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Christine Hall
University of Central Florida

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EVALUATION OF IRON AND MANGANESE CONTROL FOR A VOLCANIC SURFACE WATER SUPPLY TREATED WITH CONVENTIONAL COAGULATION, SEDIMENTATION AND FILTRATION PROCESSES

by

CHRISTINE HALL, E.I.
B.S.C.E., B.S.Env.E, University of Central Florida, 2012

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ABSTRACT

A research project assessing the effectiveness of potassium permanganate ($KMnO_4$) for the treatment of iron (Fe) and manganese (Mn) has been conducted by the University of Central Florida (UCF) on behalf of the United States Navy with regards to the water supply on the island of Guam, located in the Marianas Islands. The study consisted of three basic investigative components: one that examined the use of potassium permanganate for iron and manganese control for Fena Lake, a second that examined the existing unit operations that comprised the Navy's water treatment plant (NWTP), and a third that examined iron and manganese field sampling analytical procedures.

In the first and primary component of the research, surface water from Fena Lake located within the Naval Magazine in proximity of Santa Rita, Guam was collected at several different lake depths and initially analyzed for iron and manganese using inductively coupled plasma. Subsequent aliquots of Fena Lake collected at the various water depths were transferred to jars then dosed with varying amounts of potassium permanganate after which iron and manganese content was determined. The jars were covered to simulate actual lake to plant transfer conditions experienced at the Navy's on-island facilities. A portion of the jars was dosed with potassium permanganate prior to metals analysis in order to allow for comparisons of baseline conditions. To represent conventional treatment processes, the water samples were then coagulated with aluminum sulfate prior to filtration to remove the oxidized manganese and iron formed from the addition of the potassium permanganate. Coagulated aliquots were filtered and collected to evaluate residual dissolved iron and manganese content. Based on the results of the

jar tests it was determined that manganese was reduced by 95% or greater and that iron was completely removed to below the analytical detection limit (0.001 mg/L). It was determined that the potassium permanganate dose required for oxidation of iron was 0.94 mg/mg iron and for manganese was 1.92 mg/mg manganese. It was also observed that when the jars containing aliquots that turned brown in color after potassium permanganate dosing meant that iron and manganese were present and were being oxidized; however, water samples that turned pink were found to be over-dosed with potassium permanganate. The pink water is an undesired characteristic and could result in customer complaints when distributed to the system.

The second component of research focused on NWTP existing conditions. Water samples were collected after each key unit operation within the NWTP and analyzed for iron and manganese. This was to determine if pre-chlorination at Fena Lake was effective at removing iron and manganese that could be present in the source water. Analysis was conducted where pre-chlorination at Fena Lake was practiced as well as when no pretreatment was practiced prior to the NWTP. It was determined that the iron and manganese were not detected downstream of the coagulation unit operation within the NWTP even when pre-chlorination was not practiced. Consequently pre-chlorination of Fena Lake source water was not required for controlling iron and manganese under the conditions experienced in this study.

A third study was also implemented to confirm that 0.1-micron filters are appropriate for use in preparing samples for analytical determination of iron and manganese analysis at various points within the NWTP. The filtration step is important to delineate between dissolved and suspended iron and manganese forms. Standard Methods 3120B recommends the use of 0.45-micron filters,

although based on literature it has been shown that oxidized manganese particles may be smaller than a 0.45-micron pore size. Unless a coagulant was used, the oxidized manganese may not be fully removed via the 0.45-micron filter. To verify the effectiveness of using a 0.1-micron filter, a jar test was conducted to compare the use of a 0.1-micron filter, a 0.45-micron filter, and a 0.45-micron filter after the sample has been coagulated. It was found that the use of a 0.1-micron filter was superior to the use of 0.45-micron filters even with coagulant addition when directly comparing between dissolved and suspended iron and manganese forms. It is recommended that 0.1-microns be utilized in lieu of historically recommended 0.45-micron filters for sample preparation procedures.

This thesis is dedicated to the Hall family: Carolyn, Martin, Scott, Jennifer, and Leslie

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LIST OF EQUATIONS

LIST OF ABBREVIATIONS

B1283	Building 1283
B1285	Building 1285
BDL	below detection limit
CECE	Civil, Environmental, and Construction Engineering
CT	contact time
DBPs	disinfection byproducts
ESEI	Environmental Systems Engineering Institute
FD	field duplicate
FWTP	Fena Water Treatment Plant
HAAs	halo acetic acids
HDPE	high-density polyethylene
ICP	inductively coupled plasma
LCL/LWL	lower control limit/lower warning limit
MCL	maximum contaminant level
MG/MGD	million gallons/million gallons per day
NAVFAC	Naval Facilities Engineering Command
NOM	natural organic matter
NSDWRs	National Secondary Drinking Water Regulations
NTU	nephelometric turbidity unit
NWTP	Navy Water Treatment Plant
PWS	public water system
RPD	relative percent difference
RPM	revolutions per minute
SDWA	Safe Drinking Water Act
SM	standard methods
SMCLs	secondary maximum contaminant levels
THMs	trihalomethanes
TTHMs	total trihalomethanes
UCF	University of Central Florida
UCL/UWL	upper control limit/upper warning limit
USEPA/EPA	United States/Environmental Protection Agency
V	volts
WTP	water treatment plant

1. INTRODUCTION

Project Description

The U.S. Navy’s Public Water System’s (PWS) Fena Water Treatmen Plant (FWTP), located on the island of Guam in the Marianas Islands, draws its source water from the U.S. Navy’s Reservoir at Fena Valley; in addition, a portion of the water supply for the Navy’s water system is derived from the Bona and Almagosa Spring. Fena Lake, Bona Spring, and the Almagosa Spring are located within the Naval Magazine, a secure military compound. The Navy’s Fena Lake Reservoir serves as the primary source water for the PWS and raw water is withdrawn from a constructed screen house complex that allows supply water to be taken at depths that range from the surface to up to 50 feet (ft); water is typically drawn from a 12-ft depth. Raw water from the reservoir and the springs is pumped to, and treated by, the U.S. Navy’s FWTP, a conventional surface water treatment plant.

A schematic of the Navy’s PWS that depicts the primary water sources and identifies the key unit operations is provided as a general process diagram in Figure 3-1. Historically, chlorine was added at the Fena Lake Pump Station’s Building 1285 (B1285) for iron, manganese, taste, and odor control. The WTP processes include chemical addition and rapid mixing of alum, lime and/or polymer prior to coagulation, flocculation, and sedimentation. The coagulation and sedimentation process occurs as a combined-unit operation; the Navy operates two clarifiers either in parallel or series configuration, depending on season, demand, or quality (turbidity levels entering plant).

After the clarification process, the water is chlorinated prior to filtration. The water then proceeds through six dual-media, anthracite-sand filters, followed by post-filter fluoridation, disinfection with ultraviolet (UV) and sodium hypochlorite. The finished water then continues to a rectangular, dual-compartment, baffled clearwell for meeting contact time (CT) requirements. Finished water collected within the 1.06-million-gallon (MG) clearwell is distributed to the Naval Magazine (0.72 MG), Maanot (0.59 MG), Apra Heights (0.5 MG) and Tupo (5.0 MG) Reservoirs. From these primary finished water storage reservoirs, potable water is then distributed to secondary reservoirs and throughout the Navy's water distribution system.

In January of 2013 the U.S. Navy retained Brown & Calwell (Honolulu, HI) and the University of Central Florida (UCF) Civil, Environmental, and Construction Engineering (CECE) department to conduct research to investigate iron, manganese and DBP water quality issues within the Navy's Guam PWS. At the time that this research component reported herein was conducted, the U.S. Navy used free chlorine oxidation (from chlorine ton containers) at the Fena Lake Pump Station B1285 (B1285); it was determined that this practice contributed to the formation of disinfection byproducts (DBPs). Since the pre-chlorination was contributing to an increase in DBPs, a decision was made to cease pre-chlorination at Fena Lake. Consequently, a key portion of the research reported herein was conducted to evaluate an alternative oxidant, potassium permanganate, for use in treating Fena Lake iron and manganese in lieu of gaseous chlorine addition at Pump Station B1285.

The primary objective of this research was to conduct a study on the efficiency of potassium permanganate as an alternate oxidant for the removal of iron and manganese. To perform this research, jar tests were performed to simulate plant operations. Water samples were collected at strategic locations within Fena Lake and downstream facilities including the NWTP. Potassium permanganate was added to the samples prior to addition of coagulant to conventional process. Samples were then taken from the jars for iron and manganese analysis to determine treatment effectiveness.

2. LITERATURE REVIEW

The USEPA has established National Secondary Drinking Water Regulations (NSDWRs) that set non-mandatory water quality standards for 15 contaminants, including iron and manganese. These secondary maximum contaminant levels are not enforceable, unless a state decides to do so (for example Florida enforces NSDWRs), and are established for aesthetic considerations, such as taste, color, and odor. These contaminants are not considered to present a risk to human health at the SMCL, but iron and manganese can contribute to taste and odor problems, as well as color, which in turn, may result in consumers’ avoidance in drinking water from their public water systems, even though the water is safe. The SMCL for iron and manganese is 0.3 mg/L and 0.05 mg/L, respectively (USEPA 1979).

Manganese Chemistry

Since manganese is a transition metal, it may exist in various oxidation states as shown in Table 2-1. Within the drinking water community, the most relevant manganese species include the manganous ion (Mn^{2+}), particulate manganese dioxide (MnO_2), and the permanganate ion ($MnO_4{}^{-}{}_{-}$). These three species may exist in one of three physical-chemical forms, which include particulate, colloidal, or soluble. Of the three oxidation states and physical-chemical forms, soluble manganese, Mn^{2+}, is the most common in groundwater supplies, as well as impounded surface water supplies.

Table 2-1: Manganese Oxidation States

Oxidation State	Compound	Name	Appearance
0	Mn	Elemental	Silvery solid
II[a]	Mn^{2+}	Manganous ion	Clear in water
III[a]	Mn^{3+}	Manganic ion	Red/violet in water
	$Mn_2O_3(s)$	Manganese (III) oxide	Dark brown/black solid
IV[a]	$MnO_2(s)$	Manganese dioxide	Black solid
V	MnO_4^{3-}	Hypomanganate ion	Turquoise in water
VI	MnO_4^{2-}	Manganate ion	Green in water
VII[a]	MnO_4^-	Permanganate ion	Purple in water

a: Manganese commonly present in the drinking water industry

If oxidizing and reducing bacteria are present, they may be responsible for the cycling of manganese between the soluble and particulate manganese forms as shown in Figure 2-1 (Carlson and Knocke 1999). Anaerobic bacteria in the reservoir sediments minimize the formation of manganese dioxide precipitates during respiration, and soluble Mn^{2+} is released into the water column where it is utilized as an energy source by manganese-oxidizing bacteria. The solid manganese dioxide then precipitates to the bottom, allowing the cycle to repeat. During stratification, the anoxic conditions may disturb the biogeochemical cycle and more soluble Mn^{2+} is released than can be used by the manganese oxidizers, which results in more dissolved manganese. (Roccaro, Barone et al., 2007).

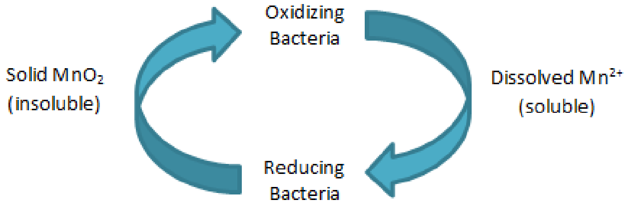


Figure 2-1: Manganese Biogeochemical Cycle (Roccaro, Barone et al., 2007)

Insoluble manganese dioxide occurs primarily as manganese dioxide while dissolved manganese occurs as a soluble free metal divalent cation. If the manganese is not oxidized, the dissolved manganese can pass easily through the water treatment processes. Once this soluble manganese is in the distribution system, it may become oxidized to insoluble manganese (manganese oxide), causing several problems, such as water discoloration, metallic taste, odor, turbidity, biofouling, corrosion, and staining of laundry and plumbing fixtures (Roccaro, Barone et al., 2007).

Manganese oxide solids involving Mn (III) or both the Mn (III) and Mn (IV) oxidation states may be present when the background water chemistry has been changed due to the addition of other oxidants (Pontius, LeChevallier et al. 2002). Therefore, manganese oxide solids are more accurately described as MnO_x(s), where x is between 1.5 and 2 and manganese oxide solids are referred to as MnO_x(s).

The permanganate species, MnO_4^-, does not occur naturally in water, but is an important manmade chemical frequently used by water utilities. The permanganate ion is a strong oxidant capable of oxidizing many contaminants that may be present in water due to its high oxidation state, +VII. Permanganate is commonly used for taste and odor control, as well as iron, and manganese treatment. Due to its high oxidation state, the permanganate ion acts as an oxidant in oxidation/reduction reactions; this results in the soluble MnO_4^- being reduced to particulate $MnO_{2(s)}$.

The species of manganese that may be present in water are controlled by the background oxidation/ reduction potential and pH of the water, along with the presence of other contaminants that can combine with manganese to form other manganese compounds. The Pourbaix diagram, or E_H-pH diagram, shown in Figure 2-2, better depicts the manganese species that may be present in the system over a range of background oxidation/reduction and pH conditions. The shaded area of Figure 2-2 represents the typical conditions of the water for the research performed by UCF. The y-axis of this diagram represents the oxidation/reduction potential of the system. The oxidizing conditions are present at the top of the diagram, and the reducing ions in acidic conditions are to the left and the basic are toward the right. This Pourbaix diagram provides basic insight to how the manipulation of oxidation/reduction potential and pH may be used to convert untreated manganese to suitable species of manganese that may be treated.

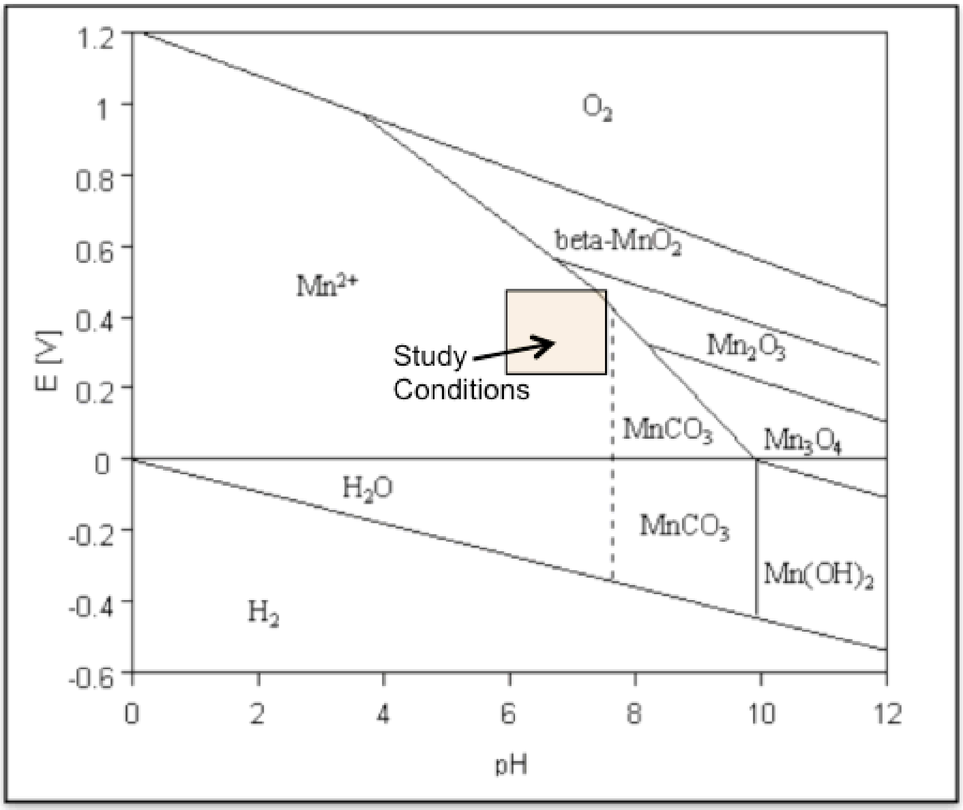


Figure 2-2: Pourbaix Diagram for Manganese (Scheffer et al., 1989)

The Pourbaix diagram presents the stable forms of manganese in pure water containing manganese and carbonate. The soluble Mn^{2+} ion is soluble and present over a wide range of pH and oxidation/reduction conditions. Based on the diagram, at a pH of less than five, manganese is highly soluble. At a moderate pH, between five and eight, manganese is highly soluble under reducing conditions, but insoluble under oxidizing conditions. At pH levels typical of a water treatment plant (pH 6.0 to 8.0), soluble Mn^{2+} may or may not be stable. This depends on the oxidation/reduction state of the water and how much carbonate is present. Under an elevated pH (greater than eight), or strongly oxidizing conditions, Mn^{2+} is unstable and will precipitate to form a visible insoluble oxide, hydroxide or carbonate solid. If the pH is further increased, the manganese forms various insoluble oxides. One of the reasons that manganese causes problems for water utilities is that typical water quality conditions are in the range from which manganese can be readily cycled between soluble and insoluble forms. This explains why water that may be colored by manganese can seem to appear and disappear from a system.

Iron Chemistry

Similar to manganese, the behavior of iron in water is primarily controlled by oxidation/reduction potential and the pH of the water in which iron occurs. This is better shown in the Pourbaix diagram for iron, Figure 2-3, where the shaded region represents the typical conditions of the water for the research performed by UCF. Like manganese, the combination of oxidation/reduction potential and pH has a strong influence on the species of iron that may be present in the source water. The species of iron present also has an influence on its solubility. In natural waters, iron is commonly present in two oxidation states, ferrous (Fe(II)) and ferric

(Fe(III)). Based on the figure shown, at a pH less than five, iron oxidation states are more soluble, like manganese. At a pH between five and eight, iron tends to be more sensitive to changes in water's oxidation/reduction potential. When the pH is greater than eight, iron tends to be insoluble like manganese (Branhuber, Clark et al. 2013).

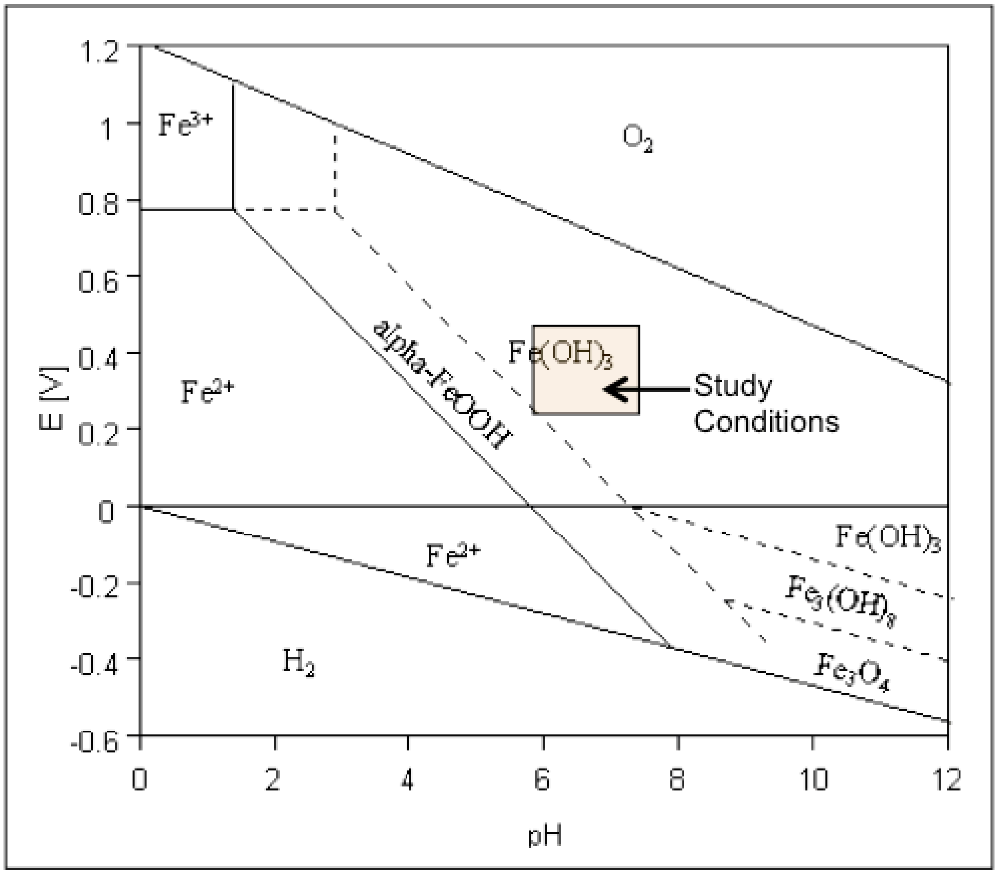


Figure 2-3: Pourbaix Diagram for Iron (Scheffer et al., 1989)

Another relevant aspect of iron chemistry is that the transfer of only one electron is needed for iron to transition from its soluble form, ferrous, to its insoluble form, ferric whereas manganese requires two electrons to transfer. Therefore, on a molar basis, twice as much oxidant is needed, in comparison to iron, for soluble manganese to convert to insoluble. In general, iron is far easier to oxidize than manganese due to the fast rate of oxidation as well as the transfer of only one electron. Therefore, the presence of soluble iron in water exerts an oxidant demand, which must be satisfied prior to completing the oxidation of manganese.

At a moderate pH, that is typical of drinking water, iron oxidation proceeds at a quicker rate than manganese oxidation. Iron is also easily oxidized at a moderate pH if chlorine or oxygen is present. Unlike iron, when chlorine or oxygen is present, the oxidation of manganese is slower. Therefore, oxygen or chlorine may be used to effectively oxidize iron when manganese is not a concern. However, it is noted that chlorine and oxygen do not provide effective removal for manganese. Utilities often believe that manganese is being oxidized and precipitated by the presence of free chlorine, when, in fact, the manganese is being removed through the process of sorption and catalyzed surface oxidation onto a media filter.

Oxidant Selection

Various oxidants are available for iron and manganese oxidation within a water treatment plant. Chemicals that can effectively oxidize dissolved manganese include potassium permanganate, chlorine dioxide, ozone, chlorine, and oxygen. These oxidants are shown in Table 2-2 and Table 2-3, as well as their stoichiometric equations, in correspondence to iron and manganese. Each oxidant only works effectively when at the appropriate pH. For the pH range between approximately 6.5 and 8.5, direct oxidation of dissolved manganese may be accomplished using one or a combination of three strong oxidants, which includes potassium permanganate, chlorine dioxide, or ozone. At a high pH, greater than nine, oxidation using chlorine or oxygen may be performed. Based on the history of the NWTP, pre-chlorination has been implemented in the past, so chlorine and the alternate oxidant of choice, potassium permanganate, will be discussed.

Table 2-2: Reactions of Fe(II) With Alternative Oxidants and the Theoretical Reaction Stoichiometry

Metal/Oxidant	Reaction	Stoichiometry
O_2 (aq)	$2Fe^{2+}+1/2O_2(aq)+5H_2O \rightarrow 2Fe(OH)_3(s)+4H^+$	0.14 mg O_2/mg Fe
$O_3(aq) \rightarrow O_2(aq)$	$2Fe^{2+}+O_3(aq)+5H_2O \rightarrow 2Fe(OH)_3(s)+O_2(aq)+4H^+$	0.43 mg O_3/mg Fe
HOCl	$2Fe^{2+}+HOCl+5H_2O \rightarrow 2Fe(OH)_3(s)+Cl^-+5H^+$	0.64 mg HOCl/mg Fe
$ClO_2 \rightarrow ClO_2^-$	$Fe^{2+}+ClO_2+3H_2O \rightarrow Fe(OH)_3(s)+ClO_2^-+3H^+$	1.20 mg ClO_2/mg Fe
$KMnO_4$	$3Fe^{2+}+MnO_4^-+2H_2O \rightarrow 3Fe(OH)_3(s)+MnO_2(s)+5H+$	0.94 mg $KMnO_4$/mg Fe

Table 2-3: Reactions of Mn(II) With Alternative Oxidants and the Theoretical Reaction Stoichiometry

Metal/Oxidant	Reaction	Stoichiometry
O_2 (aq)	$Mn^{2+}+1/2O_2(aq)+H_2O \rightarrow MnO_2(s)+2H^+$	0.29 mg O_2/mg Mn
$O_3(aq) \rightarrow O_2(aq)$	$Mn^{2+}+O_3(aq)+H_2O \rightarrow MnO_2(s)+O_2(aq)+2H^+$	0.88 mg O_3/mg Mn
HOCl	$Mn^{2+}+HOCl+H_2O \rightarrow MnO_2(s)+Cl^-+3H^+$	1.30 mg HOCl/mg Mn
$ClO_2 \rightarrow ClO_2^-$	$Mn^{2+}+2ClO_2+2H_2O \rightarrow MnO_2(s)+2ClO_2^-+4H^+$	2.45 mg ClO_2/mg Mn
$KMnO_4$	$3Mn^{2+}+2MnO_4^-+2H_2O \rightarrow 5MnO_2(s)+4H^+$	1.92 mg $KMnO_4$/mg Mn

Some undesired water qualities might be obtained from dosing too high (above the stoichiometric requirements) or too low (below the stoichiometric requirements). Therefore, dosing a specific oxidant may be constrained or controlled by undesired byproducts of the oxidant or the impacts of dosing too high or too low. The dose of chlorine dioxide may be minimal due to the byproducts chlorate and chlorite that may form. The dose of potassium permanganate must be strictly controlled, since overdosing may result in pink water formation. The addition of free chlorine can form disinfection byproducts (DBPs) due to organics being present; therefore, when selecting an oxidant, many factors must be considered.

Chlorine as an Oxidant

An elevated pH above 9.0, chlorine oxidizes manganous manganese to the manganic form relatively quickly. Based on stoichiometry, the dose for chlorine to oxidize iron and manganese is shown in Equation 2-1. When the pH is lower, the time for oxidation is longer, which may prove unfavorable to a water treatment plant. As the pH increases past eight, the time requirements decrease (Gregory and Carlson 2003). Studies performed proved that, even with chlorine doses four times greater than the stoichiometric requirements, a minimum contact time of two hours was required to reduce 1 mg/L of manganese to 0.7 mg/L at a pH of seven (Knocke, W.R. et al. 1990).

$$1.30\left(Mn, \frac{mg}{L}\right) + 0.64\left(Fe, \frac{mg}{L}\right) = Chlorine\ Dose, mg/L \qquad (2\text{-}1)$$

For free chlorine, pH has a significant and important impact on the rate of manganese oxidation. In a water treatment plant, the typical pH is between six and eight, which results in the rate of oxidation rate being relatively slow for chlorine. However, if the pH is increased to a pH of 9.0 or above, the oxidation rate relatively quick. A typical situation of using chlorine as an oxidant is when a water treatment plant applies lime and chlorine after sedimentation, but prior to media filtration, resulting in a higher pH, typically between 9.5 and 10. Based on studies, within one hour, Mn^{2+} was effectively oxidized below the SMCL of 0.05 mg/L. It has also been determined that, along with pH, temperature is also a factor in Mn^{2+} oxidation (Knocke, W.R. et al. 1990).

Not only is the high pH required for oxidation of iron and manganese an obstacle in the water treatment industry, the use of pre-chlorination at a water treatment plant may form undesired

DBPs. When chlorine reacts with natural organic matter (NOM), DBPs form. Under the Safe Drinking Water Act (SDWA), DBPs are regulated and may not exceed Maximum Contaminant Levels (MCLs) of 80 μg/L for total trihalomethanes (TTHMs) and 60 μg/L for haloacetic acids (HAAs). Since utilizing pre-chlorination may increase the overall formation of regulated DBPs, an alternate and more effective oxidant may be recommended for use.

Potassium Permanganate as an Oxidant

Potassium permanganate can be used to control taste and odor, remove color, control biological growth, and remove iron and manganese in water treatment plants. Another benefit of using potassium permanganate is that it may be useful in minimizing the formation of trihalomethanes (THMs) and other DBPs by oxidizing precursors and reducing the demand for other disinfectants (Bryant, Fulton et al. 1992). Moving the point of chorine application farther downstream of the treatment process and utilizing potassium permanganate upstream to control taste and odor, color, and algae may achieve a reduction in DBPs. Although potassium permanganate has many potential uses as an oxidant, it is not an effective disinfectant (USEPA 1999).

A primary use of potassium permanganate is iron and manganese removal. When potassium permanganate is added to water containing iron and manganese, the iron will oxidize soluble ferrous iron (Fe^{2+}) to particulate ferric iron ($Fe(OH)_3$). It will also oxidize soluble manganese to particulate manganese dioxide. In conventional treatment plants, potassium permanganate is added to the raw water intake, usually at the rapid mix in conjunction with coagulants, or at clarifiers upstream of the filter. This is due to the fact that the manganese dioxide that is formed from oxidation is small enough to pass through the filters. Therefore, it is recommended to add the potassium permanganate upstream of the coagulant due to the coagulants' ability to destabilize the particles and allow for the filtration of the manganese dioxide at the filters (USEPA 1991).

The reactions for the oxidation of iron and manganese are shown in Equation 2-2. Based on the stoichiometry, the potassium permanganate dose required for oxidation is 0.94 mg/mg iron and 1.92 mg/mg of manganese (HDR 2001). When the potassium permanganate is added to control iron and manganese, the oxidation time ranges from five to 10 minutes, provided the pH is more than seven (Kawamura 2000). As previously stated, if excess potassium permanganate is added, the water will turn pink in color.

$$1.92\left(Mn, \frac{mg}{L}\right) + 0.94\left(Fe, \frac{mg}{L}\right) = Potassium\ Permanganate\ Dose, mg/L \tag{2-2}$$

Potassium permanganate can also be used for removing taste and odor compounds. Potassium permanganate may be used to treat earthy, musty smelling compounds in drinking water (Lalezary, Pirbazari et al. 1986). The dose of potassium permanganate used to treat taste and odor compounds may range from 0.25 to 20 mg/L.

Pretreatment with potassium permanganate in combination with post-treatment chlorination will typically result in lower DBP concentrations than would otherwise occur from traditional pre-chlorination for iron and manganese oxidation (Ficek and Boll 1980). Under this approach, not only are iron and manganese oxidized, but the concentration of NOM, responsible for DBP formation, may also be reduced.

3. EXISTING CONDITIONS

Description of Raw Water Sources

The union of two volcanoes formed Guam; therefore, the island has two different geological compositions. The southern features are mainly volcanic with an elongated mountain ridge dividing the coastline and the inland, which creates the Fena Valley watershed. The Fena Valley watershed of the Naval Magazine provides water to most naval facilities, as well as some civilian communities. Additionally, the northern distribution system has groundwater wells, which supplement the primary raw water sources.

This section provides an overview of the source water that feeds the NWTP. The raw water sources include Fena Lake and the springs (Bona and Almagosa). Fena Lake is located in an inactive volcano crater and has an active storage capacity of 2,100 million gallons (MG) for the zone between the pump intake and the dam spillway. Fena Lake supplies approximately 63 percent (eight million gallons per day (MGD)) to the Navy's water system (Kennedy Engineers, 1980).

The Almagosa Spring supply is from the Upper Dobo, Lower Dobo, and Chepek springs. Approximately 22 percent (2.9 MGD) is supplied from Almagosa Spring to the water system. Bona Spring emits from two springs within limestone cavities, which supplies approximately 15 percent (1.9 MGD) to the water system. Since spring water is highly dependent upon rainfall, the yield from both springs may vary from 0.5 MGD during the dry season to three MGD during the wet season. A series of low hills of limestone formation acts as natural water storage, which allows for the continual feeding to the springs at a low rate.

Description of the NWTP Process Unit Operations

The NWTP is a conventional surface water treatment plant designed to produce 13.5 MGD of potable water to consumers within the service area. Current production varies during wet and dry seasons. According to the U.S. Navy, the flow rate may vary between 10.5 MGD during the wet season and 12.5 MGD during the dry season (Ríos 2003). The NWTP treats the combination of Fena Lake water, as well as Almagosa and Bona Springs. Prior to the start of this study, the lake water, prior to being combined with the springs, underwent pre-chlorination. Once combined with the spring water, it would enter the WTP and be treated with alum, lime and polymer addition, coagulation, flocculation, sedimentation, filtration, disinfection, fluoridation, and storage prior to entry of the distribution system. Under normal circumstances, the raw water is routed to the original conventional rapid mix, flocculation, and sedimentation unit processes. When turbidity levels are high, the raw water may be routed to the ballasted flocculation system to manage these high levels of turbidity. A diagram of the overall process is shown in Figure 3-1.

At the time this research project was initiated, the raw water was pre-chlorinated once more after pre-chlorination at the lake at the influent control structure. This pre-chlorinated water then flows into the rapid mix chamber where the alum, lime, and polymer are added. The water from the baffled chamber then flows into a rapid mixer flocculation cell in the center of a 125-foot diameter sedimentation tank where coagulation and flocculation occur.

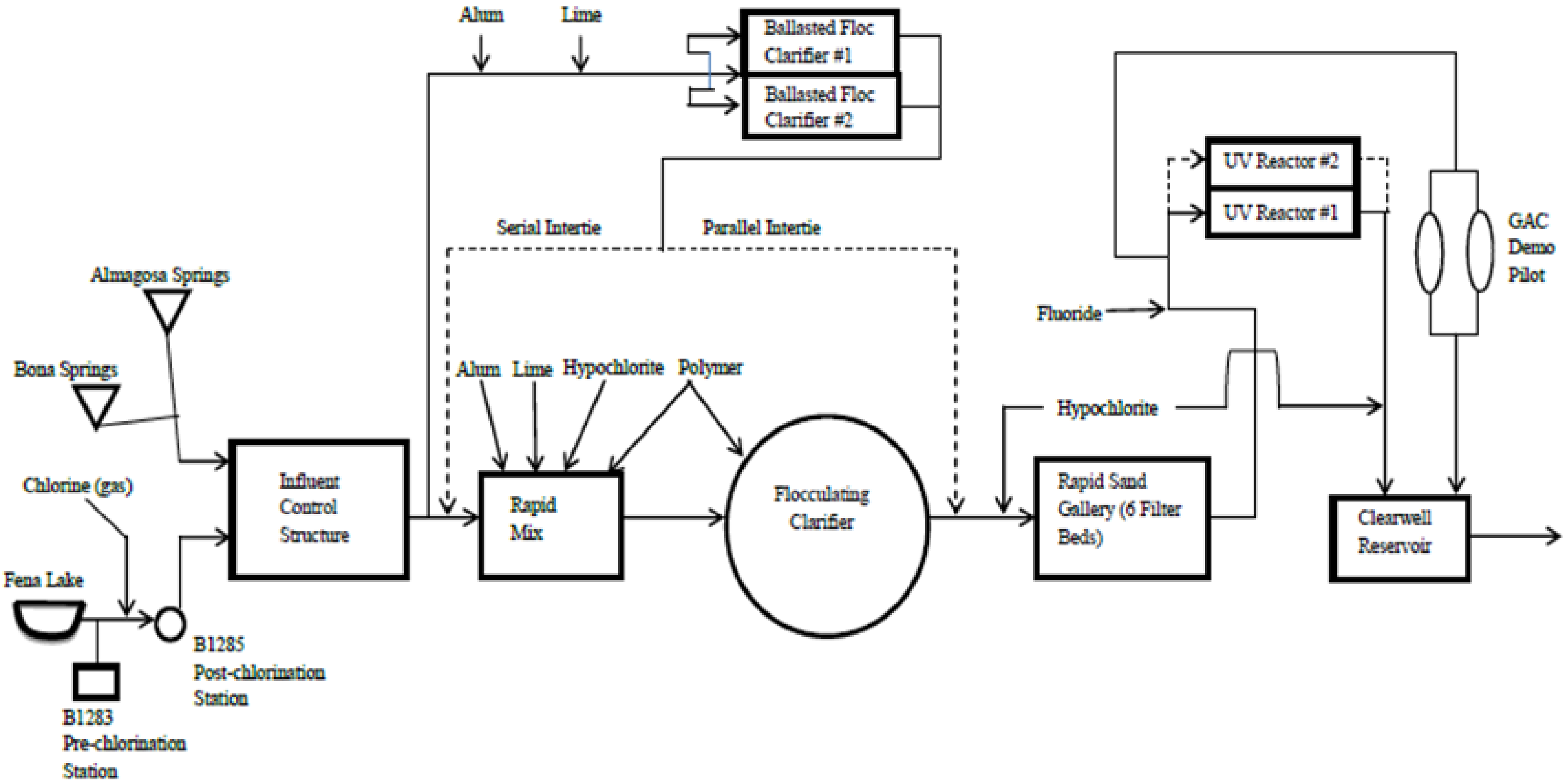


Figure 3-1: NWTP Process Flow Diagram

The coagulated/flocculated water flows under the flocculation cell skirt into the sedimentation tank. A weir around the tank periphery allows the settled water to pass onto the filters while the agglomerated solids settle to form a sludge blanket. The settled sludge, consisting of organic and inorganic solids, is raked by a rotating arm into a center hopper and then pumped to a backwash-settling tank for residual solids handling.

The settled water from the sedimentation tank is chlorinated again to prevent the algal growth on the filters. The chlorinated water then flows to six dual-media (sand and anthracite) filters to remove suspended particles. When a sand filter becomes loaded with solids, an automatic backwash system is initiated where water is used to expand and clean the bed. The solid-laden backwash water from the backwashing process is conveyed to a backwash-settling tank, where the heavy solids are separated by dewatering on sand drying beds. The clear supernatant is re-circulated to the influent control structure for blending and reprocessing with the raw water.

4. MATERIALS AND METHODS

This chapter presents the experimental plan, methods, materials, and procedures used to conduct this study. Table 4-1 provides a list of test methods and equipment used during this research. Analyses were conducted both in the field and in the laboratory, and included the parameters of pH, temperature, conductivity, turbidity, iron and manganese.

Table 4-1: List of Methods and Equipment Used

Test	Test Location	Standard Method (SM)	Equipment Description	Method Detection Level
pH	Lab/Field	SM: 4500-H+ B Electrometric Method	HQ40d Portable pH, Conductivity, and Temperature Meter	0.01 pH Units
Temperature	Lab/Field	SM: 2550 B Laboratory Method	HQ40d Portable pH, Conductivity, and Temperature Meter	0.01 °C
Conductivity	Lab/Field	SM:2510 B Laboratory	HQ40d Portable pH, Conductivity, and Temperature Meter	0.01 µS/cm
Turbidity	Lab/Field	SM: 2130 B Nephelometric Method	Hach 2100q Portable Turbidimeter	0.01 NTU
Iron	Lab	SM: 3120 B Inductively Coupled Plasma (ICP) Method/Inductively Coupled Plasma Spectrometer	Perkin Elmer Optima 2100 DV ICP-OES	0.001 mg/L
Manganese	Lab	SM: 3120 B Inductively Coupled Plasma (ICP) Method/Inductively Coupled Plasma Spectrometer	Perkin Elmer Optima 2100 DV ICP-OES	0.001 mg/L

Experimental Plan

The primary goal of this research was to determine if an alternate oxidant, potassium permanganate, could be utilized in lieu of the use of chlorine for the removal of iron and manganese at the Navy Reservoir, Fena Lake. Jar testing equipment was utilized in the experiments to evaluate oxidant effectiveness and to simulate the water treatment processes employed at the NWTP. An initial total and dissolved concentration for iron and manganese was measured using a Perkin Elmer Optima 2100 DV ICP-OES. A potassium permanganate stock solution was used to generate, and various doses that were added to the jars. The samples were then coagulated with aluminum sulfate and filtered. Water samples were collected from the jars and then analyzed for iron and manganese concentrations via Inductively Coupled Plasma (ICP).

The jar testing equipment was designed to simulate the coagulation, flocculation, and sedimentation processes that take place currently at the NWTP. The water was first dosed with potassium permanganate followed by the conventional water treatment process. Water was collected from the Navy Reservoir in plastic one-liter amber bottles. The depths varied for each jar test performed. The most common depths drawn were 40-ft and 50-ft. These depths were chosen because they had higher iron and manganese concentrations. When these depths did not have an adequate amount of iron and manganese suitable for jar testing (due to seasonal changes), iron and manganese was added to the shipped samples prior to dosing with potassium permanganate.

Also, the content of water samples collected at various locations within the NWTP were determined. Samples that were collected at the various sampling points were shipped to UCF for iron and manganese analysis. This better determined if the pre-chlorination at the Navy Reservoir was serving its purpose of oxidizing iron and manganese present in the source water.

Testing Locations

Samples were shipped monthly by the Navy to UCF for water quality analysis. In this manner, seasonal data could be collected and evaluated with regards to the Navy's Fena Lake Reservoir, Bona Spring, and Almagosa Spring. Samples were collected from various lake depths, as well as the following locations:

- Building 1283 (B1283) (before raw water chlorination)
- Building 1285 (B1285) (after raw water chlorination)
- Navy Water Treatment Plant (NWTP) (Fena Pipe Influent to the NWTP)
- Combined springs (Almagosa and Bona)
- Combined raw (Fena Lake, Almagosa and Bona Springs)
- Filtered water (post-filter)
- Clearwell

Procedures

Iron and Manganese Analysis

Sample collection and water quality analyses were performed in accordance with *Standard Methods for the Examination of Water and Wastewater* (Eaton 2005). The method followed for iron and manganese analysis was Standard Method_3120B, ICP Method for iron and manganese in aqueous solution. The samples were collected in 125-mL high-density polyethylene (HDPE) bottles for both total and dissolved analysis. The samples collected for total metals analyses were preserved with nitric acid (HNO_3) to a pH of less than two. Typically, this required 0.2-mL to 0.4-mL of concentrated nitric acid being added to the sample. The dissolved samples were first filtered through a membrane filter and then acidified.

The samples were packed into a cooler with ice packs to maintain a cool temperature and then shipped to UCF. Upon arrival at the UCF Laboratory, the samples were stored in a refrigerator at 4°C until they were prepared for metals analysis. From each sample, 10-mL were taken and placed into a 15-mL vial. The inductively coupled plasma (ICP) machine measured the interference of each sample by using an argon flame. From this value and the standard curve created, the concentration was calculated.

Potassium Permanganate Stock Solution

Since the potassium permanganate used was in a crystal form, a solution had to be prepared for dosing. The potassium permanganate stock solution was prepared by first making a stock solution that may then be diluted to provide a more accurate dose for the case of when iron and manganese concentrations were less than 1 mg/L. The stock solution was prepared by weighing out one gram of potassium permanganate crystals on a weighing dish. Next, the solid potassium permanganate was transferred to a 100-mL volumetric flask. The weighing dish was rinsed with distilled water into the volumetric flask and the potassium permanganate in the volumetric flask was diluted with distilled water to 100-mL. The volumetric flask was then covered with parafilm and mixed thoroughly. Since the stock solution of potassium permanganate is dark purple, it can be difficult to see whether or not the crystals are completely dissolved. Therefore, the volumetric flask was shaken vigorously prior to use.

Once the stock solution was prepared, the test stock solution was prepared. To prepare the test stock solution, one-mL was measured from the stock solution using an Eppendorf Pipette from the stock solution that was prepared and placed into a 100-mL volumetric flask. A one-mL aliquot was then diluted to 100-mL with distilled water. The volumetric flask was then covered with parafilm and shaken vigorously. The final solution is shown in Figure 4-1. From this solution, 10-mL was equal to one mg/L potassium permanganate.

Figure 4-1: Potassium Permanganate Test Stock Solution

Potassium Permanganate Jar Testing

It was previously noted that the U.S. Navy historically applied chlorine gas to Fena Lake raw water for iron and manganese control. Chlorine reacts slowly with manganese unless the pH is greater than nine. The pH is seven when treated with chlorine. Based on the study stated prior by Knocke et al, unless the pH is greater than nine the oxidation rate of iron and manganese is relatively slow and may take hours. Given the slow manganese oxidation reaction kinetics that may take hours at pH seven and the other competing chlorine demands, the actual required dose of chlorine to promote significant Mn^{2+} oxidation may be many times higher than the theoretical stoichiometry depending on pH. In turn may result in elevated disinfection byproduct concentrations within the distribution system (Knocke et al. 1990).

It was reported by plant operators that they believed that the decision was made to add chlorine at Fena Lake due to elevated iron and manganese concentrations. A review of data collected indicated that the iron and manganese quality varied in lake depth; however, samples taken from the depth that the water was drawn and pumped to the Fena WTP (typically around 12-ft depth) was relatively low (typically dissolved iron and manganese concentrations were found to be below the SMCLs at the shallow depths) and did not require pretreatment. The elevated iron and manganese levels that were experienced in the distribution system may have been due to pipe deposits breaking off within the distribution system and NWTP. It was also determined that iron that may have been present was removed by aluminum sulfate during the coagulation process. Preliminary findings of a parallel study revealed that the majority of the distribution system DBP concentrations were formed by pre-chlorination of Fena Lake Reservoir raw water prior to conventional treatment at the Fena WTP. Disinfection byproduct formation potential studies performed by UCF and DZSP21 confirmed that TTHMs were above the regulated MCL of 80 μg/L after a 24-hour holding time (US Navy Laboratory DZSP21, May 2013). Therefore, it was recommended that chlorine addition at the Navy Reservoir pump station be discontinued. Those DBP study component efforts will be reported under separate cover.

During times where the Navy WTP may experience iron and manganese concentrations greater than the SMCLs, was utilized as an oxidant at the Navy Reservoir pump station. In this study an alternate oxidant, potassium permanganate, was utilized as a replacement to the use of chlorine. Potassium permanganate has been used for decades as a chemical for oxidation of dissolved iron and manganese and taste and odor control in water treatment operations (HDR 2001). The oxidation kinetics of potassium permanganate with iron and manganese is fairly fast (within 5 to 10 minutes) at a pH of six or greater in comparison to chlorine, which takes hours when the pH is below nine (Brandhuber 2013).

Water was collected in bulk from Fena Lake using a crane and a container that locked in the water at the desired depth. The bulk water was then transferred to a plastic amber bottle and then prepared for shipping. Figure 4-2 shows the crane and the container used for collection. Water that was shipped was placed in a cooler with ice packs to maintain a cooler temperature. Upon arrival to UCF, the bottles were transferred to a refrigerator kept at 4°C.

The Phipps & Bird jar tester used for treatment simulations consisted of six two-liter square jars. The paddles may be altered to perform at various revolutions per minute (rpm). The volume of water in each jar was fixed at one-liter each. The bulk water that was acquired from the Navy Reservoir, after being mixed thoroughly, was allowed to warm to room temperature, measured in a graduated cylinder at 1000-mL, and then transferred to the jar. The initial conductivity, pH, temperature, and turbidity were recorded from each of the jars.

Figure 4-2: Sample Collection at the Navy Reservoir Pump Station

Next, the jars were dosed at various amounts. When potassium permanganate is added to the water, the sample will turn varying shades of brown, indicating the presence of oxidized iron and manganese. The samples that retained a brown or yellow color indicated that the oxidation process is incomplete and required the addition of additional potassium permanganate. When the water had reached its endpoint, the water exhibited a pink color. This pink color remained for at least 10 minutes. Over time, the pink color dissipates.

As shown in Figure 4-3, potassium permanganate was not added to the first jar (far left). The remaining five jars contained various doses of potassium permanganate with the recommended dose being jar four (third from right). The recommended dose was determined based on Equation 2-2. The last two jars were dosed higher than the recommended dose. These two jars resulted in pink water, which was undesirable. The jars were mixed, covered, and stirred at 120 rpm for two hours to simulate pipe flow. According to the plant operators, the water takes two hours to reach the NWTP Fena Pipe Influent from Building 1285.

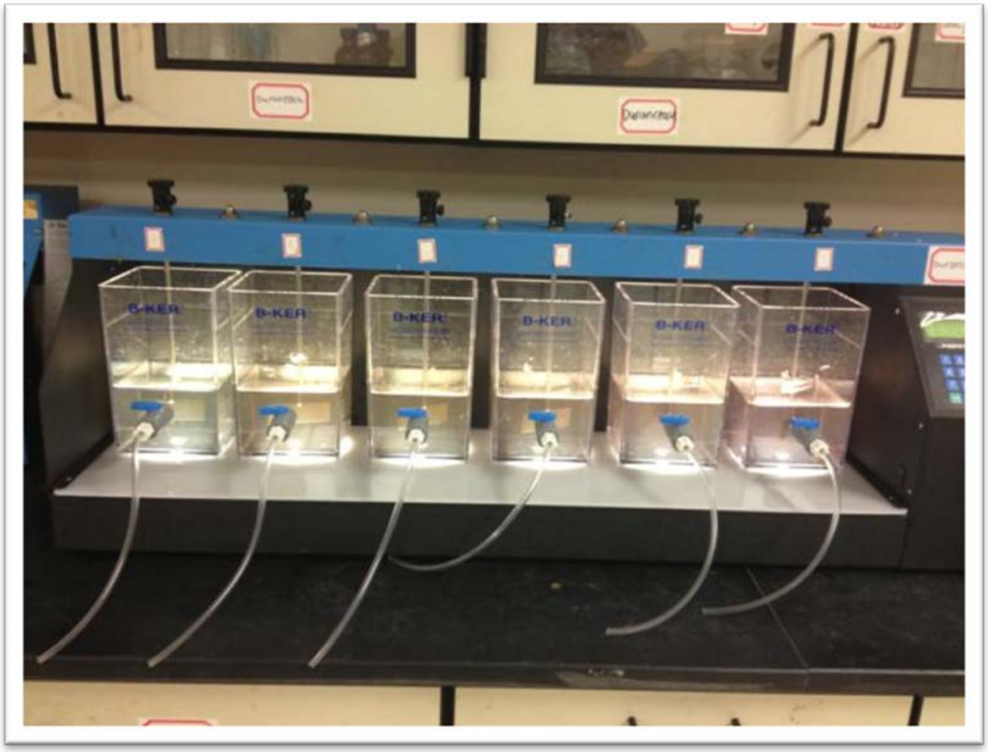


Figure 4-3: Potassium Permanganate Jar Test

As stated previously, when a strong oxidant is added, the particulate byproduct manganese oxide ($MnO_{x(s)}$) is formed. The manganese oxide that is formed is small enough to pass through 0.45-micron filters. Studies have shown that, when possible, the potassium permanganate should be added upstream prior to the coagulation and flocculation process (Branhuber, Clark et al. 2013). Manganese oxide is colloidal in nature and has a particle size below one-micron. Adding the coagulant after the oxidant is added destabilizes the particles and the particles appropriately aggregate for subsequent solid-liquid separation (Branhuber, Clark et al. 2013). Therefore, once the jars were mixed for two hours, aluminum sulfate was then added to each of the jars. The aluminum sulfate they use at the NWTP was shipped to the UCF Laboratory from the laboratory group in Guam, DZSP 21.

During the coagulation-flocculation phase, paddle speeds were chosen based on typical jar tests performed with a coagulant. The different coagulation-flocculation phases consisted of a rapid mix at a speed of 150 rpm for three minutes and a slow agitation phase at the speed of 25 rpm for 15 minutes (Zogo, Bawa et al. 2011). The water was then allowed to settle for one hour for sedimentation. The addition of the aluminum sulfate took place during the rapid mix. The dose was determined to be 35-40 mg/L based on daily plant operations data acquired from the NWTP. This was based on a day of operation when the water was the most turbid when entering the coagulation-flocculation chamber. Once settled, the final conductivity, pH, temperature, and turbidity were taken from each of the jars. Samples were also taken for metals analysis.

Once the jars were coagulated and settled, samples were then collected for analysis in 250-mL Erlenmeyer flasks. A vacuum filter apparatus was used to filter the collected samples through a

0.1-micron filter. In between each filtered sample, the vacuum apparatus was cleaned and a new filter was used for each new sample. The samples were then acidified with nitric acid to a pH less than two pH units. Once acidified, the samples were left in a refrigerator for 24 hours or longer at 4°C.

Laboratory Filter Method

Based on *Standard Methods for the Examination of Water and Wastewater* (Eaton 2005), 3120B, Inductively Coupled Plasma (ICP) Method, it is recommended to filter through 0.45-micron filters for dissolved manganese analysis. It has been shown in some literature that chemically oxidized manganese has the potential to pass through 0.45-micron filters (Branhuber, Clark et al. 2013). A study was performed to determine if naturally oxidized manganese has the potential to pass through the 0.45-micron filter. A comparison was performed between a 0.45-micron filter, 0.1-micron filter, and coagulant addition followed by a 0.45-micron filter. A sample was taken from each jar prior to coagulation. Part of this sample was filtered through a 0.45-micron filter and acidified while the rest of the sample was filtered through a 0.1-micron filter and acidified. These samples were then analyzed for iron and manganese. The remaining water in each jar was dosed with 35 mg/L of aluminum sulfate to simulate the coagulation, flocculation, and sedimentation process. Once settled for one hour, a sample was taken from each jar, filtered through a 0.45-micron filter, and acidified for iron and manganese analysis.

Cleaning Procedures

Laboratory quality control measures were taken to monitor and assess the data collected during this research. One aspect of quality control is glassware cleaning, hence, used glassware or plastic bottles were cleaned per a standard procedure. Glassware and plastic bottles were scrubbed with soap and then rinsed with tap water until soapy residues were gone. Once cleaned with soap, the bottles were rinsed with 1:1 hydrochloric acid and rinsed three times with distilled water. The bottles were then allowed to air dry. This was accomplished for the plastic one-liter amber bottles used for bulk water sampling and the 125-mL plastic bottles used for metals analysis that were shipped from Guam to UCF. Once cleaned, the bottles were shipped back to Guam for further sampling. When sampling was performed, the clean bottles were rinsed with the sample prior to filling with the sample.

Field and Laboratory Quality Control

Field and laboratory quality control measures were applied throughout the research that was conducted. Duplicate samples were collected in the field once every 10 samples, which was at the clearwell. During metals analysis, a duplicate and a spike were created for every 10 samples evaluated. A similar procedure was also implemented when collecting samples from the jars during potassium permanganate testing. Additionally, quality control requirements for data analysis were followed according to the analytical methods listed in the Laboratory Quality Assurance Procedures for the UCF Environmental Systems Engineering Institute (ESEI) housed within the Civil, Environmental, and Construction Department (Real-Robert, 2011). Quality control measures for laboratory data collection were performed according to the *Standard Methods for the Examination of Water and Wastewater* (Eaton 2005).

Accuracy

Percent recovery for each spiked sample processed through the ICP Spectrophotometer was determined using Equation 4-1. The percent recovery of each spike was plotted on an accuracy chart to assess the consistency and performance of the ICP Spectrophotometer.

$$\%\ Recovery = \frac{C_{sample+spike} - C_{sample}}{C_{spike}} * 100 \tag{4-1}$$

Where,

$C_{sample+spike} = the\ concentration\ of\ the\ spiked\ sample\ \left(\frac{mg}{L}\right)$

$C_{sample} = the\ concentration\ of\ the\ sample\ \left(\frac{mg}{L}\right)$

$C_{spike} = the\ concentration\ of\ the\ spike\ \left(\frac{mg}{L}\right)$

The upper and lower control limits (UCL and LCL) are 120 percent and 80 percent, respectively. Whenever a percent recovery was outside of these limits, the sample set was rejected, re-prepared and analyzed again.

The relative percent difference (RPD) was calculated using Equation 4-2. The RPD was used in replicate and duplicate analysis and was considered acceptable if the RPD was within the range of 90 percent to 110 percent. If outliers were present, the sample results were rejected and the samples were prepared and analyzed again.

$$RPD\ (\%) = \frac{S-D}{(S+D)/2} * 100 \tag{4-2}$$

Where,

$S = sample\ result\ \left(\frac{mg}{L}\right)$

$D = Dupicate\ sample\ result\ \left(\frac{mg}{L}\right)$

Precision

The industrial statistic, or I-statistic, was calculated using Equation 4-3 in order to create control charts relative to evaluate the precision of metals analysis. Control charts are a graphical, statistical method to monitor process variation due to either assignable causes or random variation. The industrial statistic was calculated using Equation 4-3 in order to create control charts for the precision of metals analysis. Control charts are a graphical, statistical method to screen process variation due to assignable causes or random variation (Devore 2000).

$$I = \frac{|S-D|}{(S+D)} \tag{4-3}$$

Where,

$S = sample\ result\ \left(\frac{mg}{L}\right)$

$D = Dupicate\ sample\ result\ \left(\frac{mg}{L}\right)$

The upper control limit (UCL) was defined as shown in Equation 4-4. The upper warning limit (UWL) for the precision chart was determined based on Equation 4-5.

$$UCL = 3.267 * Range_{avg} \tag{4-4}$$

$$UWL = 2.512 * Range_{avg} \tag{4-5}$$

5. RESULTS AND DISCUSSION

Fena Lake Iron and Manganese Profile

As one component of this research, a lake water quality profile was conducted for Fena Lake. Water was collected at various depths, which included 10-ft, 20-ft, 30-ft, and 40-ft. These samples were prepared for metals analysis, shipped to UCF, and analyzed using an ICP method. Results obtained determined that the lake was stratified and the iron and manganese concentrations increased with depth. There was one event in September 2013 where a storm occurred and iron and manganese were found to be below detection limits after this storm. After months passed the lake then stratified and became anaerobic once more at the lower depths and the Fe and Mn levels increased. As shown in Figure 5-1, the total manganese concentration exceeds SMCLs at a depth of 40-ft. Since the NWTP draws its water at a depth of 10-ft to 12-ft, manganese concentrations greater than the SMCL for manganese was not encountered.

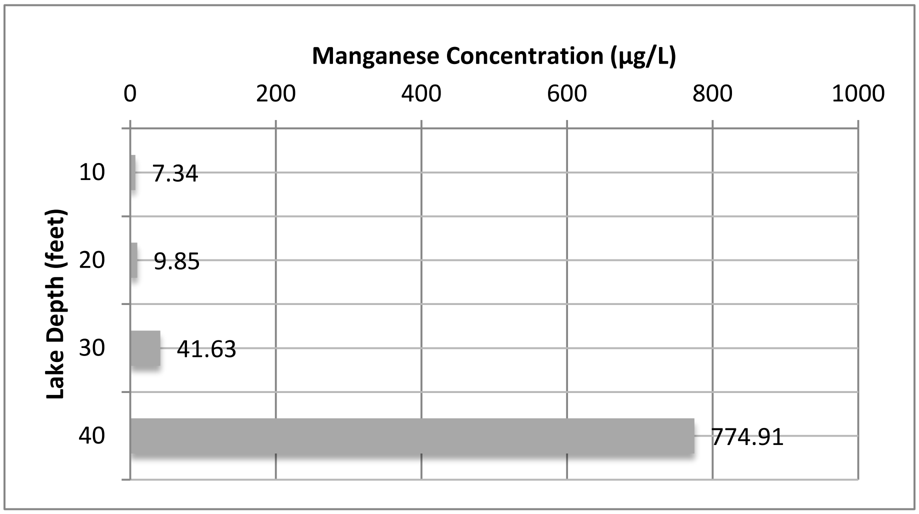


Figure 5-1: Total Manganese Concentration at Various Depths

Figure 5-2 presents the total iron concentration at various lake depths. It can be observed that once a depth of 40-ft is encountered, the SMCL for iron is exceeded. As stated prior, since the NWTP draws its raw water from a higher depth, this high concentration of iron observed at 40-ft is not of concern.

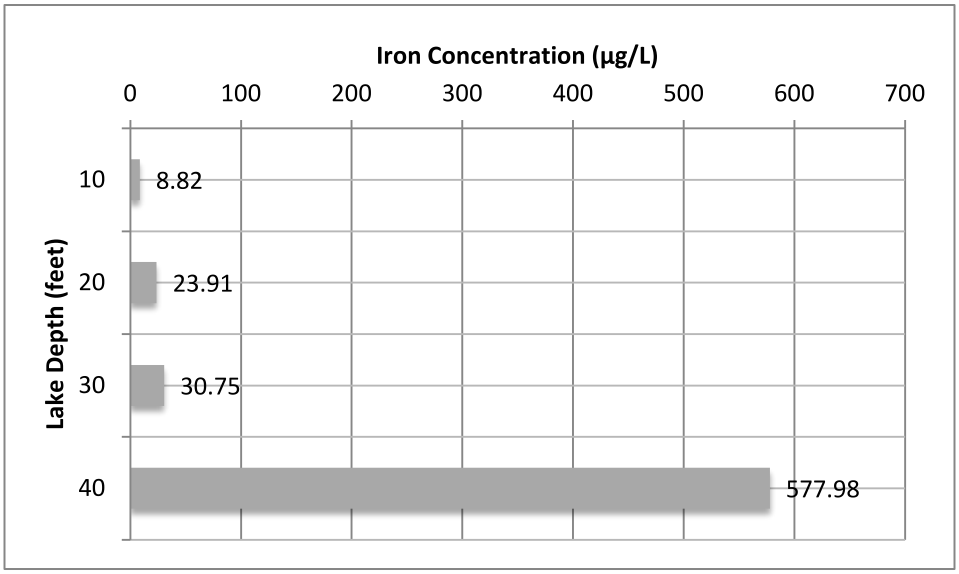


Figure 5-2: Total Iron Concentration at Various Depths

Almagosa and Bona Springs Iron and Manganese Content

During a site visit to the NWTP in Santa Rita, Guam, water was collected from Almagosa Spring and Bona Spring within the Naval Magazine. Water was for iron and manganese analysis to determine if the springs were contributing to iron and manganese concentrations. These samples were prepared for metals analysis and analyzed using an ICP method. Based on monthly samples provided by the NWTP of the combined springs and the data collected from the site visit, it was determined that the springs do not contribute to iron and manganese concentrations and in fact help to decrease the concentrations once combined with Fena Lake water. Table 5-1 shows the iron and manganese concentrations determined during the site visit in May 2013.

Table 5-1: Almagosa and Bona Springs Iron and Manganese Data

Location	Total Manganese (µg/L)	Dissolved Manganese (µg/L)	Total Iron (µg/L)	Dissolved Iron (µg/L)
Bona Springs	0.92	0.42	1.10	ND
Almagosa Springs	0.85	0.45	1.42	ND

For this particular sampling event, dissolved iron was below detection limits and therefore the iron present was oxidized. This oxidized iron would later be removed via conventional treatment processes in the plant. As for manganese there was some total and dissolved manganese present but much less than is experienced at Fena Lake, therefore this low concentration manganese water may aid in diluting manganese concentrations when combined with Fena Lake water upon entering the NWTP.

<u>Effectiveness of Fena Lake Chlorine Pretreatment for Fe and Mn Control Prior to NWTP Processes</u>

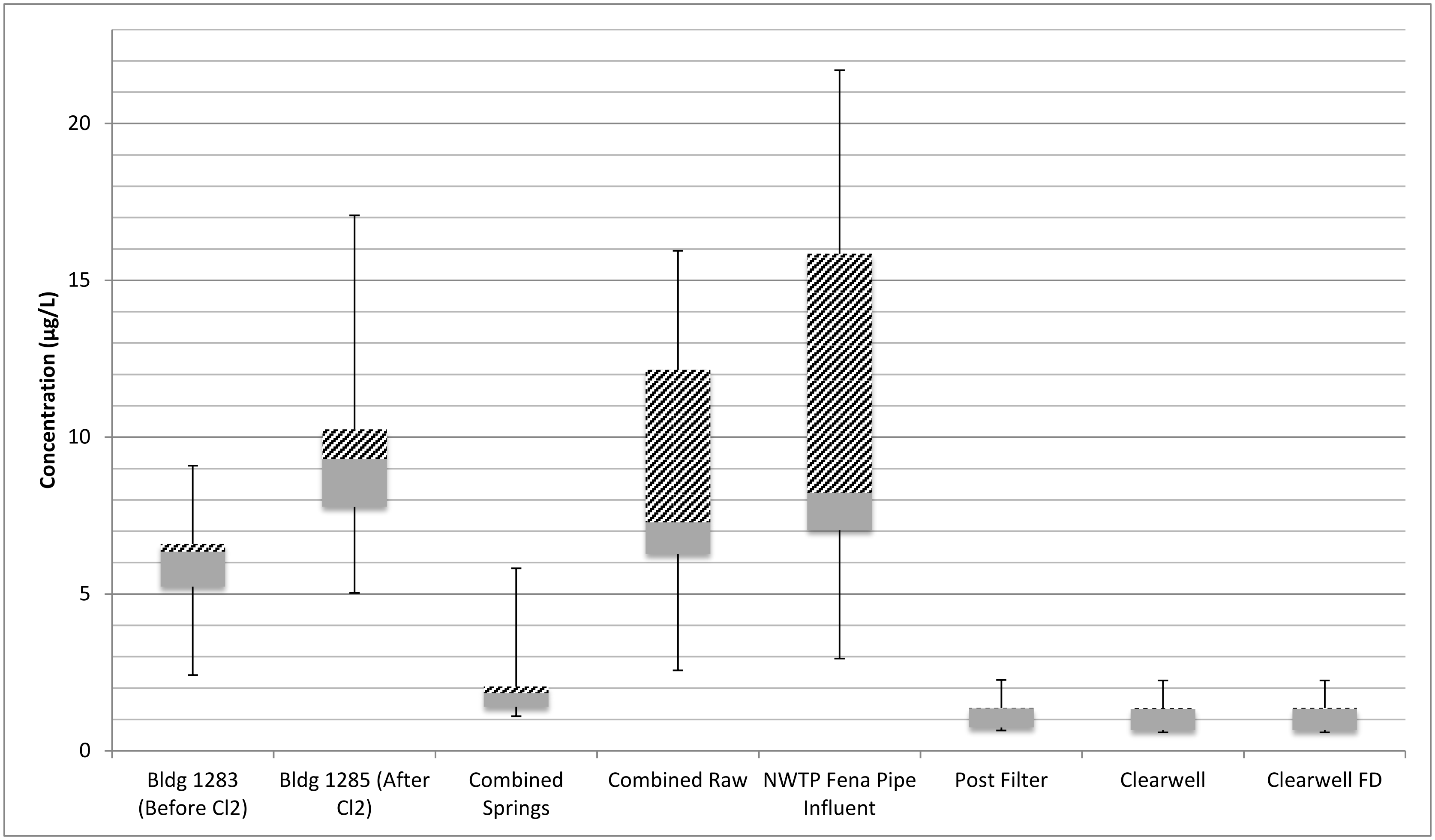
Water samples collected throughout the plant were shipped from Guam to the UCF laboratory. The samples provided were prepared for both total and dissolved iron and manganese concentration determinations. The samples were shipped in a cooler with ice packs to maintain a cooler temperature. Once the samples arrived to UCF, they were taken from the cooler and placed in a refrigerator that was maintained at 4°C.

Inductively coupled plasma was used to determine the iron and manganese concentrations following *Standard Methods for the Examination of Water and Wastewater* 3120B, Inductively Coupled Plasma (ICP) Method. This procedure states that analysis for dissolved metals must be filtered through a 0.45-micron filter. However, it has been noted through literature that MnO_x is well below one micron and, therefore, the smallest available filter was used: 0.1-micron. These samples were analyzed both prior to and after the cessation of full-scale plant pre-chlorination. Overall, the iron and manganese concentrations remained relatively low before and after the use of pre-chlorination.

Box and whisker plots were developed to better quantify and visualize the collected data. The bottom half (solid) of the box represents the fiftieth percentile where the top half (hatched) is the seventy-fifth percentile. Error bars were also constructed for maximum and minimum values based on data values and quartile values. The data analyzed is shown in Appendix A of this report. This was performed for total and dissolved iron and manganese concentrations during full-scale plant pre-chlorination. It appears that iron is removed at the point where the aluminum sulfate is added at the rapid mix. It can also be noted that there is an increase in both iron and manganese when the water reaches Building 1285 of the treatment process. At this location where chlorine gas has been added that results in a decrease in pH and an increase in both metals. This may be due to the aged pipelines containing accumulated iron and manganese within the system. The total manganese concentration leaving the plant was approximately 1.2 μg/L when lake pre-chlorination was practiced. During chlorine shutoff, discussed in the next section, the total manganese concentration was 3.1 μg/L. Note in either case the concentrations are well below the secondary maximum contaminant level of 50 μg/L for manganese.

Figure 5-3 and Figure 5-4 show the box and whisker plot for total and dissolved manganese, respectively. These samples were collected throughout 5/30/2013 to 8/15/2013. Based on the figures shown, it was determined that at Fena Lake, before chlorination, the total manganese present was approximately 21 percent dissolved (not oxidized). When the water is leaving the plant, the oxidized manganese is then removed throughout the WTP processes and the total manganese present is nearly 100 percent dissolved. As shown, when chlorine gas was added at Fena Lake there was an increase in total and dissolved concentrations. This may be due to the acidity of chlorine gas, which can lower the pH resulting in manganese pipe deposits being dissolved during the source waters transportation to the NWTP. Due to the spring water being relatively low in iron and manganese concentrations, once combined with Fena Lake water the total and dissolved manganese concentrations lowered.

The same time period that applied to manganese also applied to iron. As shown in as shown for total and dissolved manganese presented in Figure 5-5 and Figure 5-6, respectively, the iron concentration decreased when Fena Lake water was combined with the springs. As observed in Figure 5-4 for dissolved iron, when the chlorine was added to the raw water there was an increase in the dissolved iron concentration. This could be due to the acidity of the chlorine dissolving iron pipe deposits in turn increasing the dissolved iron concentration after the addition of chlorine gas or seasonal changes. As shown in the figures at Fena Lake, 7 percent of the total iron is dissolved. Once the water enters the post filter operation process, the total and dissolved iron present is removed from the addition of the aluminum sulfate added during the coagulation, flocculation, and sedimentation process.



FD: Field Duplicate

Figure 5-3: Total Manganese Throughout the Water Treatment Process (Pre-chlorination) [5/30/2013 to 8/15/2013]

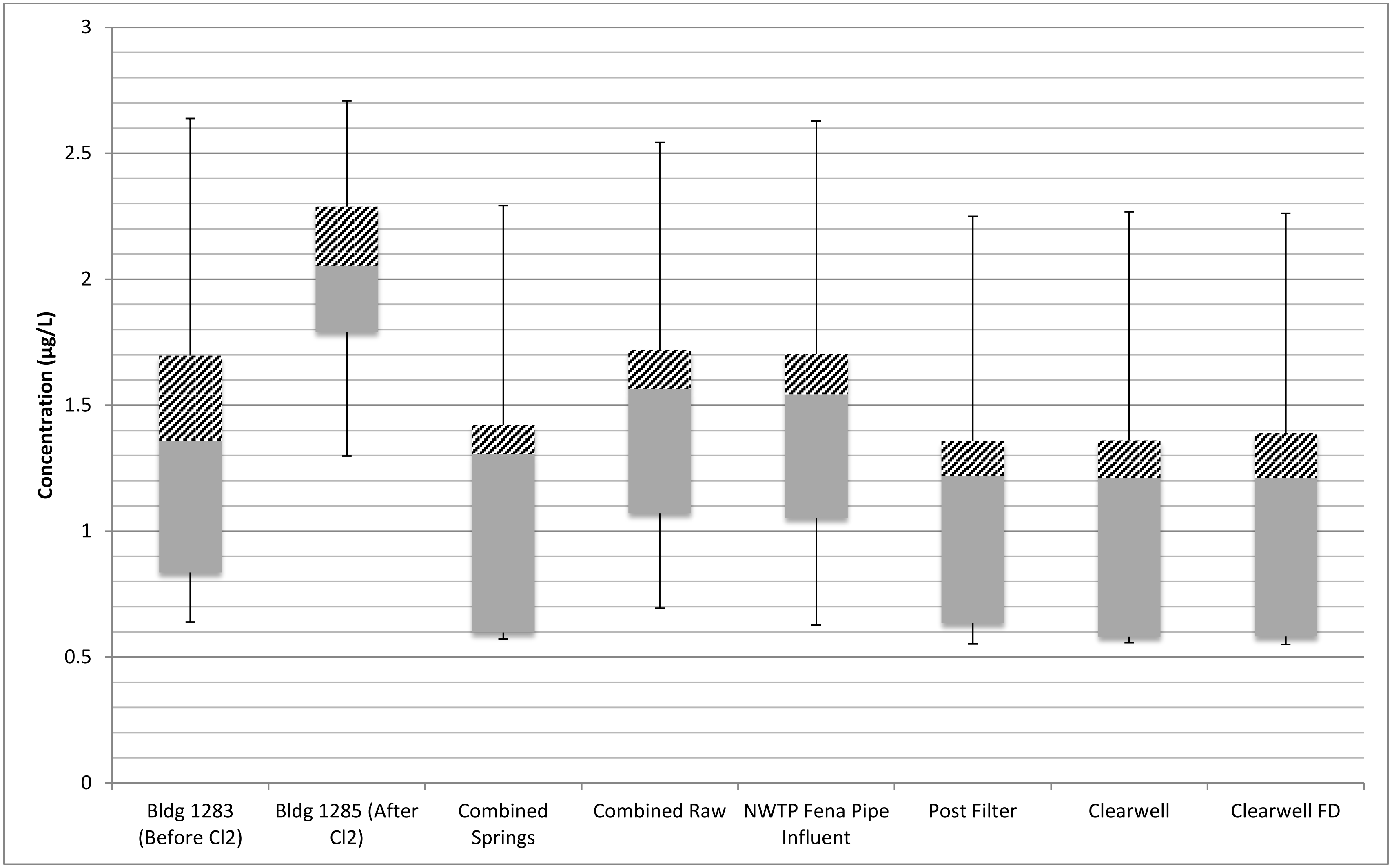
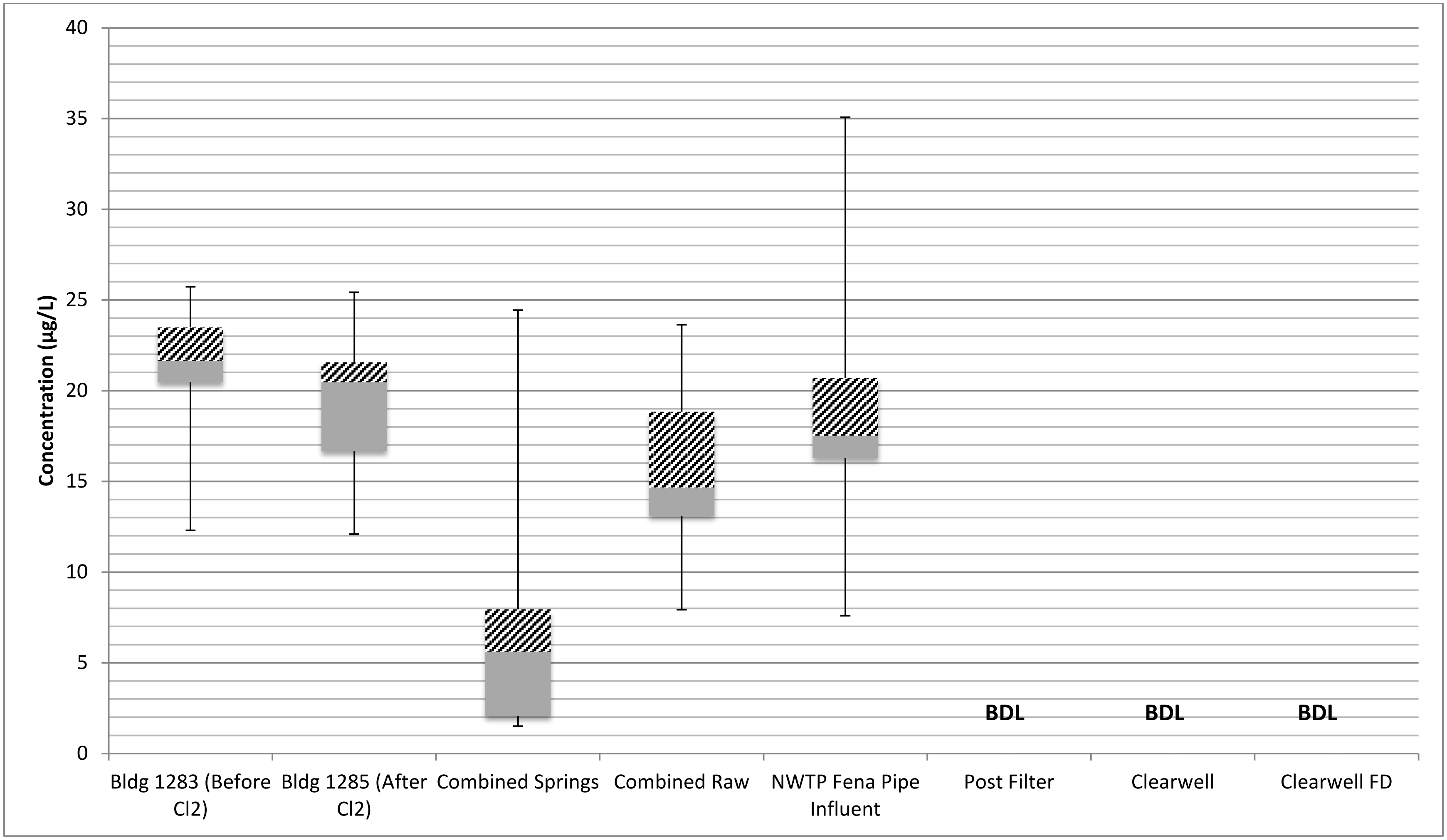


Figure 5-4: Dissolved Manganese Throughout the Water Treatment Process (Pre-chlorination) [5/30/2013 to 8/15/2013]



BDL: Below Detection Limit

Figure 5-5: Total Iron Throughout the Water Treatment Process (Pre-chlorination) [5/30/2013 to 8/15/2013]

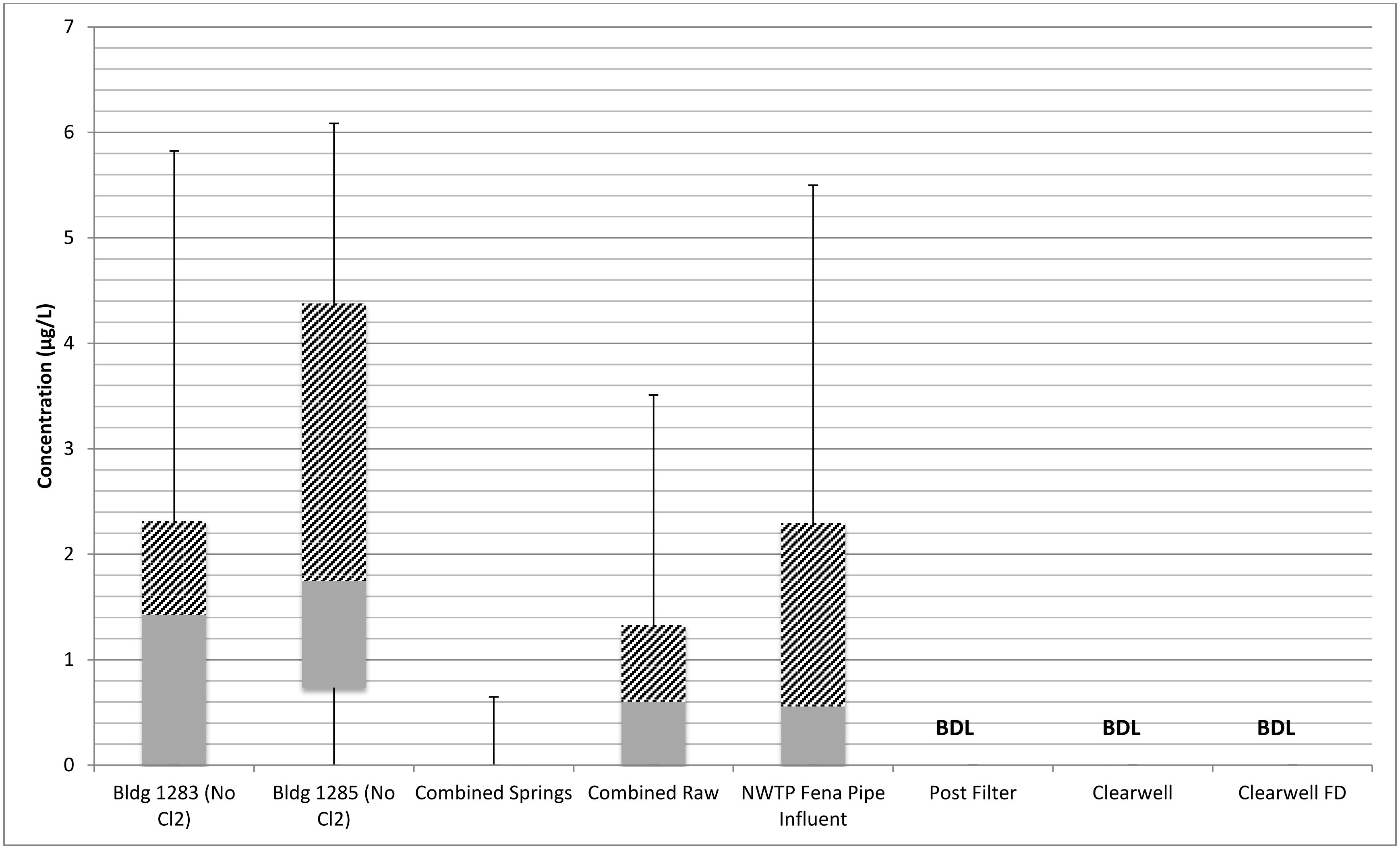


Figure 5-6: Dissolved Iron Throughout the Water Treatment Process (Pre-chlorination) [5/30/2013 to 8/15/2013]

Cessation of Fena Lake Chlorine Pretreatment and Subsequent Effects on Water Quality

Since the NWTP was exceeding the MCLs for TTHMs, it was believed that the chlorine at Fena Lake might have been the reason for this increase. Since iron and manganese concentrations being below SMCLs, an idea was proposed to shutoff the chlorine at Fena Lake. In late August, the decision was made to shut off pre-chlorination at Fena Lake. This was performed to decrease the production of disinfection byproducts.

Also, in late September of 2013, a storm occurred at the NWTP. From this, Fena Lake became more turbid, yet iron and manganese concentration were below detection limits. It is believed that soil near Fena Lake entered the lake during the storm causing adsorption to take place, explaining the turbidity in the lake and the decrease in iron and manganese. This conclusion has yet to be verified and will requires an additional study not presented herein.

Figure 5-7 and Figure 5-8 show box and whisker plots during chlorine cessation at Fena Lake for total and dissolved manganese, respectively. There was a slight increase in dissolved and total manganese at the point where pre-chlorination had previously been practiced. This could be due to the age of the pipeline and manganese deposits being present in the pipe at that location. Once mixed with the springs there was a decrease in manganese. Figure 5-9 presents a box and whisker plot for total iron. Again there was an increase at the same location as there was for manganese. The same conclusion may be speculated as was for manganese and pipe deposits. Dissolved iron was not present during chlorine cessation; therefore a box and whisker plot was not developed.

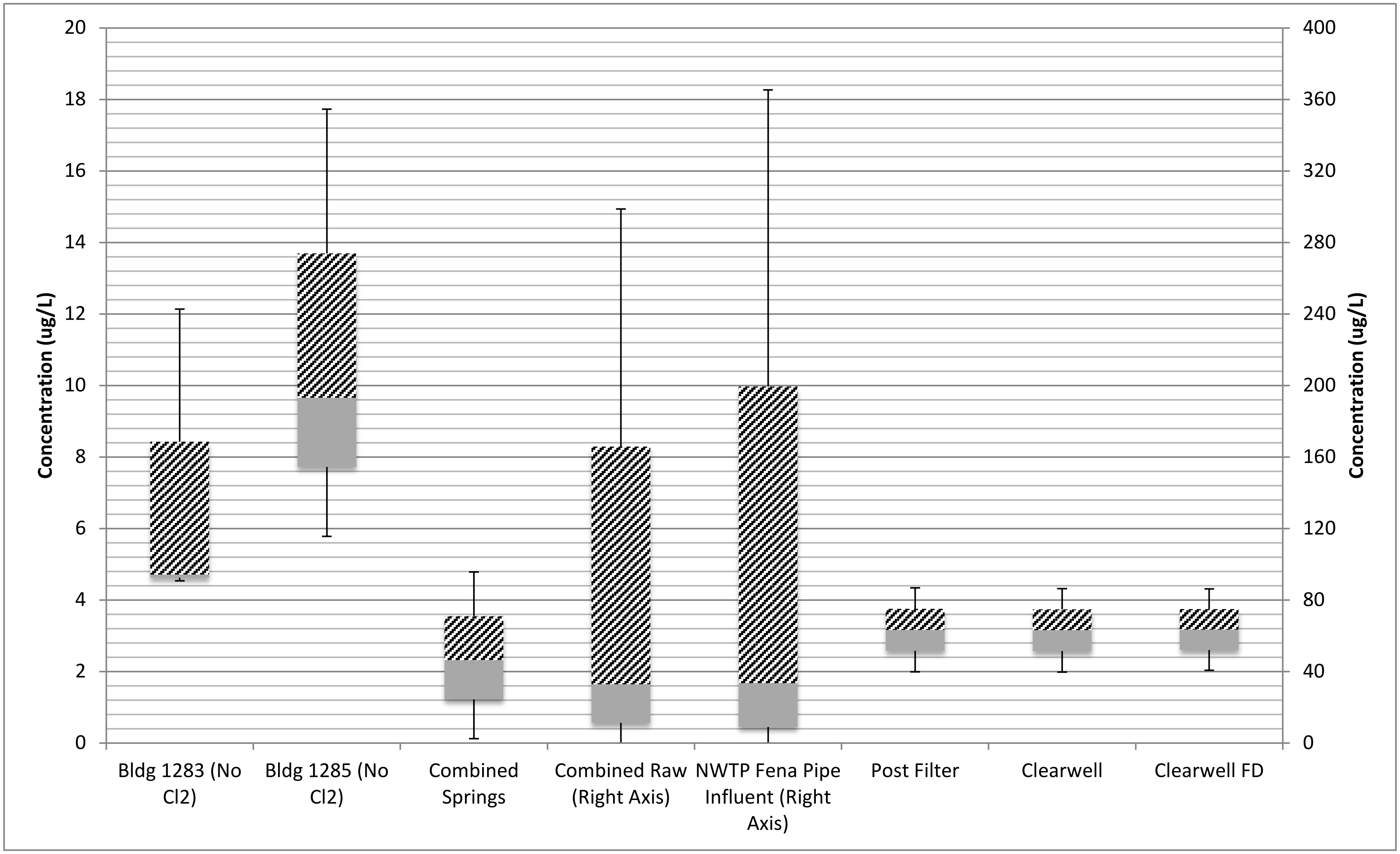


Figure 5-7: Total Manganese Throughout the Water Treatment Process (No Pre-chlorination) [8/29/2013 to 10/29/2013]

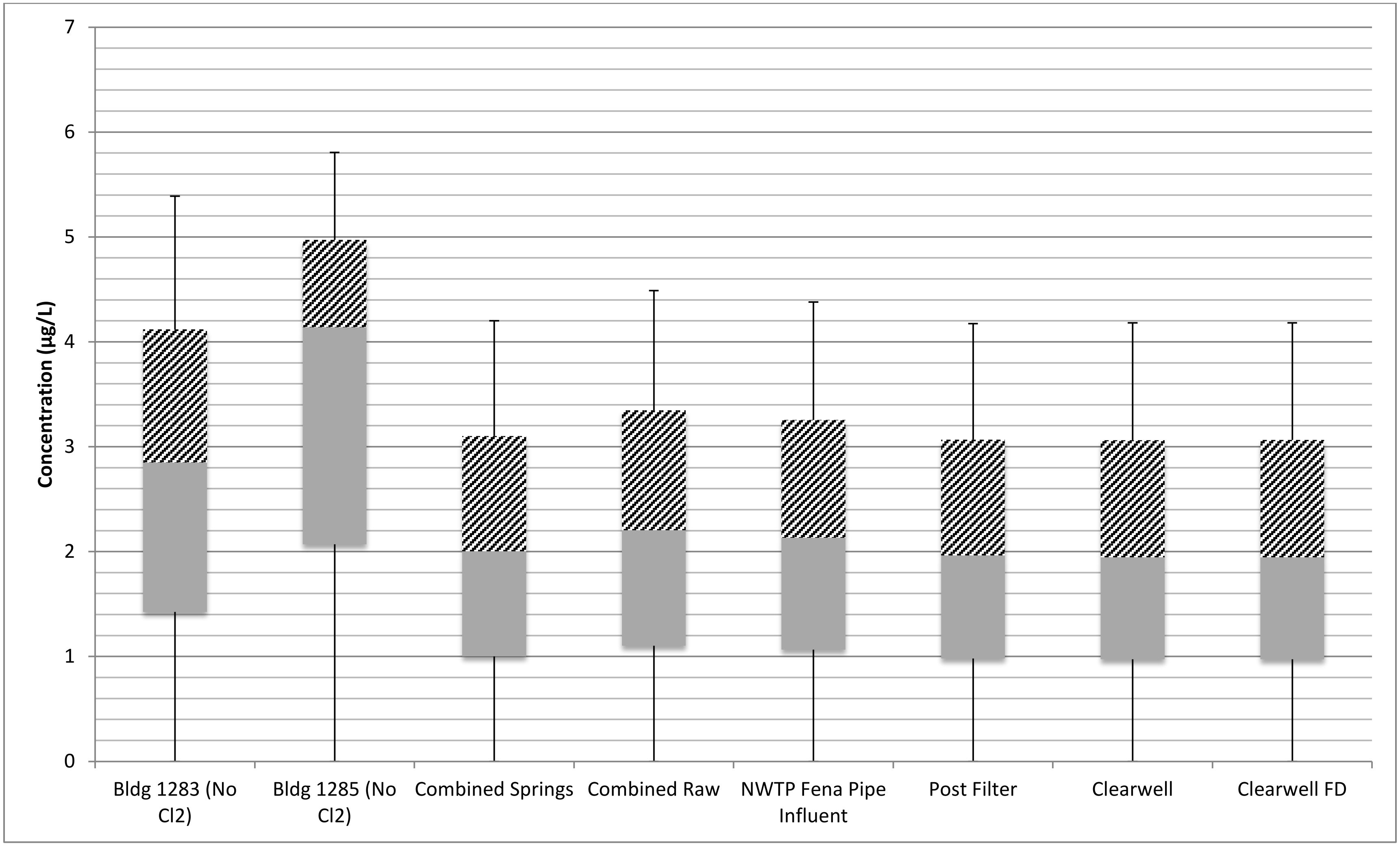


Figure 5-8: Dissolved Manganese Throughout the Water Treatment Process (No Pre-chlorination) [8/29/2013 to 10/29/2013]

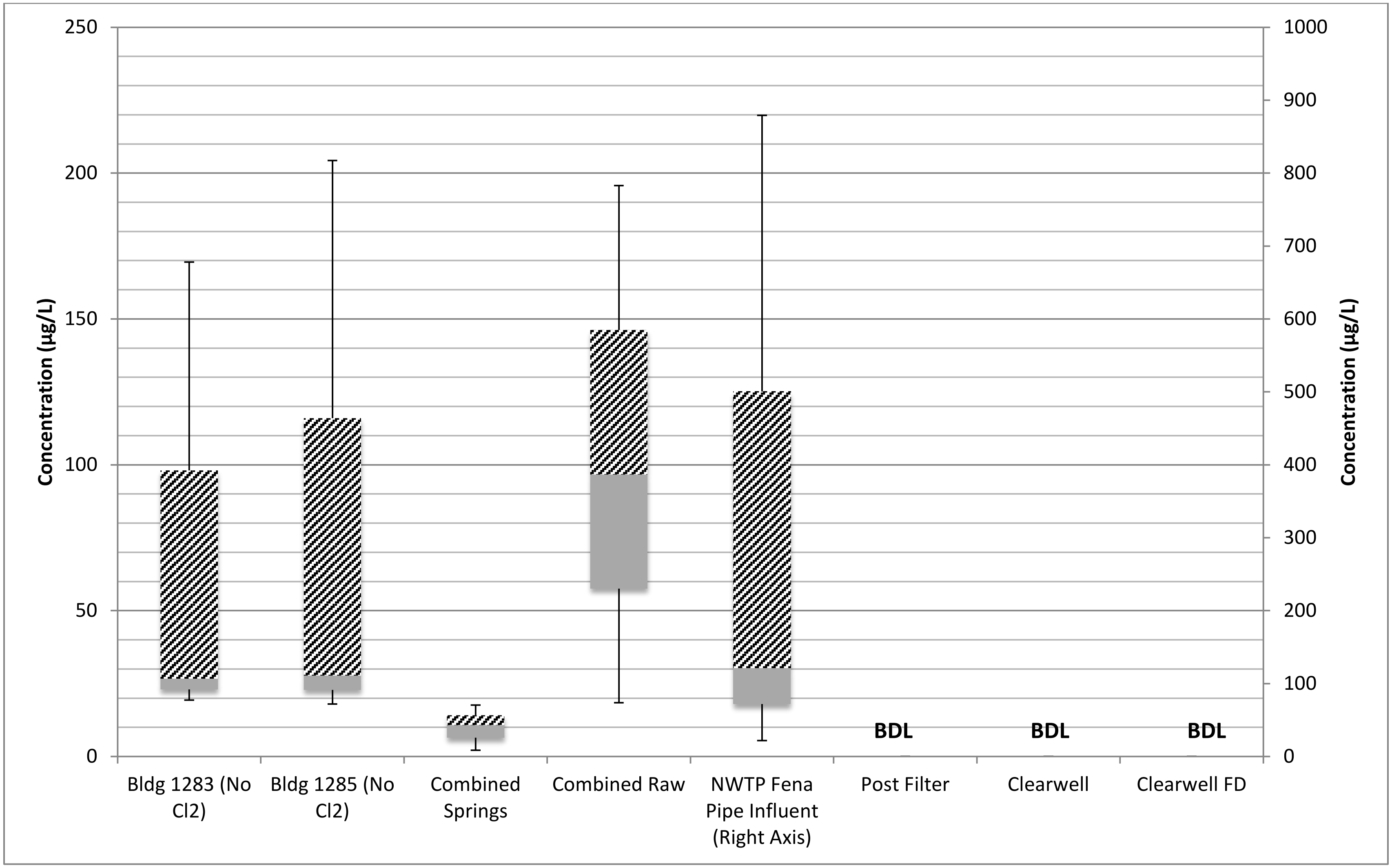


Figure 5-9: Total Iron Throughout the Water Treatment Process (No Pre-chlorination) [8/29/2013 to 10/29/2013

During chlorine cessation, three sample sets were sent to UCF for analysis. As shown in Figure 5-10 and Figure 5-11, the total and dissolved manganese was measured when the chlorine was shut off. The total manganese with pre-chlorination active was averaged and graphed, as well as the total manganese during the cessation of pre-chlorination. The data collected while pre-chlorination was practiced spans the timeframe between 5/30/2013 to 8/15/2013 whereas the data acquired without pre-chlorination is shown in the three data sets between 8/29/2013 and 10/29/2013. The corresponding data collected throughout this project is presented in Appendix A. As shown in these figures, when pre-chlorination was not practiced the iron and manganese levels slightly increased but still below the SMCL of 50 μg/L.

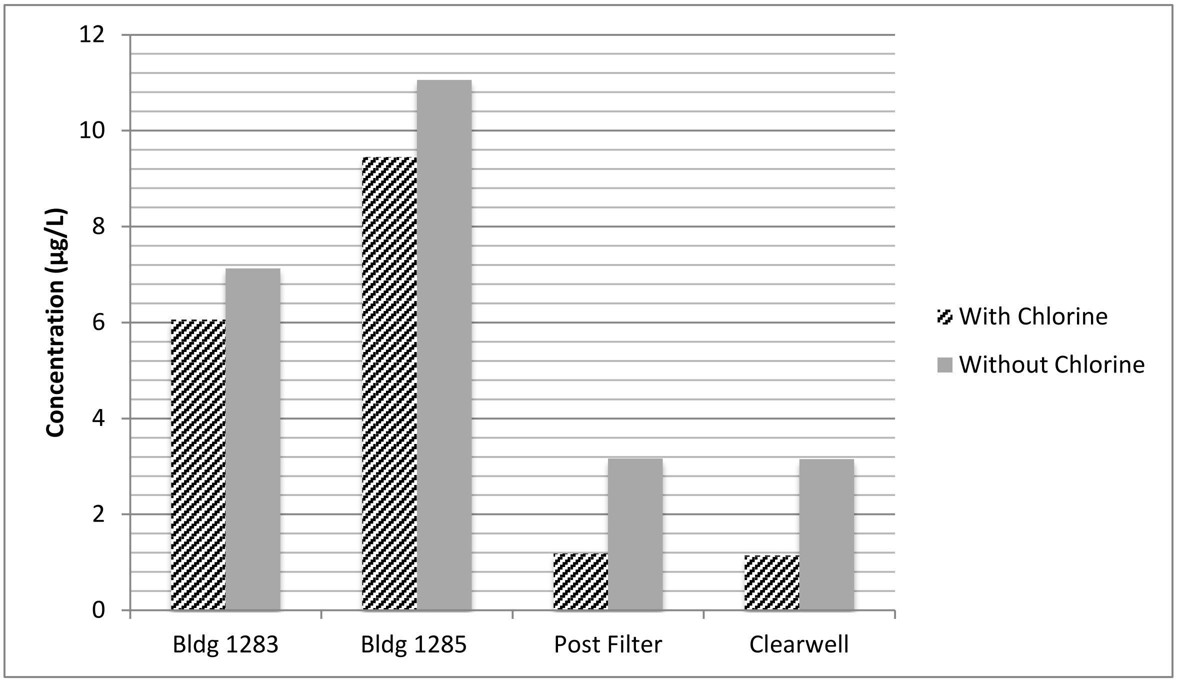


Figure 5-10: Total Manganese (With and Without Chlorine)

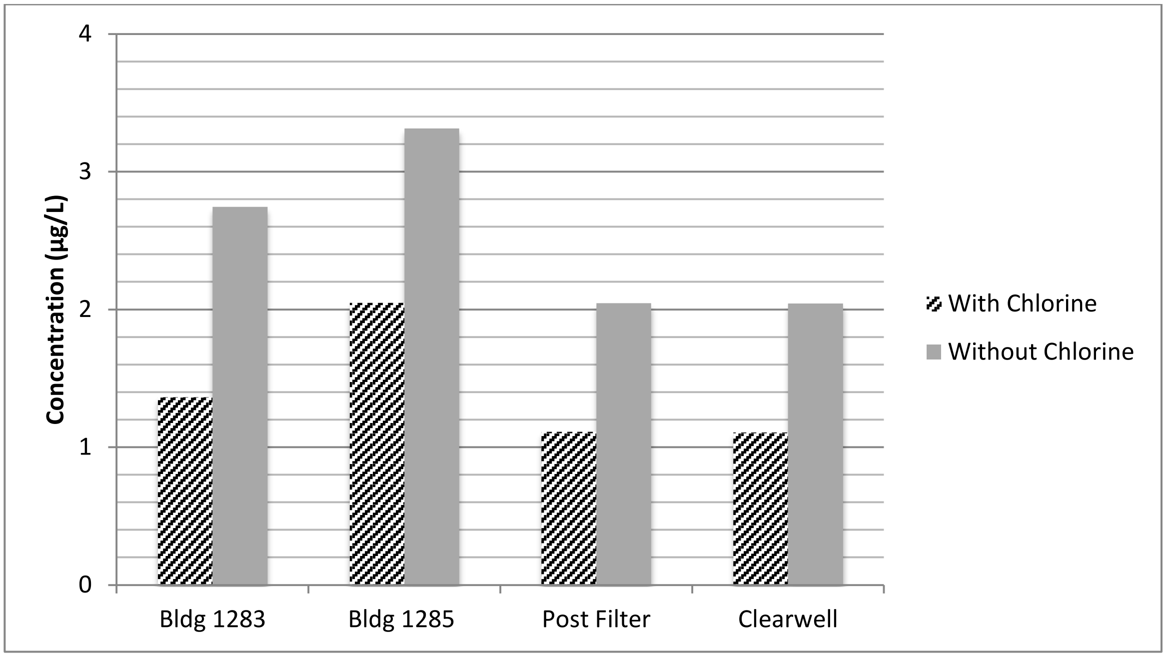


Figure 5-11: Dissolved Manganese (With and Without Chlorine)

The same was also accomplished for iron as shown in Figure 5-12 and Figure 5-13. Also, the same dates applied to iron as to applied to manganese with and without chlorine. As observed in these figures, total iron concentration increased when pre-chlorination was not practiced. Although these total concentrations increased, the dissolved concentrations were below detection limit during chlorine cessation. Since chlorine is acidic, when it is added it may dissolve iron deposits present in the pipeline. Another possible reason for the decrease in dissolved iron could be due to the time of the year and seasonal changes. Although the concentration of total iron increased during chlorine cessation, the iron concentration was still below the SMCL of 300 µg/L.

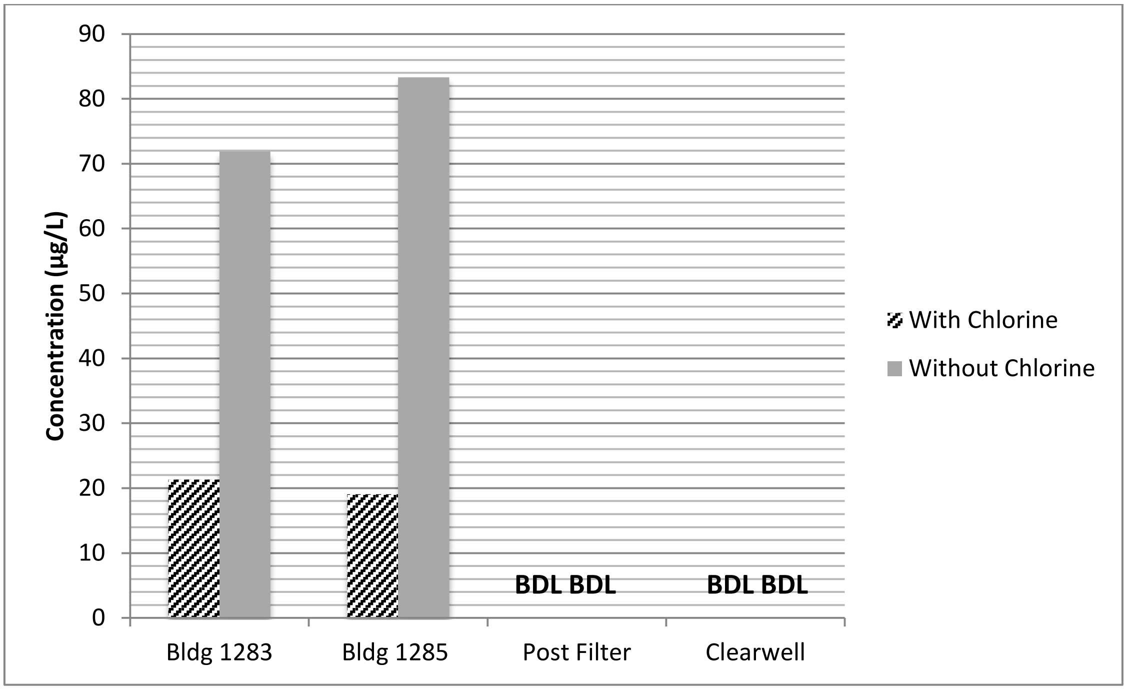


Figure 5-12: Total Iron (With and Without Chlorine)

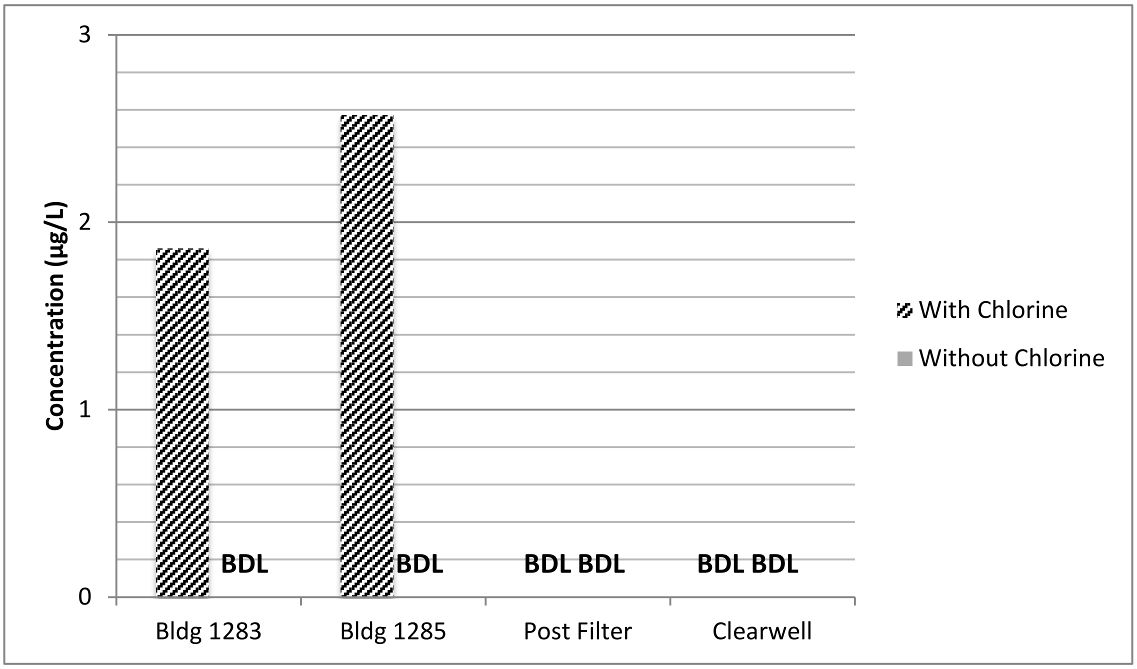


Figure 5-13: Dissolved Iron (With and Without Chlorine)

Effectiveness of Potassium Permanganate Pretreatment for Iron and Manganese Control

As shown in Figure 4-3, once the dose was increased past the recommended dose, pink water formed in jars five and six. Over time, the pink water dissipated, in some cases 30 minutes. Doses in jars two, three, and four were at or below the recommended dose, calculated using Equation 4-2. The dose varied each time depending on the initial iron and manganese concentrations measured. The jars dosed at those levels turned brown in color, which signifies that the iron and manganese was being oxidized. The jars were dosed with potassium permanganate solution, mixed, and covered to simulate pipe flow for two hours. The two-hour duration was chosen based on a typical raw water travel time from the Fena Lake Pump Station to the influent pipeline of the plant.

Once mixed, aluminum sulfate was added and the samples underwent a rapid mix at 150 rpm for three minutes, flocculated at 20 rpm for 15 minutes, and then were allowed to settle for one hour. The coagulant dose varied depending on the turbidity of the water, which usually was between the range of 25 to 40 mg/L of aluminum sulfate. Once settled, samples were then taken and filtered through 0.45-micron filters for iron and manganese analysis. The doses and water quality data is shown in Table 5-2, Table 5-3, and Table 5-4. Water quality analyzed included pH, conductivity, temperature, turbidity, dissolved iron, and dissolved manganese. The graphs correlated to the manganese concentrations after the potassium permanganate was added are shown in Figure 5-14, Figure 5-15, and Figure 5-16. The dose varied for each water shipment received and tested. As shown in the figures, once the dose exceeded the recommended stoichiometric dose, the water exhibited an undesired pink water color.

Table 5-2: Jar Test Water Quality (Run 1)

Before Permanganate Dose						
Potassium Permanganate Dose (mg/L)	pH	Conductivity (µS/cm)	Temperature (°C)	Turbidity (NTU)	Dissolved Iron (µg/L)	Dissolved Manganese (µg/L)
0	7.19	219	20.2	4.30	73.6	56.1
1	7.22	220	20.3	4.28		
1.1	7.27	220	20.3	4.37		
1.25	7.27	220	20.7	4.34		
1.4	7.39	221	20.2	4.29		
1.5	7.28	220	20.5	4.32		
After Permanganate Dose						
Potassium Permanganate Dose (mg/L)	pH	Conductivity (µS/cm)	Temperature (°C)	Turbidity (NTU)	Dissolved Iron (µg/L)	Dissolved Manganese (µg/L)
0 (Right Axis)	7.59	225	20.4	0.90	ND	43
1	7.61	224	20.5	0.88	ND	2.6
1.25	7.59	224	20.5	0.91	ND	2.4
1.75[b]	7.62	224	20.7	0.81	ND	2.3
2.25	7.63	223	20.4	0.85	ND	3.4
3	7.59	222	20.5	0.89	ND	3.1

b: Recommended dose based on stoichiometry

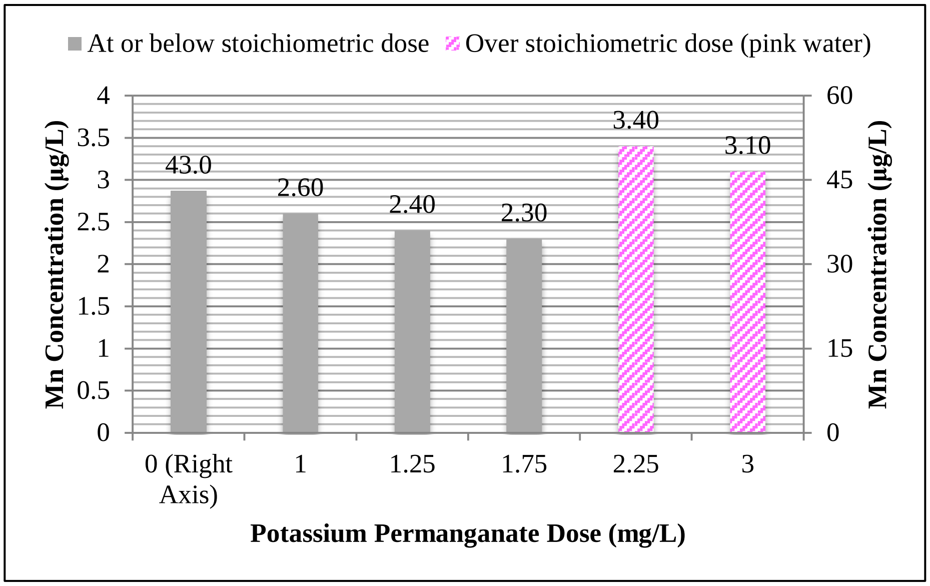


Figure 5-14: Results of Jar Test Corresponding to Table 5-2

Table 5-3: Jar Test Water Quality (Run 2)

Before Permanganate Dose						
Potassium Permanganate Dose (mg/L)	pH	Conductivity (µS/cm)	Temperature (°C)	Turbidity (NTU)	Dissolved Iron (µg/L)	Dissolved Manganese (µg/L)
0	7.13	143	20.7	5.70	130	290
0.5	7.18	144	20.6	5.74		
0.68	7.23	144	20.7	5.73		
0.85	7.29	144	20.5	5.80		
After Permanganate Dose						
Potassium Permanganate Dose (mg/L)	pH	Conductivity (µS/cm)	Temperature (°C)	Turbidity (NTU)	Dissolved Iron (µg/L)	Dissolved Manganese (µg/L)
0 (Right Axis)	7.02	182	20.9	0.99	ND	63
0.5	7.04	182	20.8	0.99	ND	4.4
0.68[b]	7.03	183	20.7	0.93	ND	4.1
0.85	7.05	185	20.6	0.95	ND	5.6

b: Recommended dose based on stoichiometry

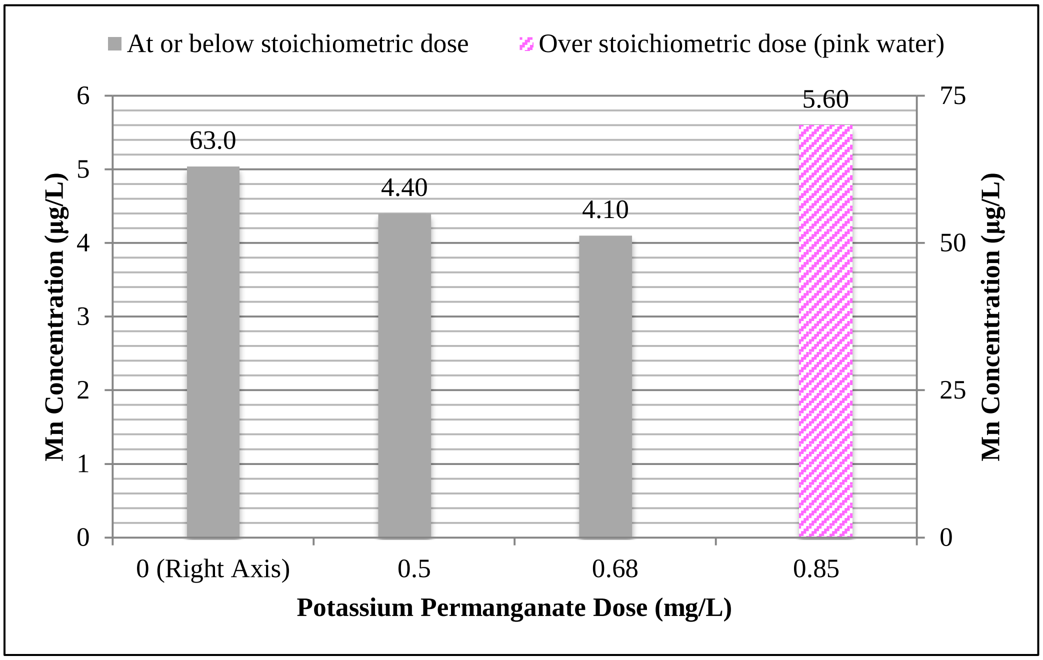


Figure 5-15: Results of Jar Test Corresponding to Table 5-3

Table 5-4: Jar Test Water Quality (Run 3)

Before Permanganate Dose						
Potassium Permanganate Dose (mg/L)	pH	Conductivity (µS/cm)	Temperature (°C)	Turbidity (NTU)	Dissolved Iron (µg/L)	Dissolved Manganese (µg/L)
0	7.12	159	20.6	5.80	150	780
1.25	7.09	158.4	20.5	6.10		
1.65	7.10	159.1	20.3	5.92		
2.05	7.16	161	20.5	5.89		
After Permanganate Dose						
Potassium Permanganate Dose (mg/L)	pH	Conductivity (µS/cm)	Temperature (°C)	Turbidity (NTU)	Dissolved Iron (µg/L)	Dissolved Manganese (µg/L)
0 (Right Axis)	7.10	205.9	20.7	0.60	ND	741
1.25	7.09	201.5	20.5	0.75	ND	47.8
1.65[b]	7.10	200	20.4	0.74	ND	3.6
2.05	7.15	199.7	20.5	0.85	ND	5.1

b: Recommended dose based on stoichiometry

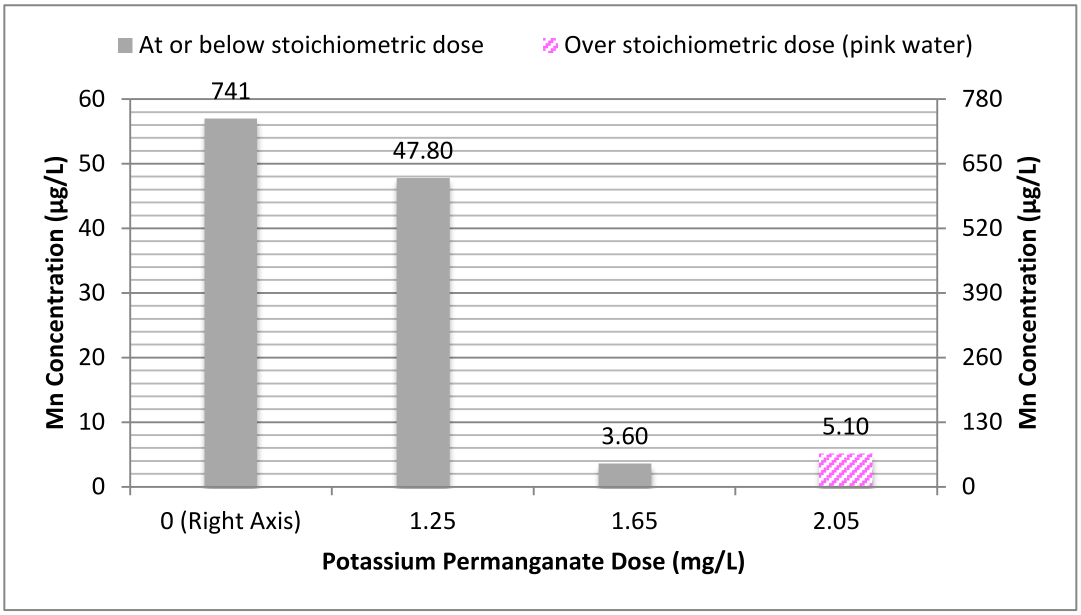


Figure 5-16: Results of Jar Test Corresponding to Table 5-4

Laboratory Filter Method Verification

Another set of studies were performed to verify that 0.45-micron filters were not removing the oxidized manganese present in the water. This specific component of the study was performed using a series of jar test. Four jars were used in total; from each jar an initial sample was taken and then filtered through 0.45-micron filters and 0.1-micron filters. These samples were then analyzed with an ICP Spectrophotometer to determine the dissolved manganese concentration. Coagulant was added to each of the jars, which then underwent rapid mix, flocculation, and sedimentation processes. Once settled, samples were then again taken and filtered through a 0.45-micron filter. Figure 5-17 interprets these results. Based on these results, this verifies that the 0.45-micron filters removed less than the 0.1-micron filters and is not effective in removing oxidized manganese particulate mater. It is recommended that when taking monthly samples from the WTP, the samples should be filtered through a 0.1-micron filter.

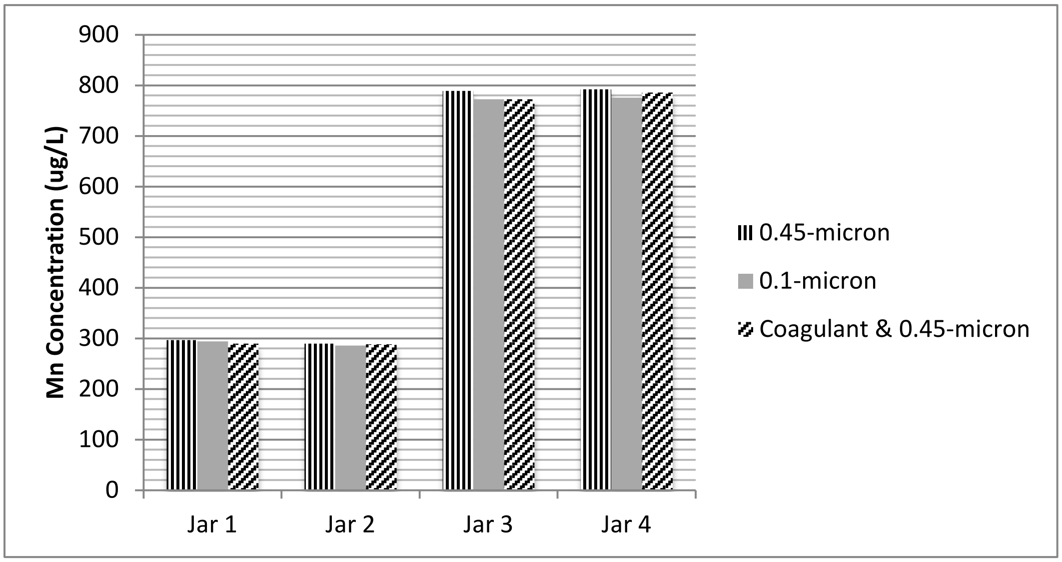


Figure 5-17: Filtering Results

Quality Control Results

Control charts were plotted for both precision and accuracy. Precision was based on the I-statistic as shown in Equation 4-3. Accuracy was based on percent recovery as shown in Equation 4-1. The graphs related for precision and accuracy are shown in Figure 5-18 and Figure 5-19, respectively. As shown in Figure 5-18 the data collected during the time of this research was within the control limits for precision and did not exceed the UWL or the UCL.

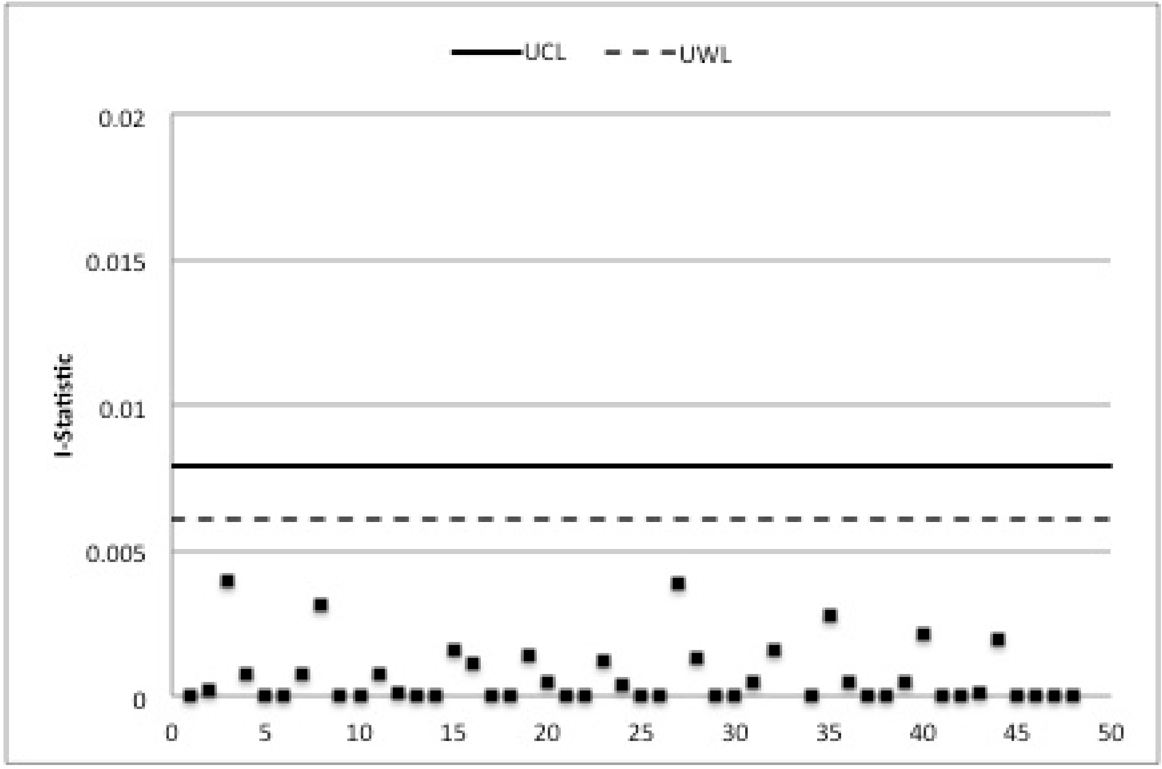


Figure 5-18: Control Chart for Metals Precision

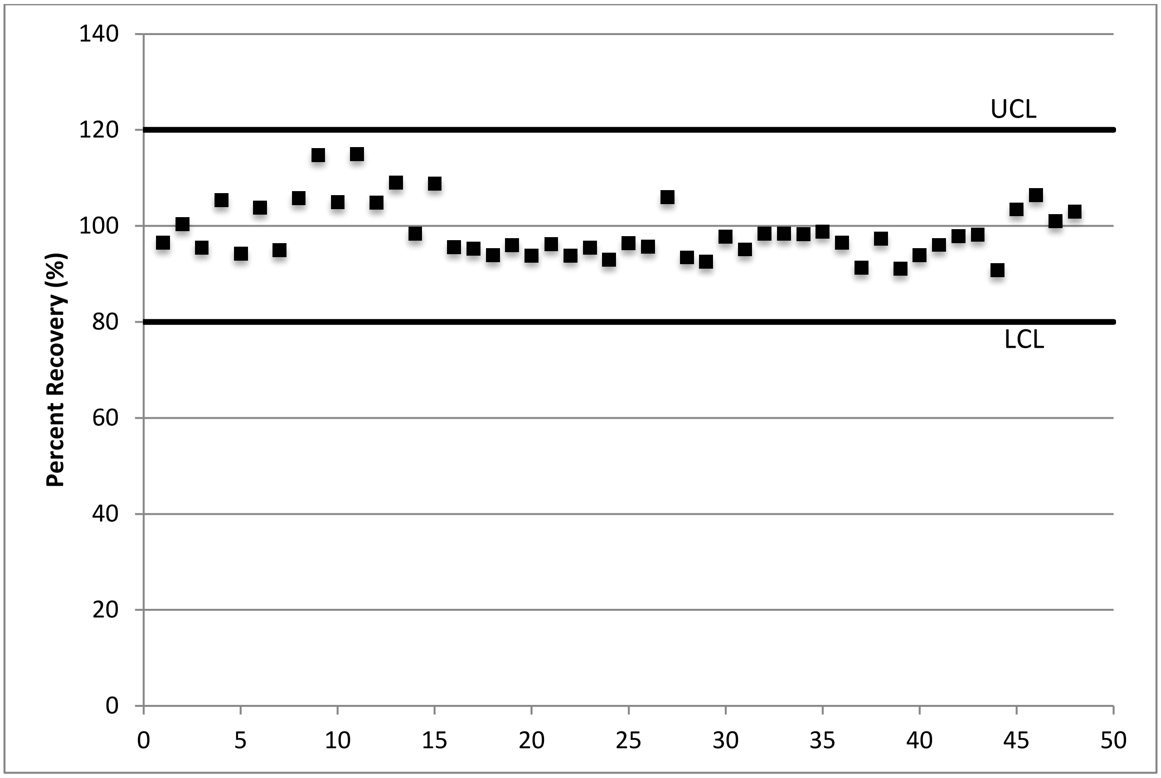


Figure 5-20: Control Chart for Accuracy

As shown in Figure 5-20, the data collected throughout this research did not exceed the UCL of 120 percent or the LCL of 80 percent. There were some cases where the data came close to the upper warning limits, but it was not necessary to discard that data due to not exceeding the upper control limit.

6. CONCLUSIONS AND RECOMMENDATIONS

Conclusions

A. Fena Lake iron and manganese concentrations increase with lake depth-. It was observed though that at lake depth of 40-ft, the manganese levels did exceed its SMCL. As for iron, at a lake depth of 40-ft, its SMCL was exceeded. Based on these results it may be concluded that the depth of 10-ft to 12-ft is sufficient for source water that does not exceed the SMCLs for iron and manganese.

B. Pre-chlorination is not necessary to control Fe and Mn levels- Based on the experiments conducted in the research reported herein, it was found that the iron and manganese concentrations throughout the WTP and at the point-of-entry are well below the secondary iron and manganese MCLs of 0.3 mg/L and 0.05 mg/L, respectively. It appeared that chlorine treatment offered no significant benefit when compared to oxygen oxidation (Fena Lake) when drawing from the surface (10-12 foot) lake level. Therefore, the chlorine at Fena Lake should be discontinued permanently as a pretreatment tool, as the chlorine does not significantly aid in manganese or iron oxidation and removal.

C. Potassium permanganate is effective in oxidizing Fe and Mn but over dosing causes pink water formation- Potassium permanganate was evaluated as an alternative to chlorine pre-treatment at the Fena Pump Station. The results showed that there was at least a 95 percent decrease, sometimes more, in the manganese concentration when potassium permanganate is added to raw Fena Lake water. The optimal doses were confirmed to be 0.94 mg $KMnO_4$ per mg Fe and 1.92 mg $KMnO_4$ per mg Mn. However, a slight over-dosage of excess permanganate leads to the formation of pink water. Caution must be taken so as to not overdose. The data developed in this work indicates that pink water formation can occur with less than 0.5 mg/L of a permanganate overdose. Therefore, iron and manganese concentrations in the source water must be monitored closely so that an accurate permanganate dose may be determined and subsequently applied if this oxidizer is to be used. An overdose that results in pink water will contribute to customer complaints.

Recommendations

A. Potassium permanganate as an alternate oxidant to chlorine pretreatment- Due to the fact that the tolerance in permanganate is so tight (< 0.5 mg/L) that the formation of pink water is possible. Consequently, the use of potassium permanganate as a pretreatment chemical is not recommended for the remotely located NWTP site.

B. Chlorine dioxide as an alternate oxidant to chlorine pretreatment- Since the use of potassium permanganate may present a difficult target for the operations staff to accurately control permanganate dosages, it is recommended that an alternate oxidant, chlorine dioxide, be researched for use as a manganese and iron control chemical. Due to the fact that chlorine was also historically used for taste and odor control during times of drought when algae could be problematic, an alternative control method would also provide possible additional benefits. Chlorine dioxide has been shown to control iron, manganese, provide taste and odor control, and does not contribute to the formation of regulated total trihalomethanes and halogenated acetic acids for many water purveyors across the U.S. (AWWA and AwwaRF 1995; AwwaRF 2009).

C. Study of storm event impacts on Fe and Mn lake water quality- It is recommended that a study be performed to verify the cause of the decreased iron and manganese concentrations that occurred at Fena Lake after the storm event that occurred during September 2013. Iron and manganese concentrations at a 40-ft depth were usually in the range of 580 μg/L and 780 μg/L prior to the storm event. After the storm event occurred, the 40-ft depth iron and manganese concentrations were below detection limits. This may be due to the increased rainfall or from the introduction of soil to the lake allowing for sand adsorption. Further studies will need to be performed to verify these conclusions.

D. Filter studies-Further studies should be performed to verify that a 0.1-micron filter should be utilized for analyzing dissolved manganese. Although this study was conducted throughout this research, it is recommended that more studies be performed to verify these results.

APPENDIX A: IRON AND MANGANESE DATA

Table A-1: Iron and Manganese Concentrations

5/30/2013	Location	Total Manganese (µg/L)	Dissolved Manganese (µg/L)	Percent Dissolved (%)	Total Iron (µg/L)	Dissolved Iron (µg/L)	Percent Dissolved (%)
	Navy reservoir 10'	4.40	0.60	14.3	8.90	ND	ND
	Navy reservoir 30'	99.9	0.80	0.80	42.6	ND	ND
	Bldg 1283 (before chlorination)	5.00	0.80	16.1	25.7	5.80	22.6
	Bldg 1285 (after chlorination)	7.40	1.70	22.5	19.9	6.00	30.3
	Combined springs	1.20	0.60	51.1	1.70	ND	ND
	Combined raw	4.50	0.70	15.4	12.5	0.60	4.80
	NWTP Fena Pipe Influent	5.20	0.60	12.0	18.8	0.30	1.40
	Filtered water	0.70	0.60	80.3	ND	ND	ND
	Clearwell	0.60	0.60	94.6	ND	ND	ND
	Clearwell field duplicate	0.60	0.60	94.4	ND	ND	ND
6/6/2013	**Location**	**Total Manganese (µg/L)**	**Dissolved Manganese (µg/L)**	**Percent Dissolved (%)**	**Total Iron (µg/L)**	**Dissolved Iron (µg/L)**	**Percent Dissolved (%)**
	Navy reservoir 10'	7.70	1.40	18.5	15.9	ND	ND
	Navy reservoir 30'	15.0	1.30	8.80	42.3	ND	ND
	Bldg 1283 (before chlorination)	6.40	1.40	21.3	23.4	2.40	10.4
	Bldg 1285 (after chlorination)	9.30	2.10	22.2	22.2	1.7	7.90
	Combined springs	1.90	1.40	71.7	1.80	ND	0.10
	Combined raw	6.80	1.80	26.3	14.3	1.10	8.00
	NWTP Fena Pipe Influent	8.20	1.70	21.0	22.4	2.20	10.0
	Filtered water	1.30	1.30	96.8	ND	ND	ND
	Clearwell	1.30	1.30	99.9	ND	ND	ND
	Clearwell field duplicate	1.30	1.40	105.3	ND	ND	ND

6/13/2013	Location	Total Manganese (µg/L)	Dissolved Manganese (µg/L)	Percent Dissolved (%)	Total Iron (µg/L)	Dissolved Iron (µg/L)	Percent Dissolved (%)
	Navy reservoir 10'	16.4	0.60	3.90	11.3	0.70	5.90
	Navy reservoir 30'	18.4	0.60	3.00	13.0	ND	ND
	Bldg 1283 (before chlorination)	9.10	0.70	7.90	21.6	2.10	9.90
	Bldg 1285 (after chlorination)	17.1	1.30	7.60	21.1	6.10	28.8
	Combined springs	1.60	0.60	38.2	24.4	0.60	2.70
	Combined raw	15.9	0.90	5.40	23.0	0.80	3.60
	NWTP Fena Pipe Influent	17.8	0.80	4.60	21.3	1.10	5.10
	Filtered water	0.70	0.60	82.7	ND	ND	ND
	Clearwell	0.60	0.60	94.5	ND	ND	ND
	Clearwell field duplicate	0.60	0.60	92.5	ND	ND	ND
6/20/2013	Location	Total Manganese (µg/L)	Dissolved Manganese (µg/L)	Percent Dissolved (%)	Total Iron (µg/L)	Dissolved Iron (µg/L)	Percent Dissolved (%)
	Navy reservoir 10'	9.00	0.60	7.00	6.70	ND	ND
	Navy reservoir 30'	30.4	6.20	20.5	17.3	0.20	1.40
	Bldg 1283 (before chlorination)	6.50	0.90	13.3	17.2	1.10	6.10
	Bldg 1285 (after chlorination)	10.0	1.40	14.4	12.2	1.50	12.1
	Combined springs	1.10	0.60	51.7	1.50	ND	ND
	Combined raw	6.10	0.80	13.4	8.20	2.20	26.8
	NWTP Fena Pipe Influent	13.9	0.80	5.80	12.2	2.30	19.2
	Filtered water	0.60	0.70	108	ND	ND	ND
	Clearwell	0.60	0.60	86.7	ND	ND	ND
	Clearwell field duplicate	0.60	0.60	90.3	ND	ND	ND

6/27/2013	Location	Total Manganese (µg/L)	Dissolved Manganese (µg/L)	Percent Dissolved (%)	Total Iron (µg/L)	Dissolved Iron (µg/L)	Percent Dissolved (%)
	Navy reservoir 10'	5.50	1.00	18.3	7.40	ND	ND
	Navy reservoir 30'	22.7	1.00	4.40	15.9	ND	ND
	Bldg 1283 (before chlorination)	5.70	1.30	22.9	20.3	1.40	7.00
	Bldg 1285 (after chlorination)	9.30	2.00	22.0	25.4	1.60	6.20
	Combined springs	1.80	1.00	55.5	7.20	ND	ND
	Combined raw	15.2	1.30	8.40	20.6	ND	ND
	NWTP Fena Pipe Influent	21.6	1.30	6.00	35.1	0.60	1.60
	Filtered water	1.00	1.00	95.0	ND	ND	ND
	Clearwell	1.00	1.00	98.6	ND	ND	ND
	Clearwell field duplicate	1.00	1.00	95.6	ND	ND	ND
7/5/2013	Location	Total Manganese (µg/L)	Dissolved Manganese (µg/L)	Percent Dissolved (%)	Total Iron (µg/L)	Dissolved Iron (µg/L)	Percent Dissolved (%)
	Navy reservoir 10'	8.80	1.50	16.8	ND	ND	ND
	Navy reservoir 30'	71.9	1.40	1.90	ND	ND	ND
	Bldg 1283 (before chlorination)	6.30	1.50	23.7	23.6	2.20	9.30
	Bldg 1285 (after chlorination)	10.5	1.90	18.1	20.8	3.20	15.3
	Combined springs	5.80	1.50	25.7	12.4	ND	ND
	Combined raw	7.30	1.60	22.5	15.9	1.50	9.50
	NWTP Fena Pipe Influent	7.40	1.60	22.0	16.2	2.50	15.40
	Filtered water	1.50	1.40	91.9	ND	ND	ND
	Clearwell	1.40	1.40	98.2	ND	ND	ND
	Clearwell field duplicate	1.50	1.40	97.2	ND	ND	ND

7/11/2013	Location	Total Manganese (µg/L)	Dissolved Manganese (µg/L)	Percent Dissolved (%)	Total Iron (µg/L)	Dissolved Iron (µg/L)	Percent Dissolved (%)
	Navy reservoir 10'	6.40	1.40	21.5	8.0	ND	ND
	Navy reservoir 30'	62.6	1.40	2.2	62.4	ND	ND
	Bldg 1283 (before chlorination)	6.70	1.70	24.8	23.2	ND	ND
	Bldg 1285 (after chlorination)	9.40	2.70	28.3	20.5	2.60	12.7
	Combined springs	2.20	1.50	67.1	2.30	ND	ND
	Combined raw	6.50	1.60	24.0	14.6	ND	ND
	NWTP Fena Pipe Influent	7.80	1.50	19.7	18.1	ND	ND
	Filtered water	1.40	1.40	100.5	ND	ND	ND
	Clearwell	1.30	1.40	101.9	ND	ND	ND
	Clearwell field duplicate	1.40	1.40	100.7	ND	ND	ND
7/18/2013	Location	Total Manganese (µg/L)	Dissolved Manganese (µg/L)	Percent Dissolved (%)	Total Iron (µg/L)	Dissolved Iron (µg/L)	Percent Dissolved (%)
	Navy reservoir 10'	2.50	1.40	57.3	4.80	ND	ND
	Navy reservoir 30'	3.30	1.40	43.3	3.10	ND	ND
	Bldg 1283 (before chlorination)	2.40	1.70	71.6	12.3	ND	ND
	Bldg 1285 (after chlorination)	5.00	2.40	47.3	12.1	ND	ND
	Combined springs	1.50	1.40	93.0	7.10	ND	ND
	Combined raw	2.60	1.80	70.0	7.90	ND	ND
	NWTP Fena Pipe Influent	2.90	2.00	68.7	7.60	ND	ND
	Filtered water	1.30	1.30	99.0	ND	ND	ND
	Clearwell	1.30	1.30	100.3	ND	ND	ND
	Clearwell field duplicate	1.30	1.30	100.1	ND	ND	ND

7/25/2013	Location	Total Manganese (µg/L)	Dissolved Manganese (µg/L)	Percent Dissolved (%)	Total Iron (µg/L)	Dissolved Iron (µg/L)	Percent Dissolved (%)
	Navy reservoir 10'	5.50	1.30	23.1	7.60	ND	ND
	Navy reservoir 30'	8.20	1.40	16.6	16.9	ND	ND
	Bldg 1283 (before chlorination)	5.50	1.80	32.3	21.1	ND	ND
	Bldg 1285 (after chlorination)	8.10	2.20	26.6	17.7	ND	ND
	Combined springs	1.90	1.30	68.8	8.70	ND	ND
	Combined raw	11.7	1.60	13.3	13.7	ND	ND
	NWTP Fena Pipe Influent	6.70	1.70	25.0	16.4	ND	ND
	Filtered water	1.40	1.20	89.7	ND	ND	ND
	Clearwell	1.40	1.20	88.0	ND	ND	ND
	Clearwell field duplicate	1.40	1.20	88.1	ND	ND	ND
8/15/2013	Location	Total Manganese (µg/L)	Dissolved Manganese (µg/L)	Percent Dissolved (%)	Total Iron (µg/L)	Dissolved Iron (µg/L)	Percent Dissolved (%)
	Navy reservoir 20'	8.10	2.30	28.1	6.00	ND	ND
	Navy reservoir 40'	989.3	986.2	99.7	685.1	5.00	0.70
	Bldg 1283 (before chlorination)	8.30	2.60	31.9	20.6	ND	ND
	Bldg 1285 (after chlorination)	10.5	2.70	25.7	15.6	ND	ND
	Combined springs	2.90	2.30	79.8	5.60	ND	ND
	Combined raw	8.80	2.50	28.8	17.0	ND	ND
	NWTP Fena Pipe Influent	9.90	2.60	26.6	16.9	ND	ND
	Filtered water	2.30	2.20	99.6	ND	ND	ND
	Clearwell	2.20	2.30	101.3	ND	ND	ND
	Clearwell field duplicate	2.20	2.30	100.8	ND	ND	ND

8/29/2013	Location	Total Manganese (µg/L)	Dissolved Manganese (µg/L)	Percent Dissolved (%)	Total Iron (µg/L)	Dissolved Iron (µg/L)	Percent Dissolved (%)
No Chlorine	Navy reservoir 20'	4.60	2.1	46.1	38.6	ND	ND
	Navy reservoir 40'	698	690	98.8	329.8	210.6	63.9
	Bldg 1283 (before chlorination)	4.50	2.8	62.8	19.3	ND	ND
	Bldg 1285 (after chlorination)	5.80	4.1	71.6	18.0	ND	ND
	Combined springs	2.30	2.0	86.6	10.7	ND	ND
	Combined raw	10.2	2.2	21.5	18.4	ND	ND
	NWTP Fena Pipe Influent	15.4	2.1	13.8	22.0	ND	ND
	Filtered water	2.0	2.0	98.6	ND	ND	ND
	Clearwell	2.0	1.9	98.0	ND	ND	ND
	Clearwell field duplicate	2.0	1.9	95.6	ND	ND	ND

9/16/2013	Location	Total Manganese (µg/L)	Dissolved Manganese (µg/L)	Percent Dissolved (%)	Total Iron (µg/L)	Dissolved Iron (µg/L)	Percent Dissolved (%)
No Chlorine	Navy reservoir 20'	16.9	4.30	25.4	38.6	ND	ND
	Navy reservoir 40'	637.4	629.3	98.7	719.0	6.20	0.90
	Bldg 1283 (before chlorination)	12.1	5.40	44.6	19.3	ND	ND
	Bldg 1285 (after chlorination)	17.7	5.80	32.8	18.0	ND	ND
	Combined springs	4.70	4.20	89.4	10.7	ND	ND
	Combined raw	298.7	4.50	1.50	18.4	ND	ND
	NWTP Fena Pipe Influent	365.4	4.40	1.20	22.0	ND	ND
	Filtered water	4.30	4.20	97.7	ND	ND	ND
	Clearwell	4.30	4.20	97.7	ND	ND	ND
	Clearwell field duplicate	4.30	4.20	97.7	ND	ND	ND

10/29/2013	Location	Total Manganese (µg/L)	Dissolved Manganese (µg/L)	Percent Dissolved (%)	Total Iron (µg/L)	Dissolved Iron (µg/L)	Percent Dissolved (%)
No Chlorine	Navy reservoir 20'	8.10	ND	ND	173.6	ND	ND
	Navy reservoir 40'	5.50	ND	ND	182.3	ND	ND
	Bldg 1283 (before chlorination)	4.70	ND	ND	169.5	ND	ND
	Bldg 1285 (after chlorination)	9.70	ND	ND	204.3	ND	ND
	Combined springs	0.10	ND	ND	17.7	ND	ND
	Combined raw	32.8	ND	ND	195.7	ND	ND
	NWTP Fena Pipe Influent	33.5	ND	ND	879	ND	ND
	Filtered water	ND	ND	ND	ND	ND	ND
	Clearwell	ND	ND	ND	ND	ND	ND
	Clearwell field duplicate	ND	ND	ND	ND	ND	ND

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