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DYNAMIC INTERACTION OF IRON CHEMISTRY IN MANTUA  
RESERVOIR AND FERRIC STAINING IN THE SECONDARY  
WATER SYSTEM OF BRIGHAM CITY, UTAH

By

Robert D. Wallace

A thesis submitted to the faculty of

Brigham Young University

in partial fulfillment of the requirements for the degree of

Master of Science

Department of Civil and Environmental Engineering

Brigham Young University

August 2007



BRIGHAM YOUNG UNIVERSITY

GRADUATE COMMITTEE APPROVAL

Thesis submitted by

Robert D. Wallace

This thesis has been read by each member of the following graduate committee and by majority vote has been found to be satisfactory.

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BRIGHAM YOUNG UNIVERSITY

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## ABSTRACT

# DYNAMIC INTERACTION OF IRON CHEMISTRY IN MANTUA RESERVOIR AND FERRIC STAINING IN THE SECONDARY WATER SYSTEM OF BRIGHAM CITY, UTAH

Robert D. Wallace

Department of Civil and Environmental Engineering

Master of Science

Water from Mantua reservoir has, during some years, exhibited reddish-brown staining when used by Brigham City for irrigation. I propose that seasonal fluctuations in the reservoir chemistry create an environment conducive to dissolving iron from the iron-rich sediments, which subsequently precipitate during irrigation, resulting in a staining event. These conditions are produced by chemical and biological decomposition of organic matter, coupled with isolation of the hypolimnetic waters, which results in seasonal low concentrations of dissolved oxygen in these waters. Under these specific circumstances, anaerobic conditions develop creating a geochemical environment that causes iron and manganese reduction from Fe(III) to Fe(II) and Mn(IV) to Mn(II), respectively. These reducing conditions facilitate reduction-oxidation (redox) chemical reactions that convert insoluble forms of iron and manganese found in the reservoir





sediments into more soluble forms. Consequently, relatively high amounts of dissolved iron and manganese are generated in the bottom waters immediately adjacent to the benthic sediments of the reservoir. Water withdrawn from a bottom intake pipe during these periods introduces iron-rich water into the distribution system. When this water is exposed to oxygen, reoxidation shifts redox equilibrium causing precipitation of soluble Fe(II) and Mn(III) back to highly insoluble Fe(III) and Mn(IV). The precipitant appears on contact surfaces as the aforementioned ferric stain. This research focuses specifically on the iron chemistry involved and evaluates this hypothesis using various measurements and models including field data collection, computer simulations, and bench-scale testing to validate the processes proposed.



## ACKNOWLEDGMENTS

First, and foremost, I wish to thank Dr. Gus Williams for his unceasing desire to provide counsel and technical assistance throughout the entire duration of this study. I would also like to thank Scott Lathen for his invaluable assistance with field data collection and the wet chemistry portion of the bench scale testing.

The project was funded in its entirety by the Division of Public Works of Brigham City, Utah.

Lastly, I want to express appreciation to my wife for her unwavering support during the long hours of research and lab work.



## TABLE OF CONTENTS

<b>1</b>	<b>Introduction.....</b>	<b>1</b>
1.1	Background.....	2
1.2	Analysis and Study Justification.....	3
<b>2</b>	<b>Theoretical Background.....</b>	<b>7</b>
2.1	Mantua Reservoir Iron Sources .....	7
2.2	Mantua Reservoir Under Oxidizing Conditions .....	8
2.3	Mantua Reservoir Under Reducing Conditions.....	10
2.4	Alkalinity .....	13
2.5	Solubility.....	14
<b>3</b>	<b>Water Sample Analysis.....</b>	<b>17</b>
3.1	Procedure .....	17
3.2	Sampling Schedule.....	18
3.3	Parameters Measured.....	18
3.4	Laboratory Methods.....	18
<b>4</b>	<b>Experiments and Simulations .....</b>	<b>21</b>
4.1	Bench Scale Simulations.....	21
4.2	Computer Modeling.....	24
<b>5</b>	<b>Results .....</b>	<b>27</b>
5.1	Field Results.....	27
5.2	Laboratory Results .....	28
5.3	Computer Modeling Results .....	35

<b>6</b>	<b>Conclusion .....</b>	<b>37</b>
	<b>References.....</b>	<b>41</b>
	<b>Appendix A: Field Data.....</b>	<b>45</b>
	<b>Appendix B: Laboratory Data.....</b>	<b>47</b>

## LIST OF FIGURES

Figure 1. Location map of Mantua Reservoir, Utah. ....	1
Figure 2. Aerial image of Mantua Reservoir. ....	3
Figure 3. Ferric staining on city-owned structures. ....	4
Figure 4. Clinograde oxygen distribution curve. ....	11
Figure 5. Temperature and Dissolved Oxygen vs. Depth measured on March 31. ....	28
Figure 6. Temperature and Dissolved Oxygen vs. Depth measured on May 19. ....	28
Figure 7. Spectrophotometer results from March 31. ....	29
Figure 8. Results from the March 31 samples using the ICP. ....	30
Figure 9. Results from the May 19 samples using the ICP. ....	32
Figure 10. Results from the May 19 samples using the spectrophotometer. ....	33
Figure 11. Results from the computer modeling predictions. ....	36
Figure B1. Calibration Curve for March 31 <sup>st</sup> Spectrophotometer Test. ....	47
Figure B2. March 31 <sup>st</sup> ICP Test Calibration Curve. ....	48
Figure B3. March 31 <sup>st</sup> ICP Test Calibration Curve. ....	48
Figure B4. May 19 <sup>th</sup> ICP Calibration Curve. ....	49
Figure B5. May 19 <sup>th</sup> ICP Validation Test Calibration Curve. ....	50
Figure B6. Calibration Curves for May 19 <sup>th</sup> Spectrophotometer Test. ....	51



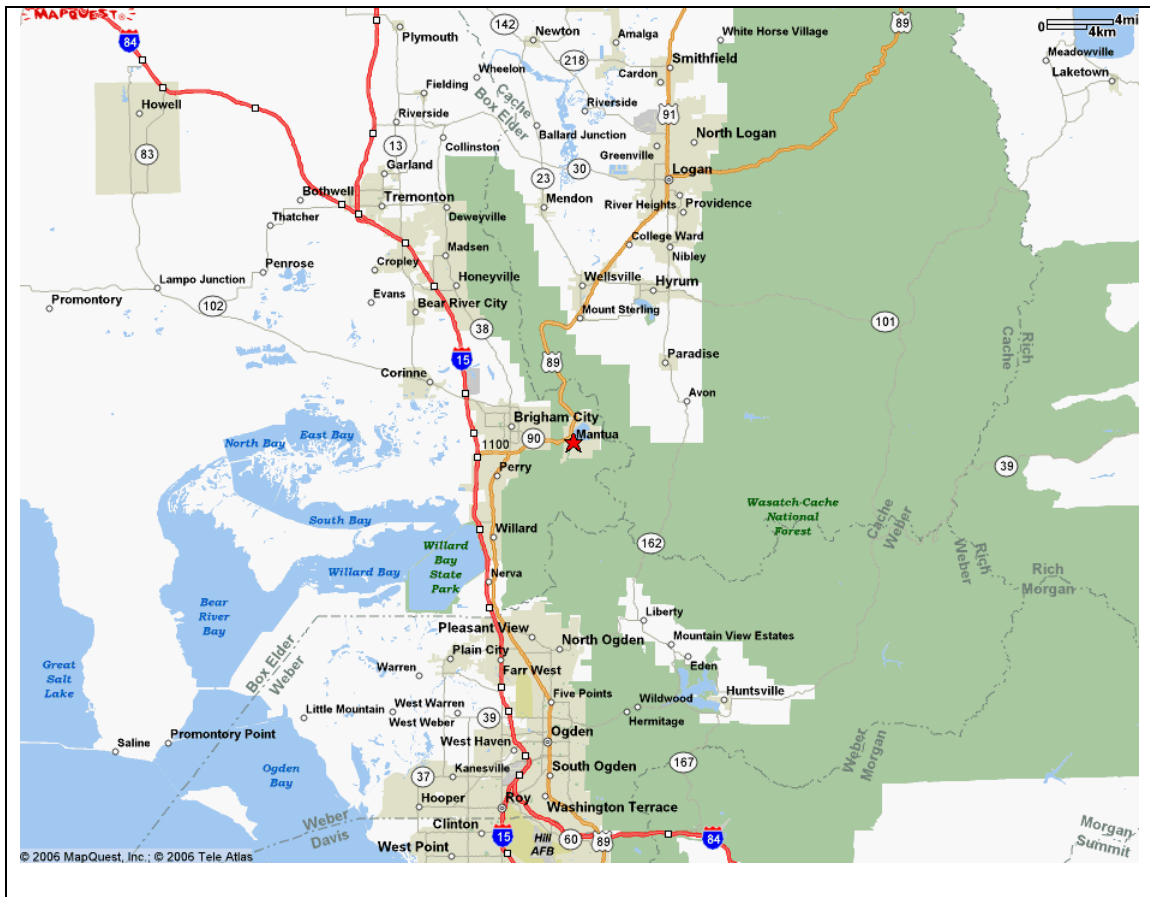


## LIST OF TABLES

Table 1. Initial Model Mantua Reservoir Staining Conditions.....	25
Table 2. Model Variance for Spectrophotometer Measurements .....	33
Table 3. Comparison of ICP and Spectrophotometer Measurements.....	34
Table 4. Computer Results From the Three Models.....	35
Table A1. March 31 <sup>st</sup> Field Data Results.....	45
Table A2. May 19 <sup>th</sup> Field Data Results.....	45
Table B1. Raw Data for Spectrophotometer Results.....	47
Table B2. Raw Data for March 31 <sup>st</sup> ICP Test.....	49
Table B3. Raw Test Results for May 19 <sup>th</sup> ICP (1 <sup>st</sup> Run) .....	49
Table B4 Raw Test Results for May 19 <sup>th</sup> Validation.....	50
Table B5 Raw Test Results for May 19 <sup>th</sup> Spectrophotometer Test .....	50



# 1 Introduction



**Figure 1. Location map of Mantua Reservoir, Utah.**

Mantua Reservoir is a relatively small reservoir, of approximately 554 acres, located in Box Elder County just east of Brigham City, Utah (DWR, 1996). It is located in the community of Mantua adjacent to Highway SR91 connecting the cities of Logan and Brigham City, Utah, as shown in Figure 1. Constructed in early 1962, Mantua

Reservoir is used for hydroelectricity, recreation and as an irrigation water supply for the town of Mantua and nearby Brigham City (DWR, 1996).

## **1.1 Background**

Mantua Reservoir is located in the Bear River watershed and is fed by three main inflows, Dam Creek and Upper and Lower Maple Creek, with a maximum volume of 10,450 acre-feet (Loveless et al, 1997). The average depth of reservoir is 14 feet. The only outlet of Mantua Reservoir, Big Creek, has an average flow rate of about 20.5 cubic feet per second (cfs) (Loveless et al, 1997). The region surrounding Mantua reservoir is mostly agricultural, as can be seen in Figure 2. The reservoir is nitrogen-limited and total phosphorus concentrations have long exceeded EPA standards (DWR, 1996). The excessive nutrient loading to the reservoir has increased the productivity levels to eutrophic. The reservoir trophic state is considered eutrophic to hypereutrophic (DWR, 1996). As a result, water quality problems of the type typically associated with eutrophic reservoirs have instigated complaints from the residents of Mantua and resulted in a reduction of recreational use (DWR, 1996). In 1982, the Utah Department of Environmental Quality ranked Mantua Reservoir in the top ten worst lakes in the State of Utah with regards to water quality (DWR, 1996). Although not completely conclusive, data have shown there has been a gradual increase in the nutrient loadings in recent years (Loveless et al, 1997). Consequently, there has been virtually no improvement in water quality since 1982 and the reservoir continues to be hampered by entangling macrophytic plant and blue-green algal growth limiting its beneficial uses (Loveless et al, 1997).



**Figure 2. Aerial image of Mantua Reservoir.**

## **1.2 Analysis and Study Justification**

In the years 2001 and 2002, objects and structures in Brigham City began to exhibit intermittent signs of a reddish-brown scale appearing after irrigation during the late summer months, as shown in Figure 3 (Hansen et al, 2002). The source of this irrigation water was Mantua Reservoir. Mantua Reservoir has a 36-inch diameter intake pipe on the west side of the reservoir which conveys water from the reservoir to a penstock for a small hydroelectric plant near Brigham City, approximately 3 miles away (Loveless et al, 1997). A pressurized irrigation diversion from the penstock, using the same water, was constructed in 1997 to serve as irrigation for the City-owned cemetery (Hansen et al, 2002).



**Figure 3. Ferric staining on city-owned structures.**

This staining has only been observed during the late summer months and has been particularly prevalent during night-time watering (Hansen et al, 2002). The staining occurred over the course of a single night's watering and was not seen as a gradual buildup over time (Hansen et al, 2002). As a result of the staining, Brigham City has sponsored water quality studies in an effort to ascertain the cause of the staining in order to design treatment alternatives (Hansen et al, 2002). Data collected during these studies provided evidence of high levels of iron and manganese within the secondary water system (Hansen et al, 2002). Additionally, the high degree of eutrophication of Mantua Reservoir was confirmed in these analyses (Hansen et al, 2002).

Recently, Brigham City performed a comprehensive feasibility study for the purpose of constructing a City-wide pressurized irrigation system (Hansen et al, 2002).

Mantua reservoir was chosen to be a primary water source for this secondary system. In order to prevent staining of private property with this system, Brigham City elected to perform another study with the technical assistance of Brigham Young University. The objective of this study is to determine the dynamic role of iron chemistry in Mantua reservoir and its interaction with the ferric staining problem in the secondary water system of Brigham City. Additionally, potential treatment options that could reduce or eliminate the potential for iron and manganese staining will be evaluated.





## **2 Theoretical Background**

For this study, we assumed that iron and manganese have very similar molecular and thermodynamic attributes. Additionally, the reduction-oxidation (redox) behaviors for the two metals under the environmental conditions discussed in this section are similar (Lith et al, 2003). However, oxidation-reduction kinetics for manganese occurs at a much slower rate than iron (Chen et al, 1983). Both iron and manganese are sensitive to redox conditions and are relatively mobile in the aquatic environment (Sawyer et al, 2003).

### **2.1 Mantua Reservoir Iron Sources**

Iron, the fourth most abundant element in the earth's crust, is present in significant quantities in the minerals that compose soils and rock. As a result, it is usually found in its solid form in most natural waters (Sawyer et al, 2003). The iron content of Mantua reservoir sediment has been found to be 16,600 mg/kg dry weight (Loveless et al, 1997). However, in spite of the available iron in the sediments, dissolved iron concentrations in the actual water column of natural waters are normally found in low concentrations (Tchobanoglous et al, 1985). Typical dissolved iron concentrations for natural well-aerated waters range between 0.1 – 2 parts per million (ppm) (DAP, 1996). Concentrations significantly above this have a potential to leave a reddish stain (DAP, 2001). In the presence of aerated (oxygenated) water, iron forms relatively insoluble

ferric oxides and iron carbonates which precipitate out of solution, leaving the water with relatively low dissolved iron levels (Sawyer et al, 2003).

Mantua Reservoir has a significant inflow from groundwater, with groundwater flows on the east side of the reservoir contributing 37.3% of the total inflow of Mantua reservoir (Loveless et al, 1997). Dissolved iron concentrations in groundwater tend to be high because groundwater systems typically have low dissolved oxygen levels (Sawyer et al, 2003). According to culinary-well reports documented by the USGS, the area around Mantua Reservoir contains high amounts of dissolved iron in the groundwater (Sanderson et al, 1999). It is possible that the groundwater contributing to the reservoir inflow has high levels of dissolved iron. Once this iron-rich water enters the reservoir and mixes with dissolved oxygen, the iron precipitates and settles on the bottom sediments. Furthermore, soils in the Wasatch Range of northern Utah have been found to be iron-rich due to their proximity to geologic iron formations (Young, 1988). Geologic data from the surrounding area support the possibility of naturally-occurring iron-rich soils that existed prior to reservoir construction becoming part of the reservoir sediment.

## **2.2 Mantua Reservoir Under Oxidizing Conditions**

The electron states of iron and manganese can be described by redox equilibrium equations (Sawyer et al. 2003). Redox potential of any element depends heavily on the amount of dissolved oxygen and pH of the system, as described in the following equation:

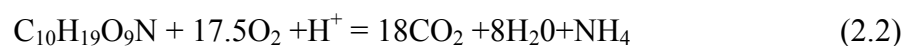
$$Eh = 1.234 - 0.058 \text{ pH} + 0.0145 \log pO_2 \text{ (1 atm and 18 degrees Celsius)} \quad (2.1)$$

Where  $pO_2$  is the partial pressure of oxygen (Chen et al, 1983).

It should be emphasized, however, that natural waters, such as Mantua Reservoir, are in a highly dynamic state and there is a significant margin of error in trying to measure redox potential (Bohn, 1971).

The atmosphere is composed 21% oxygen. As a result most shallow impoundments in temperate climates will have an adequate concentration of dissolved oxygen to remain aerobic year round due to surface solution of oxygen and subsequent dispersion and diffusion (Vance, 2002). In aerobic systems, oxygen is the terminal electron acceptor for both abiotic and biotic processes and is reduced while inorganic iron, as a reducing agent, will be oxidized to the trivalent state. As a result, iron forms relatively insoluble solids with an electron state of Fe(III) (Sawyer et al, 2003). This form of iron is poorly soluble (Sawyer et al, 2003). During most of the year, Mantua reservoir is well-aerated and can be considered under oxidizing conditions (Loveless et al, 1997). Under these conditions, iron is more thermodynamically stable as Fe(III), except at very low pH values (ESR, 2004).

In natural water systems, such as Mantua Reservoir, bio-chemical processes use oxygen (Sawyer et al, 2003). In eutrophic water systems, such as Mantua, one of the main oxygen consuming processes is the oxidation of organic material to its end products, such as carbon dioxide, ammonia, and water by aerobic bacteria, using the energy that is released for cell synthesis (Tchobanoglous et al, 1985). The decomposition of organic matter in the presence of oxygen is described in the following equation (Thomas et al, 1974):

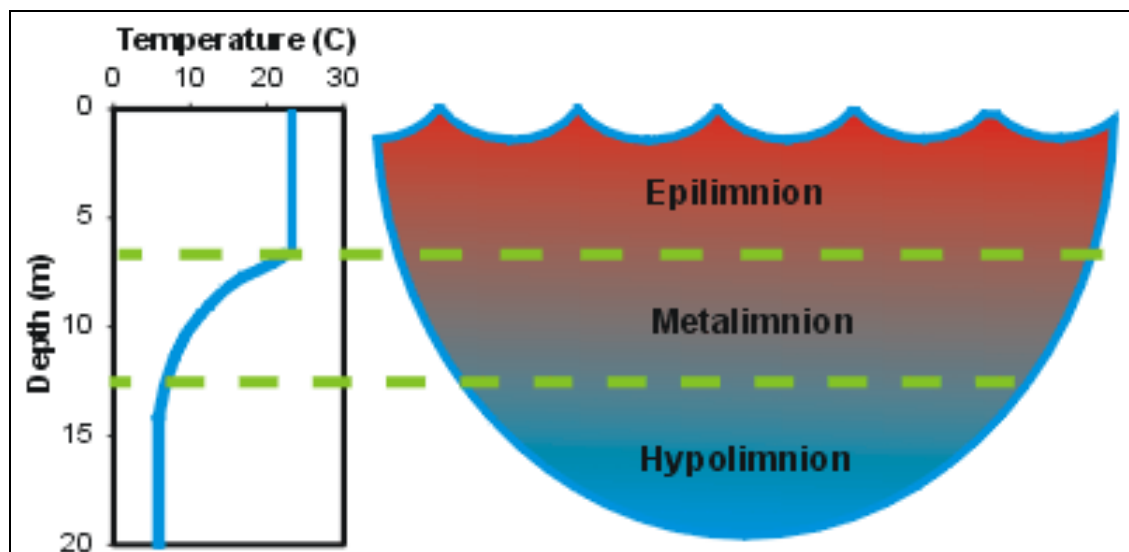


Aerobic degradation has the highest redox potential of 250 mV and, therefore, will be preferred over any anaerobic decomposition (Vance, 2002). According to principles of Gibb's Free Energy Laws, oxygen is thermodynamically preferred over iron as the terminal electron acceptor in bacterial systems having an energy content of -78.72 kJ/eq while the energy content of ferric iron reduction is -74.27 kJ/eq (Sawyer et al, 2003). As a result, elemental oxygen, when available at any concentration, is used as the oxidizing agent rather than iron (Baas et al, 1960). When oxygen concentrations are at or near zero, then microorganisms will use other electron acceptors, such as iron or manganese (Chen et al, 1983). These processes can cause a shift in equilibrium and drastically change the redox role of iron (Thomas et al, 1974). This phenomenon, in turn, significantly affects solubility (Mortimer, 1941).

### **2.3 Mantua Reservoir Under Reducing Conditions**

Many shallow and eutrophic reservoirs stratify for short periods and can go anaerobic in the hypolimnion for a period of from a few days to a few weeks during summer months (OCC, 1996). Depletion of oxygen results from chemical and biochemical decomposition of organic matter (Sawyer et al, 2003). This depletion can be offset, however, by photosynthesizing algae, which have been previously found in large populations in Mantua reservoir (DWR, 1996), wave action, or other processes that mix air with the impounded water. Respiration during the nocturnal period can quickly consume the budget of dissolved oxygen, especially during warm summer nights, of even shallow reservoirs (Tchobanoglous et al, 1985). If this oxygen is not replenished by reaeration (mixing) with the atmosphere, anaerobic conditions can occur (Thomas et al, 1974). In years past, the reservoir has been known to exceed Utah state water quality

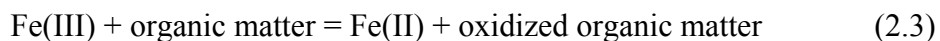
standards for dissolved oxygen and temperature (DWR, 1996). During warmer weather, dissolved oxygen profiles recorded during the late summer months in Mantua showed that dissolved oxygen concentrations decreased with increasing depth (Loveless et al, 1997). Furthermore, as indicated by the EPA temperature profiles, thermal stratification occurs in the Mantua system in the late summer and winter months (Loveless et al, 1997). As a result, layers exist in the reservoir at different temperatures and, therefore, do not mix. The density differences between the various water layers of the reservoir isolate the hypolimnion (OCC, 1996). This thermal stratification is illustrated by Figure 4 which shows the clinograde gradient.



**Figure 4. Clinograde oxygen distribution curve.**

This phenomenon, coupled with high biological oxygen demand (BOD) and high chemical oxygen demand (COD), causes very low dissolved oxygen levels in the hypolimnetic waters (Chen et al, 1983). High COD indicates the tendency for oxygen to be consumed by abiotic decomposition of organic matter. High BOD is indicative of a rapid uptake of oxygen through biodegradation of organic matter by microorganisms

(Sawyer et al, 2003). In Mantua Reservoir, the high BOD and COD is most likely caused by external phosphorus loadings from an upstream fish hatchery (Loveless et al, 1997). Furthermore, external loadings from decomposition of inundated herbaceous plants, leaves, and organically rich topsoil probably play a significant role (Chen et al, 1983). The high BOD supports organism growth in the reservoir which uses oxygen as they break down their food sources (Tchobanoglous et al, 1985). Since the reservoir is stratified, the lower hypolimnetic water does not mix with the surface water and the oxygen that is used by the organisms is not replenished, which can result in anoxic or anaerobic water (Chen et al, 1983). With the absence of oxygen, the redox couple of Fe(III) – Fe(II) can serve as a major pathway for the transfer of electrons from organic matter to ferric iron (Fe(III)) for organic matter decomposition. This can be a purely abiotic process described by the following equation (Thomas et al, 1974):



Typically the kinetics of this abiotic process are slow and do not occur to any appreciable extent without the presence of microorganisms. With the absence of oxygen as the terminal electron acceptor, the next most thermodynamically favorable terminal electron acceptor for biotic metabolic processes is iron that is used as shown in equation 2.3 (Sawyer et al, 2003). The gain of an electron changes the oxidation state of ferric iron Fe(III), which forms relatively insoluble compounds, to ferrous iron Fe(II), which forms much more soluble compounds. Therefore, when anaerobic conditions occur in the hypolimnion, iron is reduced, making the more soluble compounds favorable and the

water significantly under saturated with respect to total iron (Lovley et al, 2003). This results in the dissolution of iron and manganese from the metal-rich sediments (Mortimer, 1941).

In Mantua Reservoir, the anaerobic conditions in the hypolimnion are temporary and the water is probably reaerated each day with wind action or other mechanisms (Loveless et al, 1997). There is no evidence of long-term anaerobic conditions in any of the studies reviewed for this research. Based on observations of the reservoir, combined with measurements from the various reports, we believe that the lake does not typically have anaerobic conditions in the bottom layers and that this condition only occurs under limited conditions (Loveless et al, 1997). Since the redox reactions described above occur slower in colder temperatures, we believe these conditions occur during summer nights and in relatively warm, calm weather when biological activity would be heightened, mechanical mixing due to wind-action would be absent, and the sun would not be present to stimulate photosynthesis creating additional oxygen (Lovley et al, 2003). This is supported by the fact that no studies have measured anaerobic conditions, but that DO decreases with depth, significantly during hot weather, and that the staining only occurs intermittently in periods associated with the assumed conditions (Loveless et al, 1997).

## **2.4 Alkalinity**

The acidity, measured by pH, also contributes to conditions which affect iron solubility. There is a marked interaction between pH and the valence state and subsequent speciation of iron (Baas et al, 1960). Low pH significantly increases solubility of iron (Lovley et al, 2003). Humic acids produced as a result of aerobic decomposition are weak acids and are particularly effective in stabilizing high concentrations of ferrous iron



(Thomas et al, 1974). Past studies have found that ferrous iron is stable at low pH. In fact, even under oxygenated conditions, iron is soluble at low pH (Chen et al, 1983). Conversely, ferric iron is stable at high pH (Thomas et al, 1974). The amount of alkalinity in natural water defines the water's ability to maintain consistent pH levels (Sawyer et al. 2003). High alkalinity buffers pH change when anaerobic conditions develop in the hypolimnion (Ghosh, 1974). In fresh waters, total alkalinities range from 45 mg/L to 200 mg/L (Suchy, 2005). Based upon this range, Mantua reservoir has a relatively high alkalinity for an impounded fresh water supply with average values around 140 mg/L as calcium carbonate equivalent (Loveless et al, 1997). This is consistent with local geological descriptions stating a moderate to strongly alkaline soil surrounding Mantua reservoir (Loveless et al, 1997). Measurements indicate that Mantua reservoir is a bicarbonate system with average pH levels around 8.0 (Loveless et al, 1997). Due to the high alkalinity and the bicarbonate characteristics, the reservoir has a significant buffering capacity to resist the organic acids that result from anaerobic degradation (Sawyer et al, 2003). This buffer capacity would limit the ability of the water to have low pH conditions and would imply that dissolution of iron and manganese from the sediments is due to a change in the redox conditions, rather than a change in pH (Ghosh, 1974). This is supported by geo-chemical computer models discussed in Section 4.2 which replicate these results.

## **2.5 Solubility**

All solids are soluble to some degree in natural water systems (Sawyer et al, 2003). In the case of Mantua reservoir, the more prevalent Fe(III) mononuclear complexes are relatively insoluble with a solubility-product ( $K_{sp}$ ) for the ferric iron-

hydroxide compound,  $\text{Fe}(\text{OH})_3 (s)$  at  $25^\circ\text{C}$ , of  $6 \times 10^{-38}$  (Sawyer et al, 2003). This is the dominant iron species for Mantua reservoir in the presence of oxygen (Lathen et al, 2006). When anaerobic conditions occur, the redox conditions change. With this change, ferric iron,  $\text{Fe}(\text{III})$ , is replaced as the favorable species with ferrous iron,  $\text{Fe}(\text{II})$ , as described in Section 2.3. The solubility-product for the ferrous iron-hydroxide compound,  $\text{Fe}(\text{OH})_2 (s)$ , is  $5 \times 10^{-15}$ . This is 23 orders of magnitude greater than the oxidized form,  $\text{Fe}(\text{OH})_3$ , at  $25^\circ\text{C}$  (Sawyer et al, 2003). Therefore, under anaerobic conditions,  $\text{Fe}(\text{II})$  hydroxide complexes in the sediment of natural water systems have a greater tendency to dissolve into the water column (Lovley et al, 2003). Other iron compounds typically found in the sediments of natural water systems behave in a similar fashion (Sawyer et al, 2003).

The redox process is reversed when the water is reaerated thus reintroducing oxygen, and changing the redox potential of the system (Baas et al, 1960). When this happens, the relatively insoluble  $\text{Fe}(\text{III})$  compounds are favored resulting in iron precipitation from the water column to the sediment or onto surfaces in contact with the irrigation water (Thomas et al, 1974).

Iron reduction in the sediment is driven by both abiotic and biotic reactions which cause reducing conditions to occur. These processes are coupled to the cycling of carbon, sulfur, and phosphorus (Lith, 2005). Evidence shows, however, that iron and manganese reduction rates correspond to bacterial reduction rates involved in the oxidation of organic matter (Lith, 2005). Furthermore, because of the slow kinetics involved in the abiotic chemical reactions, it is unlikely that they occur without microbial decomposition (Fortin et al, 2005). Microbes that would use iron as an electron acceptor would tend to

accelerate dissolution (Fortin et al, 2005). Under reducing conditions, the favorable iron state changes from Fe(III) to Fe(II) (Bohn, 1971). This raises the equilibrium levels of dissolved iron in the system several orders of magnitude (Lathen et al, 2006).

### **3 Water Sample Analysis**

This study was designed to determine if the proposed mechanisms for iron solubility and precipitation were occurring in Mantua Reservoir. The study had three different parts: field sampling and measurements, laboratory experiments, and computer modeling. This section describes the water samples that were taken to support the field measurements and laboratory experiments.

All water samples collected in this study were taken off a pier in the reservoir approximately 60 yards from the outlet pipe.

#### **3.1 Procedure**

The physical location of the sampling sites was chosen for its accessibility to deeper regions of the reservoir as well as for the proximity to the outlet pipe. Samples were collected from a pier on the north arm of the reservoir. Sediment samples were obtained using a sand auger with a 10 foot extension at an approximate water depth of 11 feet.

Reservoir sampling was performed by me and Scott Lathen, a graduate student at Brigham Young University. A YSI Environmental Technologies Series 58 dissolved oxygen probe was used to measure temperature and dissolved oxygen concentration at specific depths. Anaerobic water was stored in standard BOD bottles in contact with bottom sediment and placed in the dark during transport and storage and kept at room

temperature. Aerobic waters were stored in a five-gallon bucket in contact with bottom sediment and remained exposed to the atmosphere and ambient light conditions. Sediment samples were placed in a five-gallon bucket and remained exposed to ambient light and temperature. Redundant measurements of bench scale model samples used were averaged for results. All samples were tested and stored in the Environmental Lab of the W.W. Clyde Building at Brigham Young University in Provo, Utah.

### **3.2 Sampling Schedule**

Preliminary tests used for qualitative assessments were taken from samples acquired on November 17th of 2005 at approximately 3:00 P.M. Water samples used for analysis by ICP and spectrophotometer methods were collected on the 31<sup>st</sup> of March, 2006 preceding spring turnover and then again on the 19<sup>th</sup> of May, 2006.

### **3.3 Parameters Measured**

Physical parameters measured at the reservoir site were temperature and dissolved oxygen. These results are presented below.

Chemical parameters measured at the Brigham Young University Environmental Laboratory were alkalinity and metal analyses of the water and bottom sediments. The metals analyzed were total iron, manganese, and calcium.

### **3.4 Laboratory Methods**

Aqueous and sediment samples were analyzed using Standard Laboratory Procedure Methods and EPA methods. Samples were analyzed using Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) and Spectrophotometric instrumentation.

Reaeration of anaerobic samples for the third bench scale model was done using Erlenmeyer flasks open to the atmosphere on stir plates for each given reaeration-time interval.

#### **3.4.1 Spectrophotometer**

Aqueous samples from bench scale models were prepared and analyzed according to the Phenanthroline standard method 3500-Fe D for total iron analysis (APHA, 1995). All aqueous samples were vacuum filtered using a 0.45 micron Falcon #7104 filter paper to remove suspended and colloidal particles. Deviating from the standard method, anaerobic model samples were acidified prior to filtration to prevent ferrous iron from being oxidized and precipitated onto the filter paper. This allowed an accurate measurement of dissolved iron in the water of the bench-top model and more closely represent actual conditions in the reservoir. Additionally, when developing the standard iron solutions for calibration curves, ferric chloride was used as the iron sources instead of the iron wire called for in the standard method.

Sediment samples were acid-digested according to EPA method 3050B (EPA, 2004). Upon volume reduction, sediment samples were prepared according to the Phenanthroline standard analytical method 3500-Fe D used for total iron analysis (APHA, 1995).

Calibration curves were developed from a prepared standard solution with known concentrations and fitted to a linear relationship according to Beer's Law. Unknown concentrations were then evaluated in reference to this calibration curve proportional to the absorbance of the calibrated samples. Each test used a different calibration curve. Concentrations for the calibration curves varied with each test date in an attempt to

eliminate systematic errors. All but one test used five calibration points. Bench scale models used concentrations ranging from 0.5 – 25 ppm. Larger concentrations up to 50 ppm were added to the curves for tests that included sediment samples.

### **3.4.2 Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP – AES)**

Sediment samples were prepared according to EPA Method 3050B for acid digestion of sediments, sludges, and soils (EPA, 2004). Aqueous samples were prepared according to EPA Method 200.7 for the determination of dissolved analytes in ground, drinking, and surface waters (EPA, 2001).

As with the spectrophotometer, there was a deviation from the standard methodology for the anaerobic sample preparation. The methods call for the sample to be filtered prior to method application. Anaerobic samples were acidified prior to filtration to prevent ferrous iron precipitation upon exposure to oxygen. This was done to measure the concentration of dissolved iron in an anaerobic environment in the reservoir. Otherwise, iron could have precipitated onto the filter paper because the sample was slightly aerated during filtration and handling.

Samples were created with known concentrations as calibration for the measurement of unknown concentrations. This was done according to the standard method for IPC analysis. ICP directly interpolates the average intensity of the unknown with the intensity of the known samples at their given concentrations.

## **4 Experiments and Simulations**

### **4.1 Bench Scale Simulations**

Bench scale experiments were performed to replicate reservoir conditions leading to a staining event. Three sequential models were (1) normal aerobic conditions, (2) anaerobic conditions, (3) re-aeration of anaerobic waters. These models replicate the conditions thought to cause staining and were used to describe the redox behavior of hypolimnetic waters in Mantua Reservoir throughout the year. The water resulting from these three models, were analyzed using various analytic laboratory procedures were performed to measure total iron in solution for each case. The results were then used to predict if this model of the reservoir conditions could cause ferric staining. Additionally, the reaerated model was used to evaluate a possible treatment to prevent staining.

#### **4.1.1 Aerobic Model**

The aerobic model simulates complete-mixed conditions that are the typical conditions of Mantua Reservoir and represent the water that would not cause any type of ferric staining when the water is used for irrigation. These conditions typify a shallow, well-aerated reservoir that acts as complete-mixed batch reactor. Under these conditions, most iron compounds present in the bottom muds or in the water column would be oxidized and precipitated in the form of Fe(III). This model was expected to and did have



the lowest iron concentrations. These conditions closely match the observed conditions in Mantua where dissolved oxygen and temperature levels are relatively uniform throughout all depths of the water column. (Loveless et al, 1997). This model used water sampled from the epilimnion of the reservoir that was measured to be near oxygen saturation levels for the corresponding temperature.

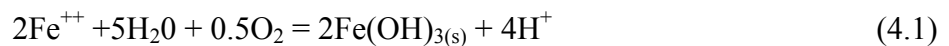
#### **4.1.2 Anaerobic Model**

The anaerobic model simulates the narrow anaerobic zone of the hypolimnion during late summer. This bench-scale model replicates that conditions that could cause iron to dissolve from the sediments. This replicates water that, through microbial processes, has had dissolved oxygen levels reduced to virtually zero. This bench-scale model was implemented by isolating the sampled reservoir water in contact with sampled bottom sediments until dissolved oxygen concentrations were 0.01mg/L, which was usually a period of approximately 5 days. The anaerobic environment developed caused reducing conditions and dissolution of iron. The bottom sediments were found to be relatively rich in iron (Loveless et al, 1997). The anaerobic bench scale model was designed with the water in contact with these sediments to replicate conditions at the bottom of the reservoir and to measure the potential amount of total iron that could be reduced to a ferrous state and dissolved into the water column. This model represents of the conditions present in the reservoir during a staining event and produced the highest dissolved iron concentrations.

#### **4.1.3 Reaeration**

The reaerated model used the water from the anaerobic model, after the iron was dissolved from the sediments. This water was stirred for a predetermined period of time.

This action reoxidized the water column and caused the Fe(II) species to oxidize and precipitate out of solution in the form of Fe(III). The time required for uncomplexed ferrous iron to undergo oxidation to the ferric state is dependent upon pH, temperature, dissolved oxygen levels, and the presence of other soluble ions (Vance, 2002). The lower the pH values and temperature the longer the time required for the completion of the oxidation reaction. Reaeration times were varied in an attempt to ascertain general trends with respect to the kinetics of iron precipitation. In the presence of sufficient concentrations of dissolved oxygen, the oxidation of ferrous iron, Fe(II), to ferric iron, Fe(III), is relatively rapid and occurred spontaneously in the laboratory models by chemical means alone and did not require a biological catalyst reaction (Thomas et al, 1974). The critical dissolved oxygen concentration is 2 mg/L. Below this value, ferrous iron oxidation occur much slower (Vance, 2002). This reaction can be described by the following equation (Thomas et al, 1974):



As a result of this reaction, total dissolved iron concentrations in the water would be less than that of the anaerobic water due to precipitation of the dissolved  $\text{Fe}^{++}$  to solid  $\text{Fe}(\text{OH})_3$  (Chen et al, 1983). The rate at which the iron would precipitate in this model is a function of reaeration duration and the reaction kinetics, which are beyond the scope of this study. The re-aeration model symbolizes the mechanisms that cause staining (reaeration of the irrigation water during sprinkling) and potential treatment strategies that could be used to prevent staining-conditions from developing. One method to

implement this treatment option would be aerating the hypolimnion of the reservoir to prevent the transition from the aerobic (low dissolved iron) to anaerobic (high dissolved iron) conditions during late summer.

## **4.2 Computer Modeling**

Computer modeling techniques were used to replicate the proposed staining mechanism. The three aforementioned bench scale models were replicated in a computer simulation to ascertain if the transition of the Mantua water from aerobic to anaerobic dissolved solid phase iron found in the bottom sediments was theoretically possible (Lathen et al,2006). As with the bench scale models, reoxidation of the anaerobic water was modeled to evaluate iron precipitation and remediation.

The software program used to evaluate the bench scale models is a geochemical program called PHREEQC and is designed to model the chemical reactions of aqueous solutions and their interaction with solid and gas phases under equilibrium conditions. (Parkhurst et al, 1999). For the Mantua study, a sequential batch model encompassing the three bench scale models was used to predict various molar concentrations in aqueous solution of various iron and manganese compounds under prescribed environmental conditions. Each bench scale model determined specific environmental conditions that were modeled using the computer code (Parkhurst et al, 1999). Input parameters for the aerobic model were based on information from the previous EPA study (Lathen et al. 2006). Anaerobic conditions were modeled by depriving previous aerobic conditions of oxygen and allowing methane to equilibrate with the natural water system replicating the processes thought to cause anaerobic conditions in the reservoir. This stage was used to determine the amount of iron that could potentially dissolve from the sediments under

these conditions. The final stage of the model was the reoxygenation of the anaerobic system to determine the amount of ferrous iron solids that could precipitate. Table 1 presents the main input parameters used to create the Mantua model in PHREEQC. It is inclusive of all elements and their corresponding molar concentrations present in the water at the time of the EPA study. Additionally, compounds present in the equilibrium phase of each bench scale model are shown for its corresponding batch model in the PHREEQC program. Note that both oxygen and carbon dioxide in the table were input as the log of the respective partial pressures in units of atmospheres (Lathen et al, 2006).

**Table 1. Initial Model Mantua Reservoir Staining Conditions**

<b>Elements</b>	<b>Concentration (mg/L)</b>	<b>Conditions</b>
Ca	27.9	pH 8.6
Mg	17.2	Temperature (°C) 23
Na	7	<b>Equilibrium Phases: Batch A and C</b>
K	1.5	
Cl	8.3	O <sub>2</sub> (g)
C as CO <sub>2</sub> (g)	-3.5	Fe(OH) <sub>3</sub> (a)
S <sup>6+</sup> as SO <sub>4</sub> <sup>2-</sup>	10	Anhydrite
Fe <sup>3+</sup>	5	Aragonite
Fe <sup>2+</sup>	1	Siderite
		<b>Equilibrium Phases: Batch B</b>
Ba	0.0423	Fe(OH) <sub>2</sub> (a)
Mn	0.0158	CH <sub>4</sub> (g)
Alkalinity as HCO <sub>3</sub>	138	
O <sup>0</sup> as O <sub>2</sub> (g)	-0.785	



## **5 Results**

### **5.1 Field Results**

Figures 5 and 6 present the temperature and dissolved oxygen readings that were recorded during field data collection on March 31<sup>st</sup>, 2006 and May 19<sup>th</sup>, 2006, respectively. Figure 5 demonstrates the inverse relationship of temperature and dissolved oxygen relative to depth. These data are typical results for a stratified reservoir and were collected just prior to spring turnover. Figure 6 is indicative of a well-mixed reservoir with temperature and dissolved oxygen levels as a function of depth remaining relatively constant.

The results shown in Figures 5 and 6 show two conditions that support the mechanisms proposed in this thesis that cause staining. The first is that Mantua Reservoir, though shallow, does demonstrate stratification under certain environmental conditions. The second is that for most conditions the reservoir is well oxygenated to that dissolved iron is relevantly low and would not precipitate causing staining.

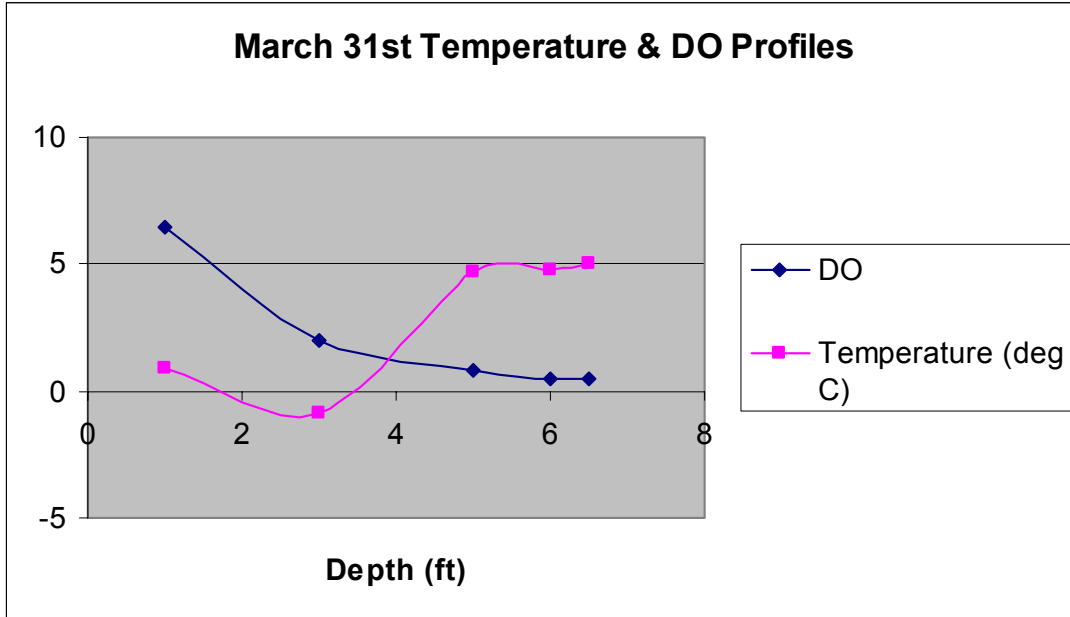


Figure 5. Temperature and Dissolved Oxygen vs. Depth measured on March 31.

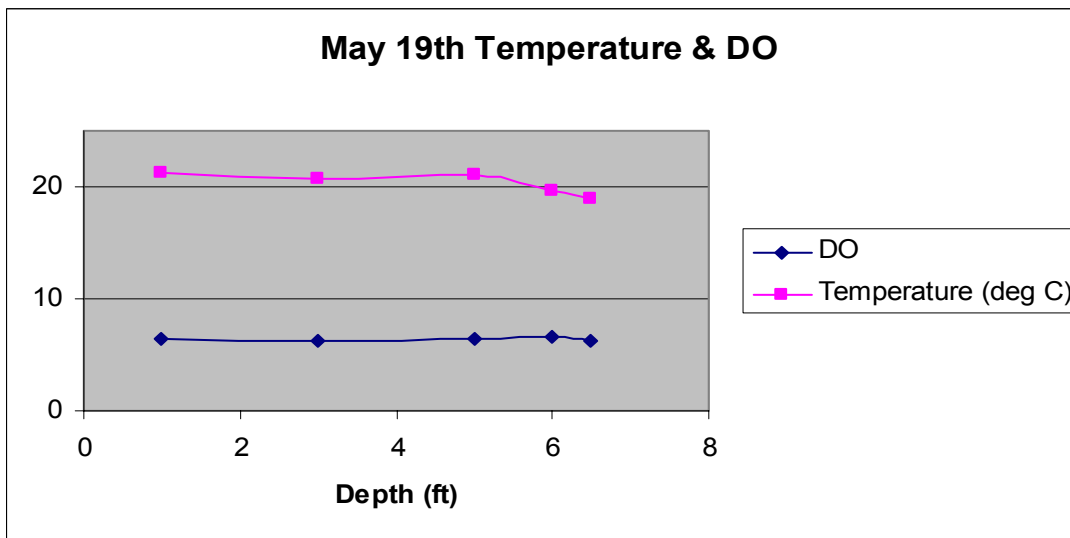
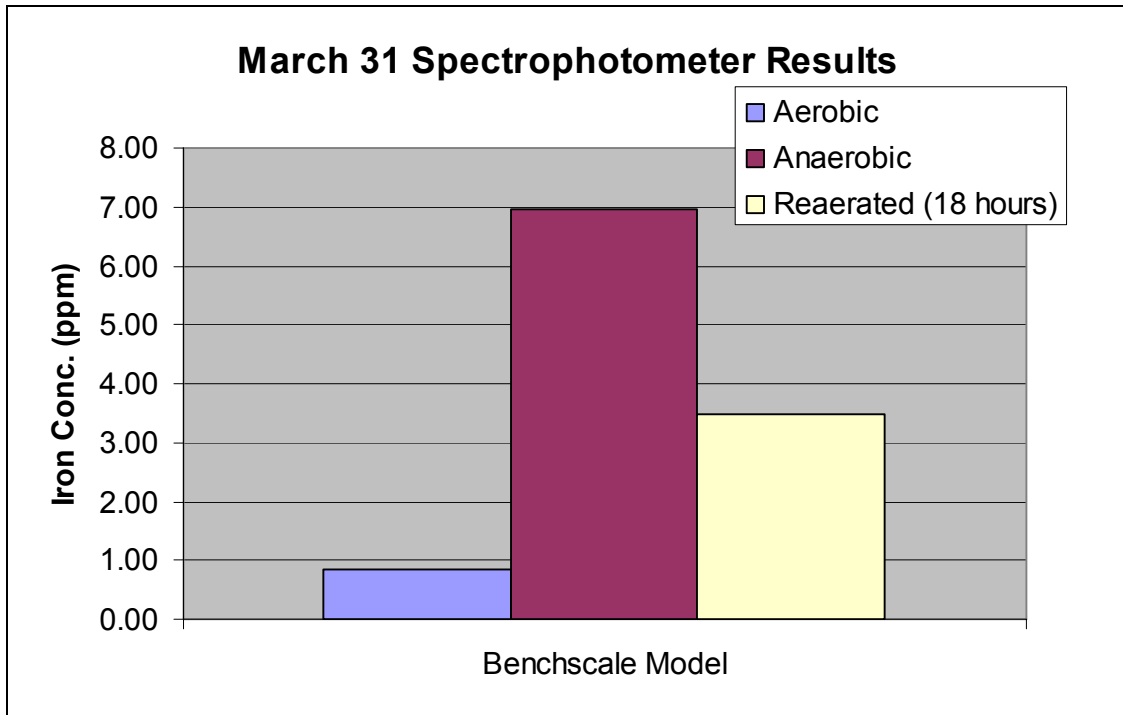


Figure 6. Temperature and Dissolved Oxygen vs. Depth measured on May 19.

## 5.2 Laboratory Results

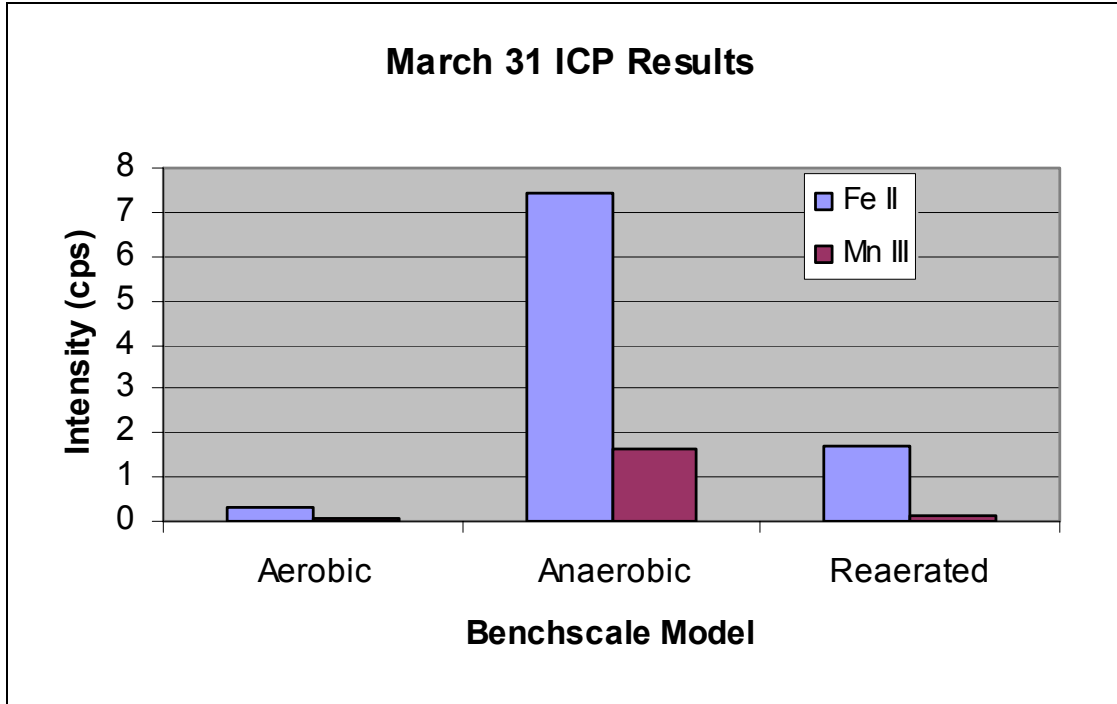
The purpose of bench scale modeling was to reproduce the ferric staining conditions that are thought to occur in the laboratory and determine if these conditions to



**Figure 7. Spectrophotometer results from March 31.**

lead to high dissolved iron and subsequent precipitation causing staining. The laboratory tests analyzed the amount of soluble iron in the water column under specific environmental conditions. Dissolved iron was measured using two separate laboratory procedures: the phenanthroline method and ICP (APHA, 1995) & (EPA, 2001). The test results are labeled by the date of field sample collection used in the laboratory procedures. Due to preparation time, tests were performed a few days after the collection dates. Dissolved oxygen concentrations were measured to be 0.01 mg/L for all anaerobic models used in this analysis. However, it should be noted that the high concentrations of BOD in the reservoir allowed for the development of the anaerobic laboratory conditions in a relatively short period of time. Due to the variability for saturation of dissolved oxygen levels in water samples exposed to the atmosphere, DO levels were not measured for the aerobic and reaerated bench scale models. It can be assumed, however, that aerobic water samples were in proximity to saturation for the given temperature.





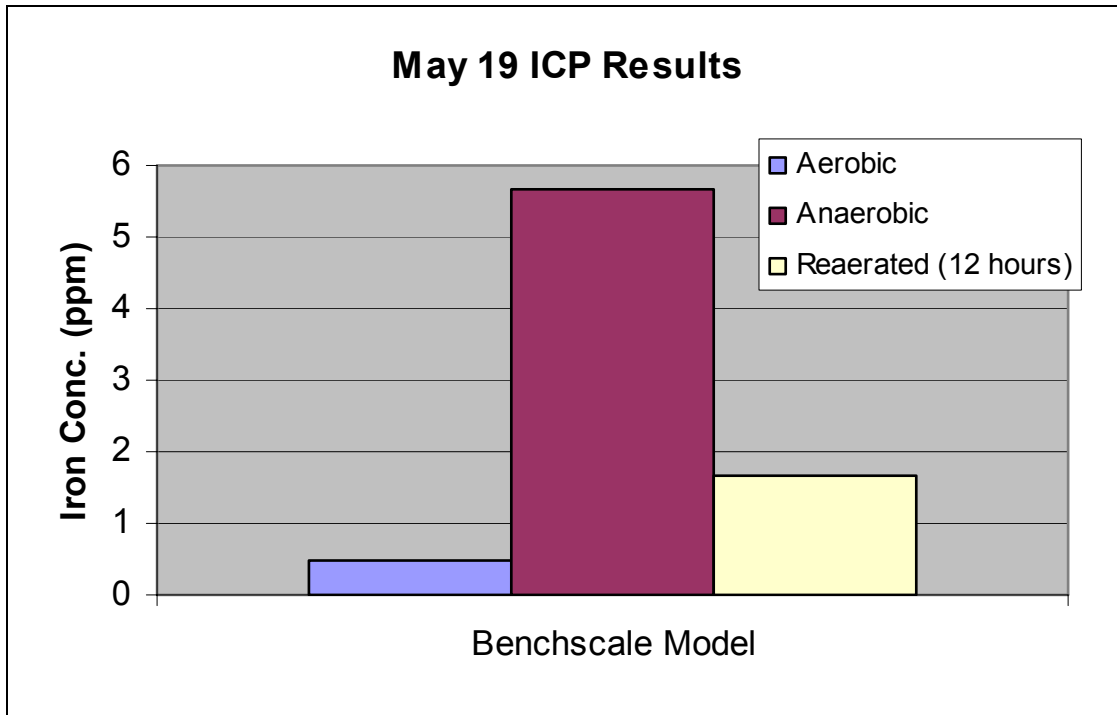
**Figure 8. Results from the March 31 samples using the ICP.**

Figure 7 qualitatively indicates that the amount of dissolved iron in the anaerobic water sample is over 7 times that of the ambient aerated water found at the surface. The anaerobic model for this test measured contained 6.94 mg/L of dissolved iron, while the aerobic model measured 0.85 mg/L of iron. For this particular test series, the ICP was used to measure dissolved manganese concentrations. Reaeration of the anaerobic model was for 18 hours and reduced the dissolved iron concentration by approximately 50% down to 3.46 mg/L. It should be noted that the anaerobic sample was measured after only 45 minutes of reaeration, however this not shown in the figure. After 45 minutes of reaeration, the anaerobic model decreased in dissolved iron concentration to 5.91 mg/L, which is about a 15% decrease. Further evaluation into the relationship of reaeration time

as a function of dissolved iron concentrations requires an in depth study into the kinetics of the equilibrium phase and is beyond the scope of this study.

Results from the ICP test were conducted on the same samples for each model, with the exception of the reaerated model, where reaeration was extended to 48 hours. Additionally, manganese concentrations were also evaluated in each model. As with the spectrophotometer, Figure 8 shows that under anaerobic conditions, iron and manganese concentrations are many times higher (approximately 20 times) than in oxygenated water typical of a well-mixed reservoir. Aerobic model concentrations for iron and manganese were 0.331 mg/L and 0.033 mg/L respectively. Anaerobic model concentrations for iron and manganese were 7.44 mg/L and 1.61 mg/L, respectively. This yields a margin of variance of about 3.5% between the ICP and spectrophotometer tests in measuring anaerobic iron concentrations. The time of reaeration for the ICP was significantly longer than what was measured for the spectrophotometer to observe any variance in metal concentrations as a function of reaeration time. After 48 hours of reaeration, the dissolved iron concentration of the anaerobic model had decreased from 7.44 mg/L to 1.7 mg/L and manganese had decreased from 1.61 mg/L to 0.13 mg/L.

Bottom sediments from samples collected on this date were analyzed for total iron content. The results were very high and out of the calibration range for both the ICP and spectrophotometer. Consequently, extrapolation from the calibration curve was considered to be crude, but it can be assumed with some certainty that total iron concentrations of the bottom sediments were over 100 mg/L or 10,163 mg/kg.

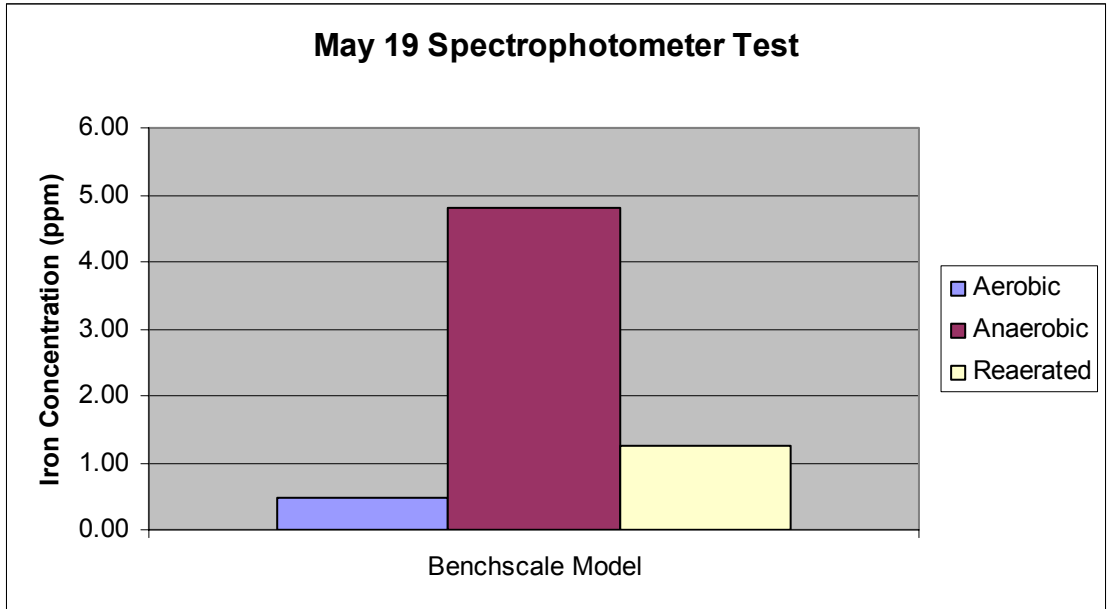


**Figure 9. Results from the May 19 samples using the ICP.**

It can be seen in Figure 9, that the data collected from the reservoir on a different date validates previous findings. The anaerobic model contains significantly more dissolved iron in the water column than that of the aerobic model. Due to the wavelength used to measure iron in the ICP, aerobic model iron concentrations were only determined to be less than 0.5 mg/L, these wavelengths could not measure below this value. Anaerobic model concentration was measured at 5.66 mg/L, a factor of at least 10 times greater. After 12 hours of reaeration the iron content in the anaerobic model decreased by 70% to 1.66 mg/L, showing significant precipitation of the iron from the anaerobic conditions.

Bottom sediment was also evaluated a second time for total iron using a larger range of calibration samples to allow higher concentration measurements. The ICP measured 167 mg/L, which was calculated to be 16,500 mg/kg dry weight of total iron in the sediments. This high amount of total iron in the bottom sediment is validated by the

metal analysis done by the Clean Lakes Study in 1996, which found that the north arm of the reservoir contained 16,600 mg/kg of total iron in the sediments (Loveless et al, 1997).



**Figure 10. Results from the May 19 samples using the spectrophotometer.**

**Table 2. Model Variance for Spectrophotometer Measurements**

Model	Variance, %
Aerobic	14.0
Anaerobic	5.0
Reaerated	3.6

The spectrophotometer test results for the water samples collected on May 19<sup>th</sup> (shown in Figure 10) mirror previous findings. The reaeration interval for this test was 36 hours. Repeat measurements were made for each of the model samples to observe precision of the spectrophotometer test. Average values for each model are expressed in Figure 10. Variances for each model are shown in Table 2.

Accuracy of the spectrophotometer for this particular data set was calibrated through a pseudo unknown. This was accomplished through taking a known concentration of iron in aqueous solution and measuring absorbance and then plotting the value on the calibration curve. The 4 ppm sample was measured at 4.38 ppm according to the calibration curve for that data set yielding 4.5% error.

An additional accuracy check was made on the May 19<sup>th</sup> spectrophotometer test results by means of ICP validation. Samples prepared for the spectrophotometer were also prepared for analysis by the ICP. Shown in Table 3 are the results of the validation test with the corresponding error percentages between the two instruments.

**Table 3. Comparison of ICP and Spectrophotometer Measurements**

<b>Model</b>	<b>ICP</b>	<b>Spectrophotometer</b>	
	<b>Fe II, mg/L</b>	<b>Fe II, mg/L</b>	<b>Variance, %</b>
Aerobic	0.81	0.46	27.6
Anaerobic	4.53	4.78	2.7
Reaerated	1.91	1.29	19.6

An unexpected, but theoretically consistent, result was observed during analysis of the data from the May 19<sup>th</sup> test. It was found that anaerobic samples that had been drawn in proximity to the sediment-water interface contain significantly higher concentrations of ferrous iron. This is due to the fact that the water in the sample flask was not evenly aerated, the water near the sediment contained less oxygen and higher iron than that near the top of the flask. Spectrophotometer readings of one such sample measured 10.72 mg/L of ferrous iron while validation with the ICP measured 10.90 mg/L of ferrous iron.

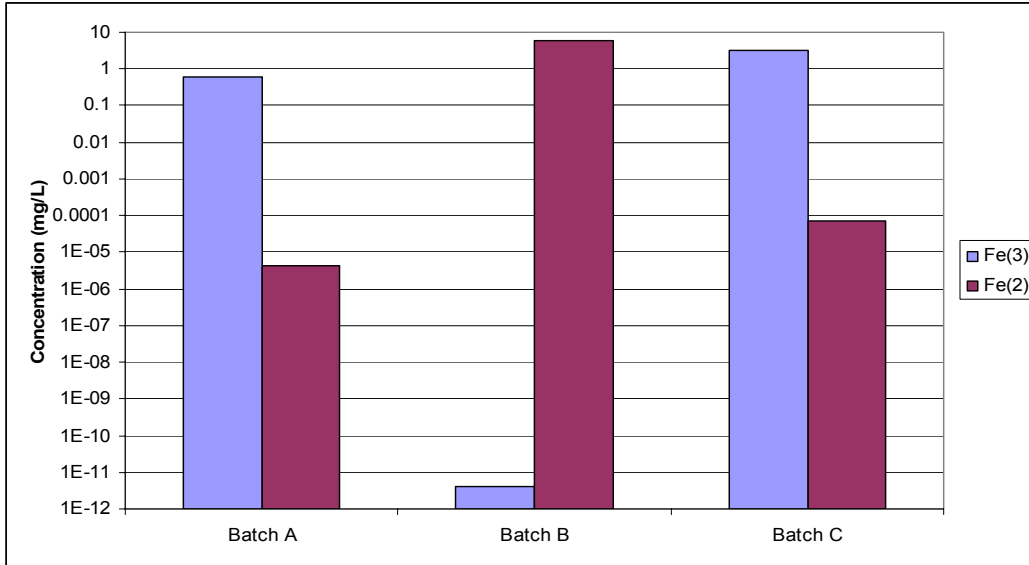
### 5.3 Computer Modeling Results

Results from the PHREEQC program validate bench scale models tested in the laboratory. Table 4 shows the results in tabular form.

**Table 4. Computer Results From the Three Models**

	Trial and Batch	Element	Atomic Mass (g/mol)	Moles in Solution	[C] (mg/L)
Aerobic Model	47-A	Fe(II)	55.8	7.73E-11	4.31E-06
	47-A	Fe(III)	55.8	1.1E-05	0.615
	47-A	O	16	0.000405	6.46
Anaerobic Model	47-B	Fe(II)	55.8	0.0686	5.97
	47-B	Fe(III)	55.8	5.37E-14	4.50E-12
	47-B	O	16	0	0
Re-Aerated Model	47-C	Fe(II)	55.8	1.33E-09	7.42E-05
	47-C	Fe(III)	55.8	5.97E-05	3.32
	47-C	O	16	0.000442	7.05

From the data presented in Table 4, it is evident that as the water becomes anaerobic, the computer predicts that levels of soluble iron significantly increase and iron compounds will dissolve in order to achieve equilibrium. As oxygen is reintroduced into the anaerobic system, iron saturation disrupts equilibrium and will precipitate. Figure 11 is a graphical representation of the results. Batch A is the aerobic model. Batch B is the anaerobic model while Batch C is the reaerated model (Lathen et al, 2006).



**Figure 11. Results from the computer modeling predictions.**

## 6 Conclusion

Through a literature review, analysis of bench scale models, field data, and computer modeling I have concluded that the ferric staining in Brigham City's secondary water system is most likely caused by seasonal anaerobic conditions in the hypolimnetic waters of Mantua reservoir that dissolve iron from the iron-rich sediments. This iron is subsequently precipitated when the water is reaerated during irrigation. Temperature gradients that prevent water column mixing combined with the high concentrations of BOD causes the dissolved oxygen deficits in the hypolimnion. The geochemical transition from aerobic to anaerobic changes the thermodynamically favorable species of iron and manganese thus changing from relatively insoluble forms to species which are highly soluble. As a result, higher concentrations of dissolved iron and manganese are found in the anaerobic water than in the oxygenated aerobic water. This was true for both laboratory tests using water from Mantua Reservoir and in the computer model results. In addition to abiotic processes driving the iron and manganese reduction, it is likely, though not proven in this research, that the iron and manganese dissolution phenomenon is catalyzed and accelerated through microbial-induced reduction of iron for energy synthesis.

Laboratory analysis of the concentration of iron and manganese in samples used in the bench scale models confirm that high amounts of insoluble iron in the form of



Fe(III) are found in the benthic sediments. Additionally, laboratory tests show that anaerobic water immediately adjacent to the bottom sediments contains higher levels of dissolved iron than water near the top of the beaker that was exposed to oxygen in the air. Laboratory results show that iron concentrations can be elevated in the bottom waters of an open system (exposed to air). Considering that the inlet pipe invert elevation for Brigham City's secondary water system is within the bottom meter of the reservoir would support the hypothesis that appreciable amounts of dissolved iron can enter the pipe at the reservoir when conditions are such that significant amounts of iron and manganese are dissolved from the bottom sediments. Since the pipe is closed to the atmosphere, atmospheric exposure to allow oxygen to dissolve into the water to initiate the redox reactions to cause iron and manganese to change to relatively insoluble forms and cause precipitation does not take place until release points where past staining events have been observed. Laboratory tests and computer models were able to replicate these conditions that cause the iron and manganese to precipitate upon reintroduction of oxygen into the equilibrated anaerobic system, molar ferrous iron concentrations of iron and manganese will decrease as molar concentrations of ferric iron and manganese increase. Subsequent precipitation of ferrous iron and manganese will result as the oxygenated system progresses towards equilibrium thus causing staining.

The results that demonstrate that increased iron and manganese aqueous concentrations increase as the result of anaerobic conditions and that these levels are reduced with the reaeration of the water suggest possible mitigation measures for the staining problems. If the water in Mantua Reservoir is aerated to prevent anaerobic conditions from developing and dissolving metals from the sediments, staining should be

eliminated or reduced. Alternatively, this aeration could be accomplished at other points in the distribution system.



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## Appendix A: Field Data

**Table A1. March 31<sup>st</sup> Field Data Results**

<b>Depth (ft)</b>	<b>Temp. C</b>	<b>DO (mg/L)</b>
1	0.9	6.50
3	-0.9	2.00
5	4.7	0.79
6	4.8	0.51
6.5	5.0	0.48

Alkalinity = 180 ppm  
DO = 7.3 ppm

**Table A2. May 19th Field Data Results**

<b>Depth (ft)</b>	<b>Temp. C</b>	<b>DO (mg/L)</b>
1	21.2	6.5
3	20.8	6.3
5	21.1	6.4
6	19.7	6.6
6.5	18.9	6.3

Alkalinity = no data  
DO = 6.7 ppm





## Appendix B: Laboratory Data

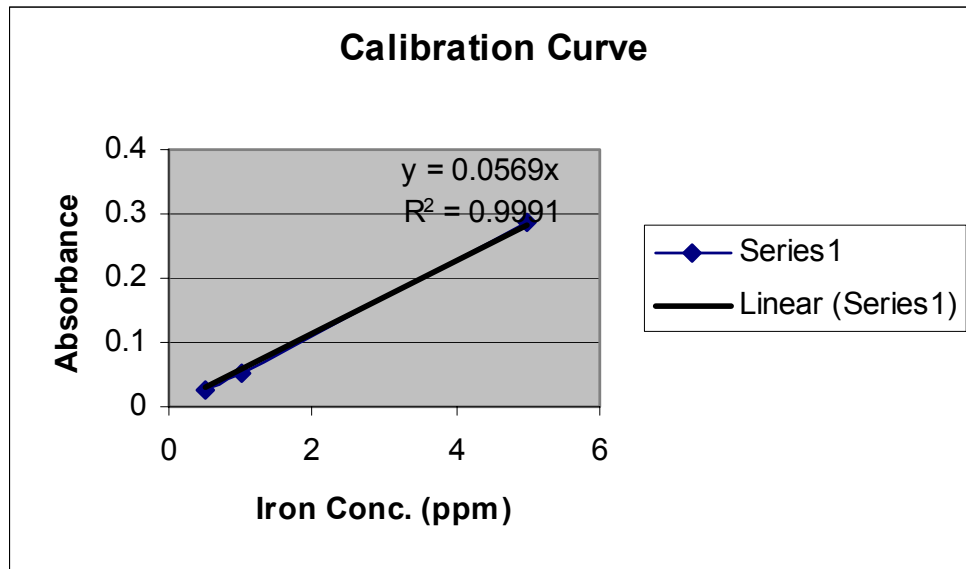
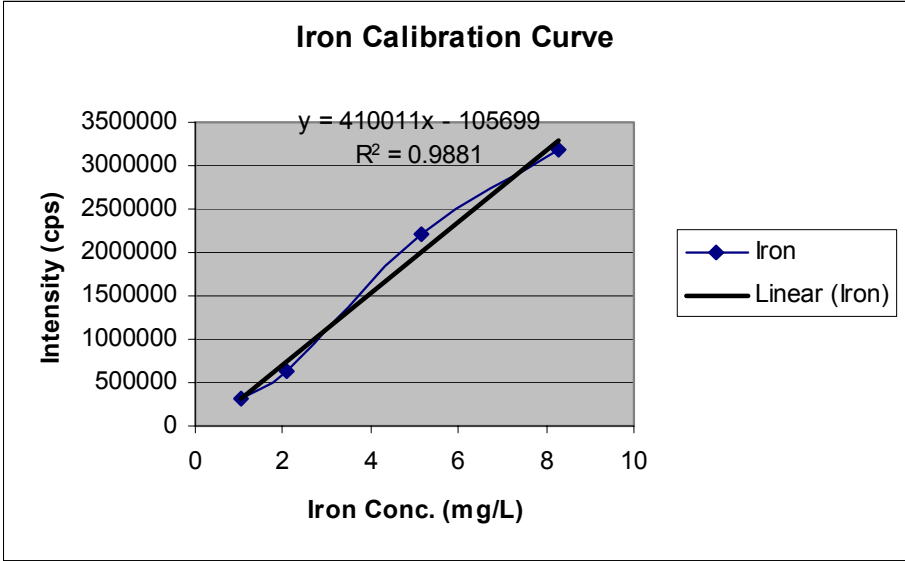


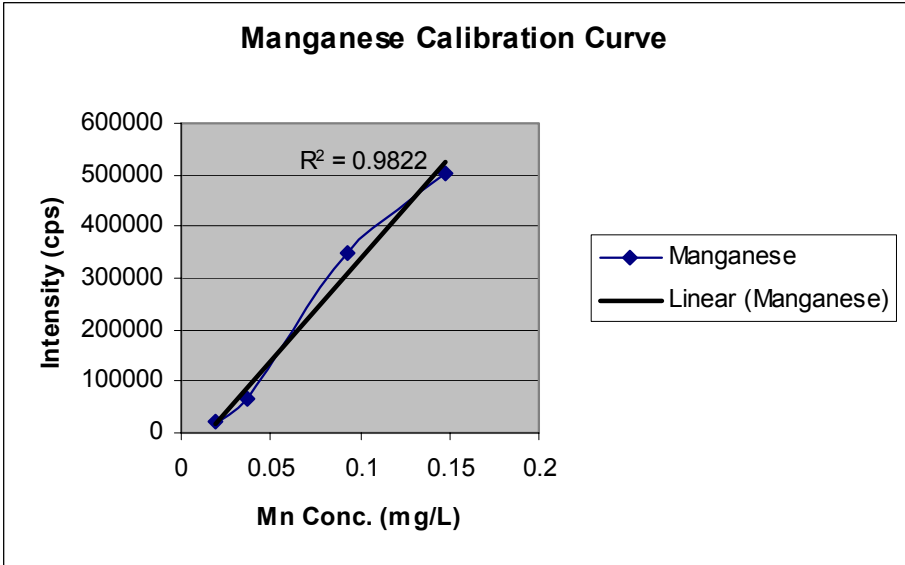
Figure B1. Calibration Curve for March 31<sup>st</sup> Spectrophotometer Test.

Table B1. Raw Data for Spectrophotometer Results

Model	Absorbance	Total Iron (ppm)	Comments
Sediment	2.275	<100	out of calibration range
Aerobic	0.043	0.85	
Anaerobic 1	0.39	6.94	
Re-aerated 1	0.331	5.91	45 min. reaeration
Re-aerated 1	0.192	3.46	18 hours reaeration
Anaerobic #46	0.875	15.47	sed-water interface
Re-aerated #46	0.211	3.80	48 hour reaeration



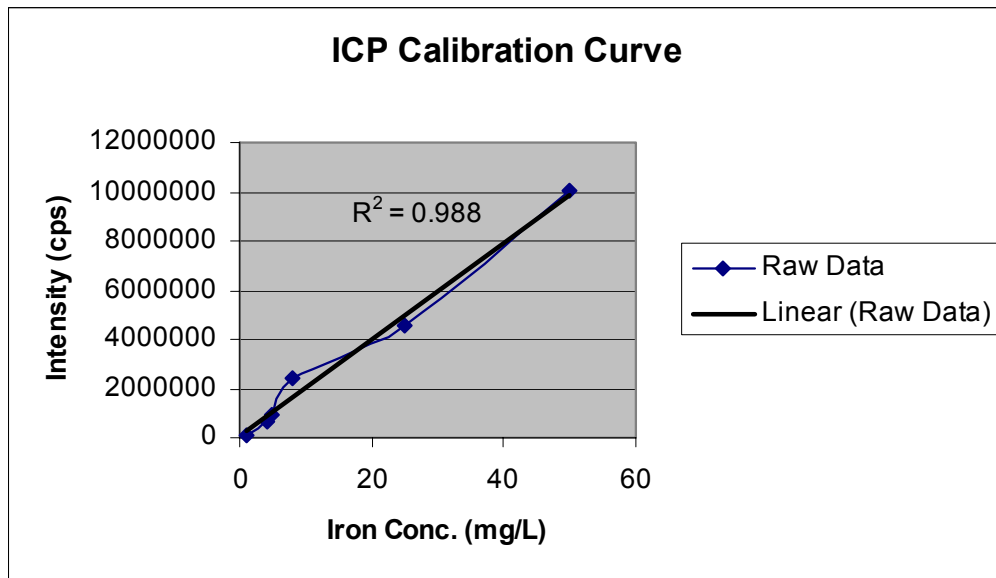
**Figure B2. March 31<sup>st</sup> ICP Test Calibration Curve.**



**Figure B3. March 31<sup>st</sup> ICP Test Calibration Curve.**

**Table B2. Raw Data for March 31<sup>st</sup> ICP Test**

<b>Model</b>	<b>Total Iron (mg/L)</b>	<b>Total Mn (mg/L)</b>	<b>Comments</b>
Aerobic	0.33	0.03	
Anaerobic	7.44	1.61	
Reaerated	1.70	0.13	48 hours re-aeration time



**Figure B4. May 19<sup>th</sup> ICP Calibration Curve.**

**Table B3. Raw Test Results for May 19<sup>th</sup> ICP (1<sup>st</sup> Run)**

<b>Model</b>	<b>Total Iron (mg/L)</b>	<b>Comments</b>
Aerobic	>0.5	
Anaerobic #46	5.66	
Reaeration #46	1.66	12 hours
Sediment	167	

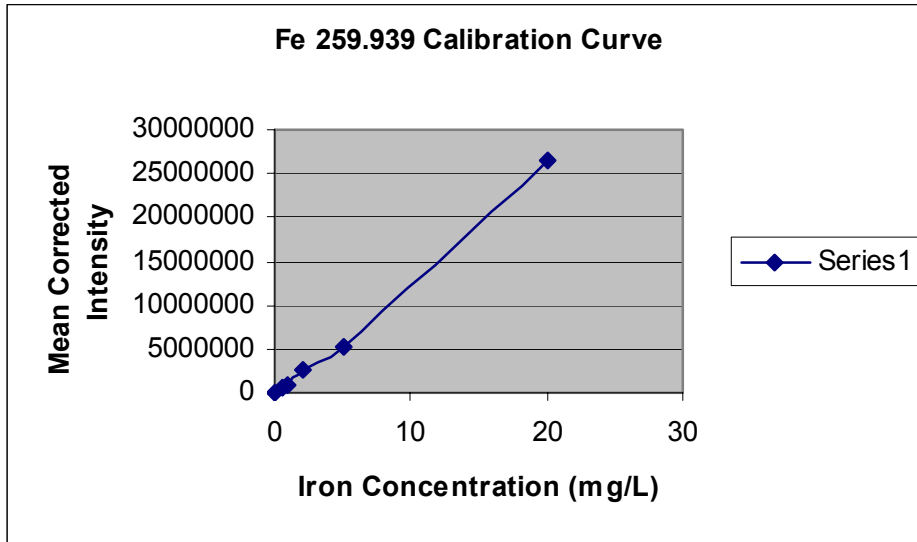


Figure B5. May 19<sup>th</sup> ICP Validation Test Calibration Curve.

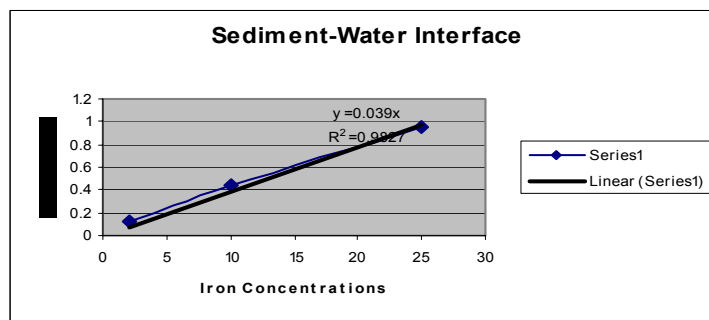
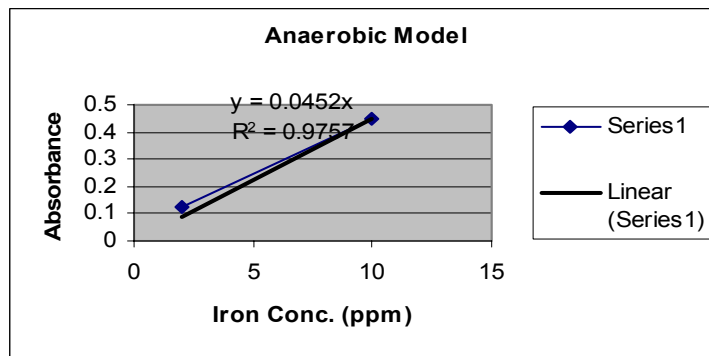
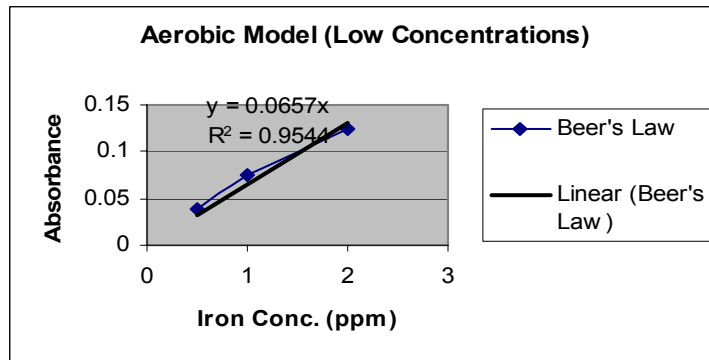
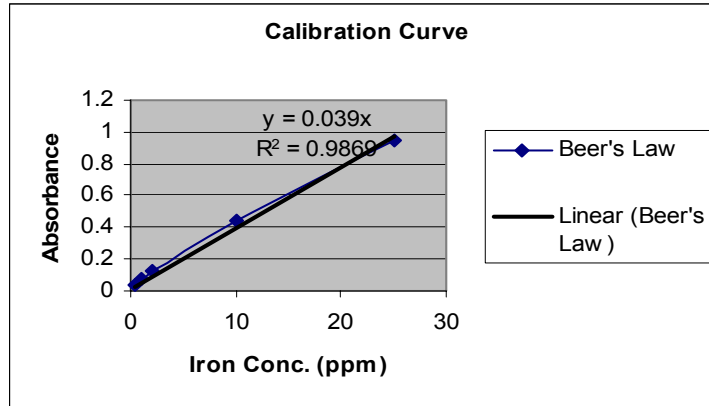
Table B4 Raw Test Results for May 19<sup>th</sup> Validation

Benchscale Model	Intensity	Iron Conc. (mg/L)	Comments
Aerobic	703933.1	0.81	~5 mg/L DO
Reaerated132	2169632	1.91	67 hours re-aeration
Anaerobic132	5625711	4.53	0.01 mg/L DO
Anaerobic132(sed)	14012267	10.90	sed-water interface

Table B5 Raw Test Results for May 19<sup>th</sup> Spectrophotometer Test

Redundant Data	Intensity	Iron Conc. (mg/L)	Comments
Aerobic 1	0.035	0.53	~5 mg/L DO
Aerobic 2	0.026	0.40	~5 mg/L DO
Anaerobic148	0.227	5.02	DO: 0.01 mg/L
Anaerobic132	0.205	4.54	DO: 0.01 mg/L
Reaerated132	0.055	1.22	36 hours reaeration
Reaerated2	0.061	1.35	
Psuedo Unknown	0.198	4.38	4 ppm
Anaerobic132 (sed)	0.418	10.72	Sed-water interface

Note: Regression Line Calibrated with Psuedo Unknown



**Figure B6. Calibration Curves for May 19<sup>th</sup> Spectrophotometer Test.**

