, dissolved oxygen, see chart or figure # A-1 at different sample points such as; raw water, mixing tank, clarifier, filter, and clear well.

D-3) Potassium Permanganate Solution

1) Wash the potassium permanganate tanks and clean the rotameter.

2) Fill the tanks with raw water from the channel.
3) Choose the percentage of potassium permanganate solution for the run.
For example: For a level KMnO4 solution of 0.5% (Solution Feed Rates)
18.9 grams /gallon x 50 gallon = 945 grams for a 50 gallon tank
4) Turn on the mixer of each permanganate tank feeder for half hour at 1750 RPM.
5) Turn off the pre-chlorine for the run, half hour to get out all the chlorine out of the line. Adjust the post-chlorine at 80 lb/24hour.
6) Check the plant flow meter and record it.

Turn the digital chronometer to check the residence time of the plant.

1) After the solution is made open the rotameter in accordance to the calibration curve for potassium permanganate.
2) Then start to fill the data sheet showed on Table D-2.
3) After the residual of the of KMnO4 solution is maintained to the expected value (0.2 mg/l), takes samples for turbidity,free chlorine, pH, each hour.
4) Calculate the residence time of the plant to see how long it takes to collect the sample for THM, iron and manganese analysis..
5) After the plant has reached steady-state., Prepare sample bottles with sodium thiosulfate to take the sample for THM analysis.
6) Take samples for metals in 250 ml amber bottles.

TABLE D-1

Factors for CAIROX®
(Potassium Permanganate)
Solution Feed Rates

KMnO4 % Solution	lb/gal	oz/gal	grams/gal	ml/min needed * 100 gpm
0.5	0.04	0.64	18.9	75.7
1.0	0.08	1.28	37.8	37.8
1.5	0.13	2.08	56.8	25.2
2.0	0.17	2.72	75.7	18.9
2.5	0.21	3.36	94.6	15.1
3.0	0.25	4.00	113.6	12.6
3.5	0.29	4.64	132.5	10.8
4.0	0.33	5.28	151.4	9.5
4.5	0.38	6.08	170.3	8.4
5.0	0.42	6.72	189.2	7.6

* The flow is equivalent to1 ppm.

For example: To make up a 4% CAIROX Solution, 1/3 pound of CAIROX was added per gallon of water. This solution should be agitated vigourosly for 15 to 30 minutes to insure dilution. Agitation with a mixer at 750-1000 rpm is recommended. Always follow the safety procedures outlined in the MSDS for potassium permanganate.

TABLE D-2
Potassium Permanganate Flow Rates (ml/min) for
Tank Feeders at Ramey Water Treatment Plant

Plant Flow GPM	3.00%	2.50%	2.00%	1.50%	1.00%	0.50%
3000	378.0	453.0	567.0	756.0	1134.0	2271.0
2900	365.4	437.9	548.1	730.8	1096.2	2195.3
2800	352.8	422.8	529.2	705.6	1058.4	2119.6
2700	340.2	407.7	510.3	680.4	1020.6	2043.9
2600	327.6	392.6	491.4	655.2	982.8	1968.2
2500	315.0	377.5	472.5	630.0	945.0	1892.5
2400	302.4	362.4	453.6	604.8	907.2	1816.8
2300	289.8	347.3	434.7	579.6	869.4	1741.1
2200	277.2	332.2	415.8	554.4	831.6	1665.4
2100	264.6	317.1	396.9	529.2	793.8	1589.7
2000	252.0	302.0	378.0	504.0	756.0	1514.0
1900	239.4	286.9	359.1	478.8	718.2	1438.3
1800	226.8	271.8	340.2	453.6	680.4	1362.6
1700	214.2	256.7	321.3	428.4	642.6	1286.9
1600	201.6	241.6	302.4	403.2	604.8	1211.2
1500	189.0	226.5	283.5	378.0	567.0	1135.5
1400	176.4	211.4	264.6	352.8	529.2	1059.8
1300	163.8	196.3	245.7	327.6	491.4	984.1
1200	151.2	181.2	226.8	302.4	453.6	908.4
1100	138.6	166.1	207.9	277.2	415.8	832.7
1000	126.0	151.0	189.0	252.0	378.0	757.0