# EFFECTS OF OXYGENATION IN STRATIFIED RESERVOIRS ON CONCENTRATIONS OF MANGANESE AND IRON IN BOTTOM SEDIMENTS

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**Buse VURAL AYDIN**

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We approve the thesis of **Buse VURAL AYDIN**

**Examining Committee Members:**

Sebnem Elci

**Prof. Dr. Şebnem ELÇİ**
Department of Civil Engineering, İzmir Institute of Technology

**Prof. Dr. Alper BABA**
Department of Civil Engineering, İzmir Institute of Technology

**Prof. Dr. Gökmen TAYFUR**
Department of Civil Engineering, İzmir Institute of Technology

**Assoc. Prof. Dr. Gökçen BOMBAR**
Department of Civil Engineering, İzmir Katip Çelebi University

**Dr. Hatice Eser ÖKTEN**
Department of Environmental Engineering, İzmir Institute of Technology

**4 December 2019**

Sebnem Elci

**Prof. Dr. Şebnem ELÇİ**
Supervisor, Department of Civil
Engineering
İzmir Institute of Technology

Sebnem Elci

**Prof. Dr. Şebnem ELÇİ**
Head of the Department of Civil
Engineering

**Dr. Hatice Eser ÖKTEN**
Co-Supervisor, Department of
Environmental Engineering
İzmir Institute of Technology

Mehtap Eanes

**Prof. Dr. Mehtap EANES**
Dean of the Graduate School of
Engineering and Sciences

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# ABSTRACT

## EFFECTS OF HYPOLIMNETIC OXYGENATION ON IRON AND MANGANESE CONCENTRATIONS IN RESERVOIRS

Iron and manganese accumulation in drinking water reservoirs is a challenging issue and should be controlled in order to prevent their adverse effects on human health. Accumulation of these elements not only clogs pipeline systems but also causes stains on fixtures and laundry. In addition, high concentrations of iron and manganese may lead to various health problems when ingested. This study focuses on the release mechanism of iron and manganese from sediments to water column and investigates methods to prevent this release. Effects of lack of hypolimnetic aeration, acid-base condition and thermal stratification on iron and manganese concentrations at water column were investigated through laboratory experiments**.** Experiments showed that total iron (Fe) and ferrous iron ($Fe^{2+}$) concentrations in the water column decreased gradually following aeration in hypoxia conditions. A similar behavior was also observed for manganese concentrations. However, the concentration of dissolved manganese (Mn) in alkaline water condition is observed to be less than the aerated water case. This is an indication that iron and manganese react differently under different acidity of water in consideration.

# ÖZET

## TABAKALAŞMIŞ REZERVUARLARDA OKSİJENLEŞTİRMENİN DİP SEDİMANDAKİ MANGAN VE DEMİR KONSANTRASYONLARINA ETKİSİ

İçme suyu rezervuarlarında demir ve mangan birikimi önemli bir konudur ve insan sağlığı üzerindeki olumsuz etkilerini önlemek için kontrol edilmelidir. Bu elementlerin birikmesi sadece boru hattı sistemlerini tıkamakla kalmaz, aynı zamanda armatürlerde ve çamaşırlarda lekelere neden olur. Ayrıca, ağız yoluyla vücuda alındığında sağlık sorunlarına neden olabilir. Bu çalışma, sedimanlardan su kolonuna demir ve manganın salım mekanizmasına odaklanmakta ve bu salımın önlenmesi için yöntemleri incelemektedir. Deneylerde hipolimnetik havalandırma, asit-baz durumu ve termal tabakalaşmanın demir ve mangan konsantrasyonları üzerine etkileri incelenmiştir. Deneyler, su sütunundaki toplam demir (Fe) ve ferröz demir ($Fe^{2+}$) konsantrasyonlarının, oksijensiz ortamın oluştuğu hipoksi su kolonunda havalandırma uygulaması ile birlikte zaman içerisinde azaldığını göstermiştir. Benzer bir davranış mangan konsantrasyonları için de geçerli olmaktadır. Fakat alkali koşullarda, suda çözünmüş mangan konsantrasyonu havalandırma koşuluna göre daha az olmaktadır. Bu da demir ve mangan elementlerinin su kolonunun farklı asidite koşullarında farklı reaksiyon verdiklerinin göstergesidir.

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# INTRODUCTION

## 1.1. Motivation

In a reservoir, wind stress pushes warmer surface water in downwind direction and an upwelling occurs to replace loss of water. Warm epilimnion water accumulates at the downwind direction and is pulled downward by gravity. A counter current flows back near thermocline in the upwind direction. The thermocline gets tilted downward leading to oscillations. These thermal oscillations help mixing of nutrient rich bottom water. Thus, wind induced currents and structure of thermocline mainly control the vertical distribution of heat, dissolved substances and nutrients in water column.

Hypolimnetic water is desirable because it is cooler and has fewer chemicals than the other zones. However, lower dissolved oxygen concentrations in hypolimnion affect the drinking water quality negatively. In summer months, as thermal stratification takes place hypolimnion becomes cut off from the surface layer (epilimnion), where active oxygen transfer is occurring. Moreover, organic residues tend to sink to hypolimnion and due to degradation of these organic residues in sediments, remaining oxygen is depleted. Anoxic or anaerobic microbial degradation tend to change the pH of sediment and eventually of hypolimnion towards acidic conditions. Under anoxic conditions (less oxygen) some elements are soluble in water. In general, these soluble elements accumulate in the hypolimnion zone. It may lead to failing to meet the drinking water quality, aquatic problems such as fish kills, cloggings of pipeline system, stains on fixtures and laundry. Moreover, a high intake of these elements may cause various health problems.

The purpose of this study is to investigate the measures to prevent release of elements from sediments to water column using different experimental methods. A comparison of iron (Fe) and manganese (Mn) concentration distributions in the water column provides strong evidence for redox cycle. During redox reactions, Fe (II)- Fe (IV) and Mn (II)- Mn (IV) presents different properties with respect to solubility, adsorption, and complexation.

In this study, effects of aeration, acidity level and the degree of thermal stratification on release rates of iron and manganese from sediment to water column were investigated in seven experiments. The first experiment could be defined as a base experiment for the other experiments and represented the simplest case. Its aim was to observe iron and manganese release from sediment to water column. The second experiment aimed to investigate how total iron (Fe), ferrous ion ($Fe^{2+}$) and manganese (Mn) behaved in case the system was deprived of oxygen. The third experiment aimed at investigation of how aeration affected the dissolution of Total Fe, $Fe^{2+}$ and Mn in the hypolimnetic water layer. However, aeration was applied to the system very carefully to keep air diffusion at the nominal level. The purpose of the next experiment, the fourth experiment, was to show how acidic water conditions affected iron and manganese solubility in case of hypoxia. The tank was filled, and the elodea plant was used to create hypoxia in the tank. When the DO level was reached around 5, the elodea was removed from the tank. The fifth experiment investigated the effect of basic (alkaline) conditions of water on iron and manganese concentrations. In order to increase water pH to an approximate value of 11, the NaOH solution was prepared before the tank was filled. The main purpose of the sixth experiment is to investigate thermal stratification effects on soluble iron and manganese concentrations. The last and seventh experiment aimed to investigate how aeration effects the dissolution of Total Fe, $Fe^{2+}$ and Mn in case of stratification and the hypoxia together.

## 1.2. Literature Review

Morgan (2004) investigated that in aqueous geochemistry increasing the Mn (II) by the reaction to the high oxidation states of Mn (III) and Mn (IV) which is the sparingly soluble solid phases, with dissolved oxygen is one of the major processes that regulate the manganese cycle. The product after reaction (Mn (III) and Mn (IV)) is subject to removal of the sediments of a water body and/or further oxidation to a $MnO_2(s)$ phase in the water column. After that, to reduce the solid phase of manganese to manganese (II) phase, it is subjected to organic carbon compounds and another reductant. With this process of manganese which is called the dynamics of oxidation and reduction, vertical and horizontal profiles of dissolved manganese (largely Mn (II) species) in fresh and marine water bodies are established. Bacterial oxidation, elements oxide catalysis, homogeneous solution oxidation is the pathways of Mn (II) oxidation. Kinetic Analysis of Homogeneous Oxidation requires to be understood in a more fundamental and quantitative way. Reaction stoichiometry, energetics, the experimental rate law, a proposed scheme of elementary reactions, and a rate expression based on the proposed scheme are the needs for kinetic analysis on several levels. Morgan (2004) has studied the rate of $O_2$ oxidation of dissolved Mn (II) species (including free $Mn^{2+}$ ions and their hydrolysis products, carbonate complexes, and complexes with other ligands such as sulfate and chloride) to Mn (III) product at 25°C. He has also evaluated and interpreted the rate of oxidation in terms of the solution species of Mn (II) in natural waters. For this purpose, experiments in three different laboratory buffers and in seawater have been performed. He defined a kinetic rate expression for parallel paths expressing the total rate of Mn (II) oxidation in terms of multiplication of ki and aij; where ki is the rate constant of species i and aij is the species concentration fraction in solution j. As a result of his experiments, the range of kinetic rate for the dissolution of Mn (II) varied from 8.6 x 10 -5 to 2.5 x 10 -2 ($M^{-1}$ $s^{-1}$), between pH 8.03 and 9.30, respectively. Moreover, he observed values of oxidation rate constants (M -1s -1) for the most reactive species. These rate are stated as 1.66 x $10^{-2}$, for manganese (I) hydroxide ion ($MnOH^+$); 2.09 x 101, for manganese (II) hydroxide ($Mn(OH)_2$) and 8.13 x 10 -2 , for manganese (IV) carbonate ion $Mn(CO_3)_2^{2-}$ respectively. These rate constants were yielded from the observed rates to the species kinetic rate expression that fits with a multiple linear regression analysis. The species kinetic rate expression accounts for both carbonate on oxidation rates of Mn (II) and influence of pH, by the way of complex formation and acid-base balance of reactive and unreactive species. So finally, when pH is higher than, 8.4, contributions of the species manganese (IV) carbonate ion ($Mn(CO3)_2^{2-}$ ) and manganese (II) hydroxide ($Mn(OH)_2$) at greater contributions and at pH 8 contribution of manganese (II) hydroxide (MnOH) at a greater fraction of the total rate was observed.

The thermal stratification is an important natural process which represents temperature change at different depths in a lake. Temperature change also causes change in water density, leading to three discrete layers of water: warm surface layer (epilimnion) and cold bottom layer (hypolimnion) and thermocline behaving as a barrier between cold and warm layers. Production of ammonia, sulphide, algal nutrients and increasing concentrations of iron and manganese are results of the potential changes in chemical contents in water due to stratification that may have a significant effect on water quality. A good understanding of the behavior of the reservoir may help to identify several measures for the improvement of water quality. For this purpose, Baharim et al. (2011), have studied one of the water supply reservoirs located in Johor, Malaysia facing high iron and manganese concentrations caused by the thermal stratification process, for over 13- months on a weekly basis. Moreover, concentrations of iron and manganese throughout the water column were analyzed by procedures in Standard Methods for the Examination of Water and Wastewater (APHA, 1998) and the effects of thermal stratification on the water quality in the reservoir were evaluated. Four water sampling sites were chosen randomly in the reservoir with a depth of 16.5 m, 15.9 m, 10.5 m and 10.3 m, respectively. In-situ monitoring for temperature and dissolved oxygen concentrations were done at every one-meter depth, using YSI600 XL. The sondes of YSI 600XL measure eleven parameters simultaneously; DO (% and mg/L), ORP, temperature, depth or level, conductivity, total dissolved solids, specific conductance, resistivity, salinity and pH. It is an economical logging system for long-term, in situ monitoring and profiling (YSI Environmental Instruction Manual). Water samples for iron and manganese analysis were taken from the surface, middle and at the bottom layers (0.5 m above the sediment) using Hydro-Bios Water Sampler. Results showed that during the observation period level of thermal stratification in the reservoir varied and at the strongest period of stratification, dissolved oxygen content decreased with an increase of water depth while the highest iron and manganese concentrations were observed. And, the significant period of rainfalls lead to natural destratification (decreasing of concentrations of iron and manganese) in reservoir until the start of the thermal stratification.

Munger et al. (2016) investigated that iron and manganese elements accumulation in stratified drinking water reservoirs reduce water quality. Hypolimnetic oxygenation has been used by some drinking water utilities to create more oxygen in the water column. Thus, iron and manganese concentrations could be reduced. On the other hand, while dissolved oxygen concentration has been controlled, studies show that not only dissolved oxygen affects iron and manganese concentration but also pH and elements-oxidizing microorganisms affect the concentration of these two elements in the water. The aim of this study was to investigate the effects of hypolimnetic oxygenation on Fe and Mn dynamics in a shallow, dimictic drinking water reservoir. So, iron and manganese concentration were studied under hypolimnetic oxygenation condition in a shallow drinking water reservoir in Vinton, Virginia, USA by sequentially activating and deactivating an oxygenation system over two summers. The results showed that maintaining well-oxygenated conditions prevent or reduce soluble iron concentration accumulation in the hypolimnion. This process is not valid for manganese concentration, while the rate of manganese oxidation increased, soluble manganese still accumulated in acidic to neutral (pH 5.6 to 7.5) hypolimnion. Moreover, it was performed laboratory incubation experiments, which showed that the presence of Mn-oxidizing microorganisms increased the rate of Mn oxidation in comparison with rates under oxic, abiotic conditions. After field and laboratory experimental results combined, the results showed that increasing dissolved oxygen levels in the water column is important for stimulating the oxidation of iron and manganese. However, the more efficient method for manganese is tied to the activity of manganese-oxidizing organisms in the water column and favorable (neutral to alkaline) pH. In summary, hypolimnetic oxygenation can be a favorable management strategy for controlling soluble iron, but it was decided that future work is needed to optimize its effectiveness in promoting soluble Mn oxidation. As a summary, they investigated the effects of hypolimnetic oxygenation on Fe and Mn dynamics in a shallow drinking water reservoir. They studied the response of Fe and Mn concentrations to activation and deactivation of the oxygenation system. They found that oxygenation prevented the accumulation of soluble Fe in the hypolimnion. However, it was not the case for manganese. They observed that soluble Mn still accumulated in the hypolimnion even under well oxygenation conditions. They pointed out the need for future work to optimize the effectiveness of oxygenation systems.

Other researchers (Gantzer et al., 2009; Zaw and Chiswell,1999) have stated that oxygenation systems can decrease soluble Mn concentrations by increasing DO levels causing manganese oxidation and adsorption to other particles and causing subsequent precipitation to the sediment. They pointed out that oxygen dynamics and biogeochemical processes are variable at the sediment water interface and thus changes in the sediment oxygen uptake rate may occur. In these studies, the influence of oxygenation on sediment water fluxes of manganese is also stated as unclear.

Bryant et al. (2011), also looked at the impact of oxygenation on manganese concentrations and they found that soluble Mn levels increased when oxygenation was turned off and the upper sediment became anoxic. After several weeks of anoxic conditions, they also observed a higher release of Mn from the sediment. However, they also stated that diffusive flux of manganese from the sediment also increased in response to the oxygenation which contradicted to their previous remarks.

L. Liboriussen et al. (2009), studied and realized that especially during the summer months because of high air temperature, stratified eutrophic lakes mostly suffer from depletion of hypolimnetic oxygen. It causes low redox conditions and accumulation of phosphate and ammonia in the hypolimnion layer. To improve the water quality hypolimnetic oxygenation was used as a method of lake management strategy. For that purpose, oxygen was applied about 4-20 years to the five different eutrophic dimictic Danish lakes. Only one lake has shown high oxygen concentration in the hypolimnion, while the other four lakes could not show any difference and still low average summer levels. Oxygenation increased the water temperature generally between 0 to 2˚C; however, in one lake water temperature increased about 4-6 ˚C. During stratification, in all lakes ammonia and phosphorus concentration has been reduced by oxygenation. Oxygenation was helped to decrease of accumulation of ammonia and phosphorus concentration by 40 to 80%. It was stopped two lakes oxygenation in around 1 and 2 years hypolimnion concentrations of ammonia and phosphorus increased again in this period. In the subject of surface water came up, its quality improved in only one lake. However, improving also was based on simultaneously occurring changes in external nutrient loading. At the end of this study, it is concluded that oxygenation can only minor improve the oxygen level in most of the lakes; however, ammonia and phosphorus accumulation has been reduced by hypolimnetic oxygenation. Also, hypolimnetic oxygenation prevents a lack of oxygenation (anoxia) in deeper parts of the lake. Moreover, if it is aimed to ensure a long-lasting solution to improve in the quality of water lake, oxygenation treatment should be accompanied by reduced nutrient intake to the specified lake.

M. Kawashima et al. 2009, studied manganese preparation mechanisms with the perspective of adsorption onto suspended solids and microbial oxidation of Mn in Lake Biwa. The concentration of dissolved manganese, which is $Mn^{2+}$, decreased at pH > 7 by microbially mediated oxidation in aerobic water samples maintained in the laboratory. In the end, it was observed that autoclaving, irradiation of ultraviolet light and filtration of water samples and the addition of $NaN_3$ prevented $Mn^{2+}$ precipitation. In addition, in the suspended solid the adsorption of $Mn^{2+}$ was appreciable at pH > 7 and it was reached equilibrium point within the minimum 30 minutes. When the $Mn^{2+}$ oxidation rate has been compared with $Mn^{2+}$ adsorption rate, it is much less than adsorption. In different parts of the lake, for example, bottom water, river mouth or sediment surface, subsequent slow oxidation mediated by bacteria and initial adsorption of $Mn^{2+}$ might require for the $Mn^{2+}$ precipitation mechanism process.

## 1.3. Hypolimnetic Anoxia in Reservoirs

Thermal stratification of reservoirs, where warm and cold water form layers in the water column, results in poor mixing during the summer and water can become anoxic due to the lack of light for photosynthesis. This eventually leads to poor downstream quality resulting in water treatment problems in respect of taste/odor and iron/manganese soluble salts. Low DO levels have a negative impact on aquatic life. In water-supply reservoirs, low DO may lead to the release of soluble reduced iron and manganese from the sediments.

Chemical and thermal stratification occur during the summer months because of the lack of oxygen in the hypolimnetic zone. Under anoxic conditions, some elements become soluble in water. According to water quality standards, dissolved oxygen concentration must not drop below 5 ppm. Generally, these soluble elements accumulate in the hypolimnion and can lead to water treatment problems.

High concentrations of soluble elements such as manganese (Mn) and iron (Fe) often cause water quality problems. Iron and manganese threshold values are given as 50 µg/l and 200 µg/l respectively for drinking water (EPA, Microbiological, Chemical and Indicator Parameters in 2014 Drinking Water Regulations 2014). These two soluble elements react sensitively to changes in redox conditions. During redox reactions, Fe (II)-Fe (IV) and Mn (II)-Mn (IV) presents different properties with respect to solubility, adsorption, and complexation.

Also, hypolimnetic anoxia can occur in reservoirs due to the decay of phytoplankton. This ecologic process degrades the water quality by releasing the anoxic sediments as phosphates, ammonia, sulfides, methylmercury, iron, and manganese (Marc W. Beutel, Hypolimnetic anoxia and sediment oxygen demand in California Drinking Water Reservoirs,2003).

In bottom water, anoxia can occur due to ecological processes that degrade the water quality.

There are several studies about hypolimnetic aeration and oxygenation in the reservoirs (Marc W. Beutel, Hypolimnetic anoxia and sediment oxygen demand in California Drinking Water Reservoirs,2003). The hypolimnetic oxygenation is about the dissolved oxygen and reducing the chemicals. Several ecological can be a reason for anoxia like contamination, eutrophication, phytoplankton, and bacteria. This study was based on reducing the amount of Mn and Fe by using the aeration and improve the water quality.

## 1.4. Hypolimnetic Oxygenation

Hypolimnetic aeration systems are installed in the reservoir in order to prevent hypolimnetic anoxia. Hypolimnetic aeration can increase dissolved oxygen while preserving thermal stratification in water bodies. In many reservoirs, the aeration systems are accepted as the sole solution for improving the water quality for better management strategies. There are several types of systems to help do this, by injecting air or through mechanical mixing. Generally, three primary devices are preferred; airlift aerators, bubble plume diffusers and speece cone.

In airlift aerators, injected air is delivered to the aerator and then air bubble released from the diffusers and at the top, the air bubble is transferred to the atmosphere. Oxygenated water goes down through the vertical tube resulting in the increased levels of oxygen concentration at the hypolimnetic zone. Bubble plume diffusers are generally used for hypolimnetic zone oxygenation while preserving stratification of water bodies. These systems are most suitable for deep lakes where the bulk of the bubbles dissolves in the hypolimnion and the momentum generated by the plume is low enough to prevent significant erosion of the thermocline (Wüest, A.1992). In speece cone systems, water and oxygen bubbles are entered at the top of the cone and water flows downward through the cone. Cone cross-sectional area increases as it goes down, so the water velocity decreases. Water velocity is designed to be less than the rising bubble velocity at the deep of the cone. Of these methods, bubble plume diffusers are preferred for preservation of stratification.

## 1.5. Kinetics of Iron and Manganese

In the water column, iron and manganese may be present in different forms. $Fe^{2+}$, $Mn^{2+}$ ions existing in the water column are mostly present in soluble form and when enough oxygen is supplied, they change their forms to $Fe^{3+}$, $Mn^{4+}$ ions which then become insoluble and precipitate to the bottom sediments underlying the hypolimnetic water layer. According to one of Minnesota Rural Water Association publications, it takes 0.14

mg/L of dissolved oxygen to oxidize 1 mg/L of iron, and 0.27 mg/L of dissolved oxygen to oxidize 1 mg/L of manganese.

Through the process of aeration to the system, it should be very careful to keep water flow at the nominal level. In case water flow is too high, iron and manganese can not oxidize because of insufficient air. On the contrary, if water flow is too low, water can saturate with dissolved oxygen and it leads to corrosive water in the system. This type of water can cause lead and copper level increase at the taps.

Homogeneous oxidation is the oxidation of $Fe^{2+}/Mn^{2+}$ to $Fe^{3+}/Mn^{3+}/Mn^{4+}$ ions and the subsequent hydrolysis which results in flocs that precipitate on and between the sand grains (Sung and Morgan, 1980; Tamura et al., 1980; Beek et al., 2012; Vries et al.,2016). Homogeneous oxidation is pre-dominant in the zone where an oxidant is present and no adsorbent material, like (coated) sand grains, is present.

Iron homogeneous oxidation can be described by oxidation and hydrolysis equations (Equation 1.1 and 1.2).

$$Fe^{2+} + \tfrac{1}{4}\ 0_2 + H^+ \rightarrow Fe^{3+} + \tfrac{1}{2}\ H_2O \qquad (1.1)$$

$$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3 + 3\ H^+ \qquad (1.2)$$

Leading to the overall reaction as given (Equation 1.3).

$$Fe^{2+} + \tfrac{1}{4}\ O_2 + 2\ \tfrac{1}{2}\ H_2O \rightarrow Fe(OH)_3 + 2\ H^+ \qquad (1.3)$$

The reaction rate of homogeneous oxidation (Equation 1.4) is described by a kinetic rate (Beek et al., 2012) where the rate of Fe (II) removal is dependent on Fe (II), oxygen and pH (Vries et al.,2016):

$$\frac{d}{dt}[Fe^{2+}] = -k_{Fe,hom}\frac{[Fe^{2+}][O_2]}{[H+]^2} \qquad (1.4)$$

The reaction rate constant is determined at $2.20\text{x}10^{-15}$ $(mol/l)^{-2}s^{-1}$ with the aid of different residence times and measurements of ferric iron (Beek et al., 2012; Vries et al.,2016). This constant value is used for all model simulations.

Manganese homogeneous oxidation and hydrolysis equations are provided as (Equation 1.5, 1.6, 1.7, 1.8);

$$Mn^{2+} + \tfrac{1}{4}\ 0_2 + H^+ \rightarrow Mn^{3+} + \tfrac{1}{2}\ H_2O \qquad (1.5)$$

$$Mn^{3+} + \tfrac{1}{4}\ H_20 + H^+ \rightarrow Mn^{4+} + \tfrac{1}{2}\ H_2O \qquad (1.6)$$

$$Mn^{2+} + \tfrac{1}{2}\ 0_2 + 2\ H^+ \rightarrow Mn^{4+} + H_2O \qquad (1.7)$$

$$Mn^{4+} + 2\ H_20 \rightarrow MnO_2 + 4\ H^+ \qquad (1.8)$$

The rate of reaction constant is measured with the following equation (Equation 9);

$$\frac{d}{dt}[Mn^{2+}] = -k_{Mn,hom}\,[OH]^{2,56}[Mn^{2+}] \qquad (1.9)$$

For the reaction, constant $k_{Mn,hom}$, a value of $2.08 \times 10^{-2}$ $(mol/L)^{2.56}s^{-1}$ was adopted (Davies and Morgan, 1989) which has been determined at 298 ° K (Vries et al.,2016).

During thermal stratification, reductive dissolution of Fe and Mn from the sediments to the water column occurs. In anoxic conditions, when dissolved oxygen (DO) levels fall below 0.5 mg/l, conditions become favorable for the reduction of Fe and Mn to soluble forms ($Fe^{2+}$, $Mn^{2+}$). When these elements are oxidized by aeration, they often precipitate as Fe and Mn oxyhydroxides that are subject to sedimentation.

Even in oxic conditions, sediments can continue releasing elements as reported by other researchers (Gantzer et al 2009, Bryant et al. 2011). Thus, for accurately describing the processes controlling elements concentrations, the governing mechanism must be further studied for good management practices of drinking water supply reservoirs.

## 1.6. Acceptable Limit of Iron and Manganese

Soluble elements such as iron and manganese are present in water suppliers and often reach the high concentration level during the summer season. These elements have occurred as a result of the natural process of earth and the most common caused by erosion. Moreover, iron and manganese may also occur when the water has been contacted with the rock in deep wells, but the process takes a long time. Especially in groundwater iron and manganese occur together; however, the concentration of iron always much more than manganese.

In nature, iron and manganese have been found in soils, minerals, and rocks in the form of less soluble oxide and hydroxide. Therefore, these two elements are very rare in surface waters.

Due to The Safe Drinking Water Act (SDWA) the maximum level of iron and manganese to be of no use is accepted as 0.3 mg/L Fe and 0.05 mg/L Mn. The recommended level of these two should be;

1. Iron (Fe) - acceptable limit < or = 0.3 mg/L
2. Manganese (Mn) - acceptable limit < or = 0.05 mg/L

Moreover, due to the deterioration effects of iron and manganese on water quality, World Health Organization (WHO) has set limits maximum allowable concentration as 0.3 and 0.1 mg/l respectively.

Corresponding to approximate concentrations above, iron, and manganese does not present a danger to the environment or human health much but cause aesthetic problems that not be desired such as changing of taste and color of the water, the turbidity of the water, dishes staining.

## 1.7. Water Quality Effects on Health

Water has an important role for the people, animals and plants' life. It can be used as drinking, cleaning water or daily needs for the population. On the other hand, it is used for agriculture, industry and domestic purposes. This kind of usage of water creates some problems as environmental contamination and serious human health problems.

Water quality means the basic characteristics of water in order to determine its suitability for the population uses. There are some diseases due to the degradation of water quality and contamination. Today, 1.1billion people lack access to an improved water resource and over three million people, mostly children, die annually from water-related diseases (UNICEF, 2008).

Also, the proportion of some chemicals and toxic materials like iron and manganese can be a reason for the decrease in water quality in terms of taste, pH, and color. Contaminated water as chemicals in drinking water can have serious health effects and water-borne diseases. Furthermore, low water quality transmits some diseases, bacteria or viruses to human skin. If this condition continues in the long term, the skin will have a risk for cancer.

Overconsumption of iron is known to increase risks for Alzheimer's disease.

Moreover, manganese is a very common compound that can be found everywhere on earth. Manganese is one of three toxic essential trace elements, which means that it is not only necessary for humans to survive, but it is also toxic when too high concentrations are present in a human body. Manganese effects occur mainly in the respiratory tract and in the brains. Symptoms of manganese poisoning are hallucinations, forgetfulness, and nerve damage. Manganese can also cause Parkinson and bronchitis. A syndrome that is caused by manganese has symptoms such as schizophrenia, dullness, weak muscles, headaches, and insomnia.

# CHAPTER 2

# MATERIALS AND METHODS

## 2.1. Introduction

Iron and manganese accumulation in drinking water reservoirs is a challenging issue and should be controlled in order to prevent their adverse effects on human health. Accumulation of these elements not only clogs pipeline systems but also causes stains on fixtures and laundry. In addition, high concentrations of iron and manganese, especially in pregnant women, lead to various health problems. This study focuses on the release mechanism of iron and manganese from the sediments to the water column and investigates the methods to prevent this release. The effects of lack of hypolimnetic aeration, acid-base condition and thermal effects on iron and manganese concentrations at the water column were investigated through laboratory experiments**.** Experiments showed that Total Fe and $Fe^{2+}$ concentrations in water column decreased in time in case aeration application in hypoxia, it was also the case for manganese concentrations. However, in alkaline water condition, the concentration of dissolved Mn in water is less than the aeration condition.

Iron and manganese are two similar elements that commonly exist in Earth’s crust. Iron is the element most widely found together with manganese in water supplies. These two elements are found frequently in water systems that use groundwater. Moreover, surface water generally does not contain large amounts of iron or manganese. Water infiltrated through soil or rock can cause dissolving of iron and manganese in the solid material. Moreover, iron pipes can cause water with a high concentration of iron.

When iron and manganese accumulate in drinking water reservoirs, they result in clogging of pipeline systems and cause orange-brown or black stains and particulates on fixtures and laundry, metal tastes and aesthetic problems. Water contains iron and manganese mineral is not health-threatening in case of no bacteria in water. However, bacteria in drinking water can cause problems in human health. Besides these visual effects, intake of high concentrations of these elements may also result in several health problems. Overconsumption of iron is known to increase risks for Alzheimer's disease, whereas overconsumption of manganese affects the respiratory tract and the brain, leading to increased risks for bronchitis and Parkinson disease.

Due to the deterioration effects of these elements on water quality, World Health Organization (WHO) has set limits for their concentrations in drinking water. Maximum allowable concentration limits for iron and manganese are set as 0.3 and 0.1 mg/l respectively and treatment of these elements is mostly required in drinking water reservoirs. Mostly oxidation and filtration techniques are utilized. However, the accumulation of iron and manganese in raw water increases the cost and difficulty of the water treatment process and thus in situ treatment is preferred in most cases.

Iron and manganese are colorless and clear from in the water with low oxygen content. In this type of water, two elements are in dissolved form. When the water contained iron and manganese exposed to air, these elements are oxidized and change their forms from colorless to colored and occurred very small solid particles. Aeration of pure oxidation process can change iron from white to yellow finally red-brown solid particles.

Thermal stratification generally occurs during summer months due to lack of oxygen in the hypolimnetic zone. Under anoxic conditions, iron and manganese are soluble in water.

In general, soluble elements accumulate in the hypolimnetic zone and it can lead to drinking water problems and aquatic problems such as fish kills. The common application for the treatment of iron and manganese at the reservoir raw water is to oxygenate the hypolimnion. Hypolimnetic oxygenation systems increase dissolved oxygen concentrations by injecting air/oxygen nearby the water intake structures in the reservoirs. When dissolved oxygen (DO) concentration increases in hypolimnion through oxygenation method, oxidized iron and manganese are precipitated to bottom sediments. However, bottom sediments can continue to release elements as a result of combined effects of DO concentration, pH and microbial activity, where these effects need further research and are not fully understood.

According to the form of iron and manganese in water, it should be used the proper treatment method. As it is known, iron and manganese present in water both solved and dissolved forms. If the water is initially clear but then forms change to brown-orange and/or black particulates at the bottom of the source, it is called “dissolved or reduced” form of iron and manganese. The reduced form of iron and manganese have a pH of less than 7.0 and these are most common in groundwater.

In the case of solid iron and manganese particles appear in the water column, the elements are already oxidized. It shows that water's pH is higher than 7.0 and oxygen is available in the water column.

Water pH plays a significant role in the oxidation of iron and manganese. According to Mazzei Technical Bulletin No. 2, the ideal water pH range is 7.5 to 8.0 for the oxidation of iron. For the manganese, water pH should be at least 9.5. Oxidation of manganese is quite slow below this pH level.

The purpose of this study is to study the release mechanism of these elements from sediments to the water column and to investigate the methods to prevent this release. The effects of lack of hypolimnetic oxygenation and thermal effects on iron and manganese concentrations at the water column and at sediments were investigated in this study. To examine the effects of oxygenation on iron and manganese concentrations, a laboratory experiment was set up in two 1m*0.4m*0.5m glass water tanks. Sediment was placed at the bottom of the tanks and the iron and manganese concentrations were monitored in time by collecting samples from water column and sediment, which were initially contaminated at known concentrations.

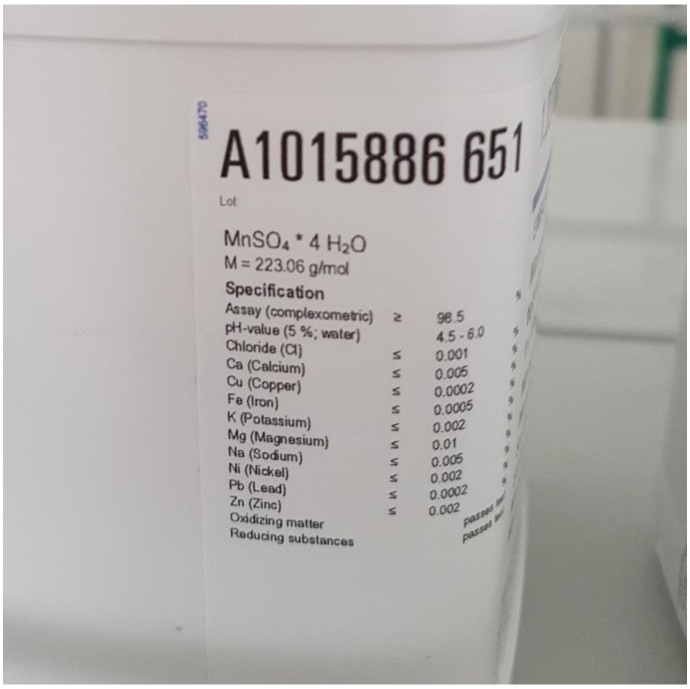
## 2.2. Preparation of Iron and Manganese Solution

In the water column, iron and manganese may be present in different forms. $Fe^{2+}$, $Mn^{2+}$ ions existing in the water column are mostly present in soluble form and when enough oxygen is supplied, they change their forms to $Fe^{3+}$, $Mn^{4+}$ ions which then become insoluble and precipitate to bottom sediments underlying the hypolimnetic water layer.

Iron and manganese solutions were prepared to contaminate the sediments and the water column. Manganese(II) Sulfate Tetrahydrate ($MnSO_4.4H_2O$) and Ferrous Chloride Tetrahydrate $FeCl_2*4H_2O$ chemical compounds were used as a source of $Mn^{2+}$ and $Fe^{2+}$ for the experiments. $MnSO_4.4H_2O$ and $FeCl_2*4H_2O$ compound's specification is shown in Table 2.1, Figure 2.1 and Figure 2.2.

Table 2.1. Mass of Mn and Fe and their compounds

| | |
|---|---|
| Molar mass of $MnSO_4*4H_2O$ | 223.06 g/mol |
| Atomic waste of Mn | 54.94 g |
| Molar mass of $FeCl_2*4H_2O$ | 198.83 g/mol |
| Atomic waste of Fe | 55.85 g |



596470

A1015886 651

Lot

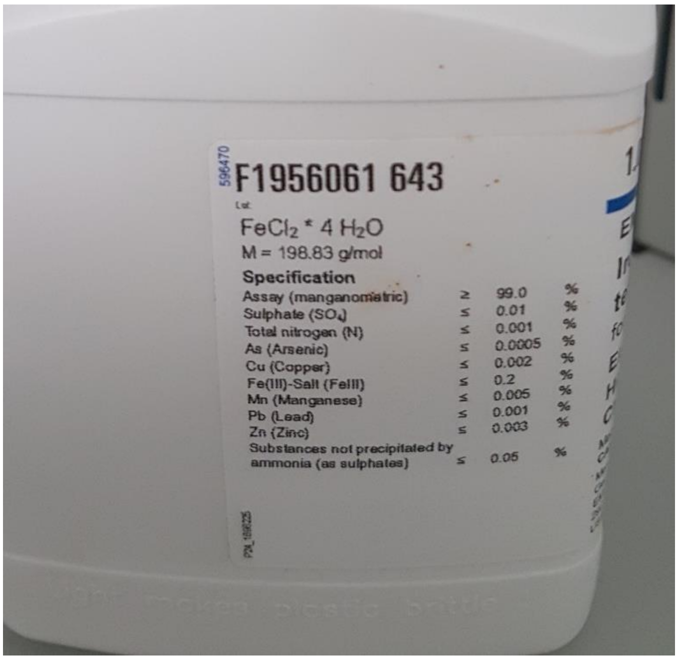
$MnSO_4 * 4 H_2O$

M = 223.06 g/mol

**Specification**

| | | |
|---|---|---|
| Assay (complexometric) | ≥ | 98.5 |
| pH-value (5 %; water) | | 4.5 - 6.0 |
| Chloride (Cl) | ≤ | 0.001 |
| Ca (Calcium) | ≤ | 0.005 |
| Cu (Copper) | ≤ | 0.0002 |
| Fe (Iron) | ≤ | 0.0005 |
| K (Potassium) | ≤ | 0.002 |
| Mg (Magnesium) | ≤ | 0.01 |
| Na (Sodium) | ≤ | 0.005 |
| Ni (Nickel) | ≤ | 0.002 |
| Pb (Lead) | ≤ | 0.0002 |
| Zn (Zinc) | ≤ | 0.002 |
| Oxidizing matter | | passes |
| Reducing substances | | passes |

Figure 2.1. $MnSO_4.4H_2O$ Specification



596470

F1956061 643

Lot

$FeCl_2 * 4 H_2O$

M = 198.83 g/mol

**Specification**

| | | | |
|---|---|---|---|
| Assay (manganometric) | ≥ | 99.0 | % |
| Sulphate ($SO_4$) | ≤ | 0.01 | % |
| Total nitrogen (N) | ≤ | 0.001 | % |
| As (Arsenic) | ≤ | 0.0005 | % |
| Cu (Copper) | ≤ | 0.002 | % |
| Fe(III)-Salt (FeIII) | ≤ | 0.2 | % |
| Mn (Manganese) | ≤ | 0.005 | % |
| Pb (Lead) | ≤ | 0.001 | % |
| Zn (Zinc) | ≤ | 0.003 | % |
| Substances not precipitated by ammonia (as sulphates) | ≤ | 0.05 | % |

Figure 2.2. $FeCl_2*4H_2O$ Specification

The solution contained iron and manganese were prepared to aim to reach 3 g/L concentration of each element. With this scope, in total 12.18 g, $MnSO_4.4H_2O$ and 10.68 g $FeCl_2*4H_2O$ were used to prepare a solution with a concentration of 3 g/L of both $Mn^{2+}$ and $Fe^{2+}$ showed in calculations of Equation 2.1 and 2.2.

$FeCl_2*4H_2O$ → (198.83 g x 3 g) / 55.85 g = 10.68 g (2.1)

$MnSO_4*4H_2O$ → (223.06 g x 3 g) / 54.94 g = 12.18 g (2.2)

Figure 2.3. $FeCl_2*4H_2O$ Weighing with Digital Precision Scales

Iron and manganese compounds that already measured were mixed with one liter of water. The prepared solution was used for contaminated sediments.

## 2.3. Elodea Plant

Elodea is an aquatic plant that native to most of North America. Some records show that the plant was a pest on canals and rivers in the United Kingdom, especially in the 19th century. Some botanic gardens in the United Kingdom aided to distribute this plant to every continent. It is found in all areas south of the Arctic, including Australia, Asia, Africa, and New Zealand.

Elodea plant has stems and generally its length branches out between 20 and 30 cm. The numerous overlapping, dark green, translucent, and minutely toothed leaves are about 1 cm long, and 2-3 mm wide (CABI, 2005; GISD,2018). In addition, the leaves have a non-waxy texture and are rigid (Herault et al., 2008). This species contains flowers, either white or pale purple, that appear at the surface of the water (DAISIE, 2009; GISD,2018). The flowers have also been described in color as being rose-white. The flowers are carried to the surface on a long slender stalk, which is 2-15 cm long, with a sheathing, two-lobed spathe (CABI, 2005; GISD,2018). In addition, there are fruits, which are capsules having a length of less than 1 cm (DAISIE, 2009; GISD,2018) and 3 mm in width. The roots are white, unbranched and thread-like (CABI, 2005; GISD,2018). The plant has multiple apical growth points (Herault, Bornet & Tremolieres, 2008; GISD,2018). In winter the stems build turions, specialized overwintering buds (Cook & Urmig-Koenig, 1985).

Photosynthesis is a process by which light energy is converted into chemical energy. Photosynthesis primarily happens in green leaves. Some more factors are needed for photosynthesis; carbon dioxide, water and sunlight.

- Carbon Dioxide – the plant absorbs the gas through pores called stomata located on its underside of the leaf. The stomata can close at night when no photosynthesis is taking place, or during the heat of the day when the plant is in danger of too much water evaporating from its leaves.
- Water – the plant absorbs the water by the roots and sent up to its leaves through the xylem part of the plant’s vascular tissue.
- Sunlight – the sun provides the energy that enables the process to work.

Elodea is a plant that is good for studying factors related to photosynthesis (Figure 2.4). But the main reason for preferring this plant in the presented study was the ability of this plant to consuming oxygen rapidly when exposed to no sunlight.

Figure 2.4. Elodea Plant

In the case of cultivating elodea in a water column where no light is provided and with limited air contact, the elodea plant can not photosynthesize. Thus, the water tank where Elodea was placed, the tank was covered with black nylon to prevent sunlight and air diffusion to the tank (Figure 2.5).

Figure 2.5. Container Cover with Black Nylon to Prevent Air and Light Diffusion

## 2.4. Measurement of Dissolved Oxygen, pH and Temperature

According to the previous studies conducted on the topic, water quality parameters affect the solution of iron and manganese in the water. In order to investigate the effect of water quality parameters on the dissolution of iron and manganese in water including dissolved oxygen, pH and temperature were monitored during the experiments.

Dissolved oxygen (DO) was monitored via the water quality meter produced by Hach Lange and is shown in Figure 2.6. This device is designed for water quality applications measuring potential of hydrogen (pH), conductivity, total dissolved solids (TDS), salinity, dissolved oxygen (DO), oxidation-reduction potential (ORP) and ion-selective electrodes (ISE) in water. The Hach HQ40D portable multimeter is composed of two channels advanced handheld digital meter. The Hach HQD digital multimeter combines reliability, flexibility, and ease of use. The HQD portable meters connect with a wide range of intellectual smart electrodes addressing different parameters, sample types and operating environment for water quality, environmental and treatment process purposes (Hach Lange, Instruction Manual).

Dissolved oxygen sensor is oxygen impermeable and clear hard substrate. A dye of oxygen-sensitive luminescent and a scattering agent is on the substrate. A last overlay of dark pigment is added to keep stray light out of the measurement cell. When exposed to blue light the luminescent dye gives a red light.The scattering agent distributes the light in the sensor matrix. Also, it contributes to the opacity of sensor. Pulses from a red LED are used as an internal reference. The duration of the luminescence is proportional to the concentration of dissolved oxygen in the sample (Hach Lange, Instruction Manual).

According to the Instruction Manual, the device firstly calibrated. Then before each analyzing, the probe was rinsed with water and dried. The probe put the tank that contains the solution. It was not allowed to probe touch bottom or sides of the tank. It is led to remove air bubble under the probe tip moving the probe up and down. Then pushed the “read” button. The lock icon is shown when the measurement is stable. The value of dissolved oxygen was recorded with time. At the end of each analysis, the probe clean well to avoid the accumulation of elements.

Figure 2.6. Hach HQ40D Portable Multi Meter

Temperature and pH were measured with Hach Sension 2 (Figure 2.7). This device provides pH and ISE meters for applications from pH measurements to accurate Ion Selective Electrode work. Hach Sension™2 Portable is used for pH/ISE/mV/Temperature Meter measurements (Portable pH/ISE Meter Instruction Manual).

A combination pH electrode develops a potential at the glass/liquid interface. At a constant temperature, this potential varies linearly with the pH of the solution. The pH is the hydrogen ion activity in a solution and is defined as –log10a($H^+$), where a($H^+$) is the activity of the hydrogen ion. The sample pH can change when carbon dioxide is absorbed from the atmosphere. In water that has high conductivity, the buffer capacity is typically high, and the pH does not change much (Portable pH/ISE Meter Instruction Manual).

The device measures from -2.0 to 19.99 pH units and the sample temperature. pH values are temperature corrected using the measured sample temperature or a default temperature setting. In the ISE mode, the meter measures from 0 to 19900 with the highest resolution as 0.001 (Portable pH/ISE Meter Instruction Manual).

Before analyzing of the experiments, the probe Hach Sension™2 Portable was calibrated to analyze the highest level of accuracy according to the instruction manual. Hach Sension™2 Portable working method is almost the same as Hach HQ40D Portable Multi Meter. The device was rinsed before analyzing and then put into the tank slowly to avoid probe contact with sidewalls or bottom of the tank. Pushed the "read" button and then pH and temperature values recorded after device stabilizing.

Figure 2.7. Hach Sension 2

## 2.5. Analysis of Sample

All samples were analyzed using the device “UV-2600 UV-Vis Spectrophotometer from Shimadzu” (Figure 2.8). This device is a universal, research-grade spectrophotometer that can be used in a wide range of fields, and easily expanded to suit the measurement objective. By using the optional integrating sphere, the measurement wavelength range of the UV-2600 can be extended to the near-infrared region of 1400 nm (Shimadzu UV-2600 Instruction Manual).

This spectrophotometer measure the amount of light with a specific wavelength that is absorbed by a sample. This device generally is used chiefly to measure the concentration of analytes in solutions. However, it is also used to characterize liquid and solid samples. The simplest spectrophotometers send a single wavelength beam through a single sample, measure the intensity of the beam to determine the absorbance, and then display the result (Labcompare, Spectrophotometer Overview).

Figure 2.8. Shimadzu UV-2600 Spectrophotometer

Moreover, powder pillow reagents were used for photometric precision. For one determination, each powder pillow contains the exact amount of reagent. All necessary information is printed on every powder pillow and also written on Method of Powder

Pillow Manual Sheet. As a powder pillow, Hach was preferred. For analyzing each type of element, different powder pillows were used as follows.

| | |
|---|---|
| Total Iron (Fe) | ; Ferrover Iron Reagent for 10 ml Sample |
| Ferrous ($Fe^{2+}$) | ; Ferrous Iron Reagent for 25 ml Sample |
| Manganese (Mn) | ; Buffer Powder Citrate Type + Sodium Periodate |

According to Hach Total Fe, $Fe^{2+}$ and Mn Instruction Manuals (DOC316.53.01053, DOC316.53.01049, DOC316.53.01058) all analyzing was completed. Before the analyzing started, the wavelength of the device was specified. The program was started 265 iron for ferrover, 295 for manganese and 255 for ferrous ion. For all types of elements, the specified amount of samples were prepared based on the instruction manual. The samples mixed with pillow powder was poured 5 ml cell holder (Figure 2.9). Put a stopper on the sample cell and invert it to mix. After waiting a specified time in the instruction, the cell holder was inserted into the spectrophotometer and reading was completed (Figure 2.10).

Figure 2.9. Spectrophotometer Cell Holder

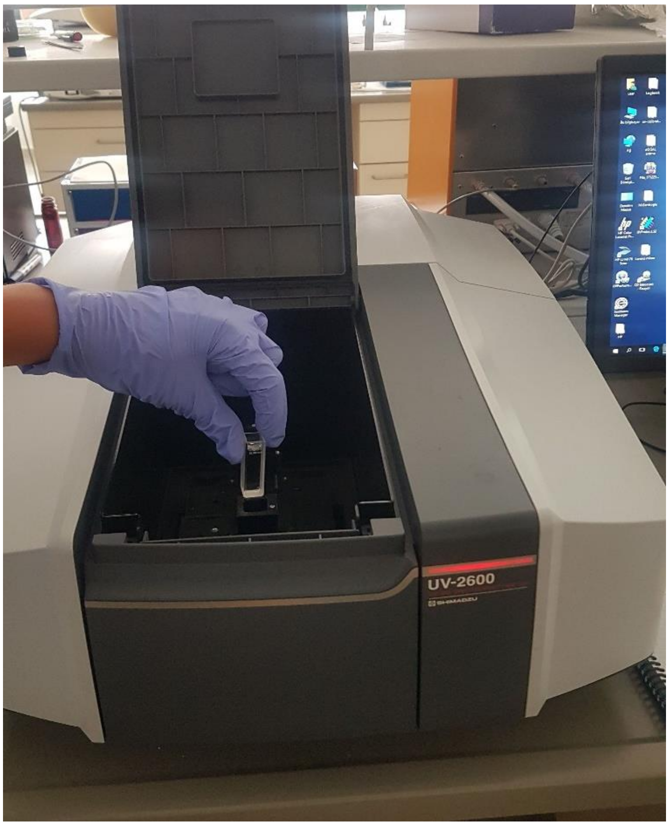


Figure 2.10. Inserting Cell Holder to the Spectrophotometer

## 2.6. Experiments

Two different glass water tanks were used to examine the effects of oxygenation, acid-base condition and thermal stratification on iron and manganese concentrations (Figure 2.11 & Figure 2.12). These two tanks have the same sizes and it is 1 m*0.4 m*0.5 m. The tank (Figure 2.12) was used in another experiment before and have the holes at the bottom. These holes were closed with a suitable material before the experiments start.

To represent an actual reservoir, sediment size distribution observed in Tahtali Reservoir in earlier studies was used as a reference. Based on this data, sediments consisting of 60% sand and 40% silt and clay were obtained by sieve analysis. Totally 1.2 kilogram sediment was distributed homogeneously to the container and remaining sediments would be preserved.

Before the experiment starts, the iron and manganese stock solution was prepared. The solution was mixed with sediments slowly (Figure 2.13).

Figure 2.11. First Water Tank Used in Experiments

Figure 2.12. Second Water Tank Used in Experiments

Figure 2.13. Sediment Mixed with Stock Solution

The purpose of this study is to determine the release mechanism of iron and manganese from the sediments to the water column and investigates the methods to prevent this release. The effects of lack of hypolimnetic oxygenation on iron and manganese concentrations at the water column, iron and manganese concentration in case of acid and alkaline water condition and stratification effects on iron and manganese concentration in the water column were investigated through several experiments. These experiments were performed in a series as the stated table below according to groups (Table 2.2, 2.3 and 2.4). In each experiment, only one parameter was changed while all parameters were kept the same to observe which parameter is more effective on the concentrations of iron and manganese.

Table 2.2. Summary of Group #1 Experiments

| **Group #1** | | |
|---|---|---|
| **Experiment #1** | **Experiment #2** | **Experiment #3** |
| Contaminated Sediments, Clean Water in Neutral Water Condition. | Contaminated Sediments, Clean Water with Hypoxia in Neutral Water Condition (pH=7).<br>No aeration is applied. | Contaminated Sediments, Clean Water with Hypoxia in Neutral Water Condition (pH=7). Aeration applied at a rate of 60 L/s of air discharge. |
| The soil sample is contaminated with a 500 mL of stock solution with a concentration of 3 g/L both $Mn^{2+}$ and $Fe^{2+}$ while the water is free of iron and manganese elements. | Elodea plant is placed in the middle of the full water tank to help reducing the oxygen concentration. After the tank reached low level DO, soil sample that has already contaminated with a 500 mL of stock solution with a concentration of 3 g/L both $Mn^{2+}$ and $Fe^{2+}$ placed the tank. | The water tank is deoxygenated using the elodea plant. The same stock solution is used to contaminate the soil sample. The system is aerated through half an hour with the rate of 60 L/h, at certain intervals. |

Table 2.3. Summary of Group #2 Experiments

| **Group #2** | |
|---|---|
| **Experiment #4** | **Experiment #5** |
| Contaminated Sediments, Clean Water with Hypoxia in Acidic Water Condition (pH=5).<br>No aeration is applied. | Contaminated Sediments, Clean Water with Hypoxia in Basic Water Condition (pH=11).<br>No aeration is applied. |
| Using the elodea plant, the tank full of water is deoxygenated. Then, the specified amount of HCl is used for creating acidic conditions in the water. The contaminated soil samples with the same concentration of stock solution have placed to the bottom of the tank. | Elodea plant is also used to reduce oxygen concentration in water. To create basic conditions in the water tank, a specified amount of NaOH is used for creating basic water. Then, soil contained the same concentration of the stock solution is placed to the tank bottom. |

Table 2.4. Summary of Group #3 Experiment

| **Group #3** | |
|---|---|
| **Experiment #6** | **Experiment #7** |
| Contaminated Sediments, Clean Water with Hypoxia in Neutral Water Condition (pH=7). No aeration is applied. Water column is stratified with a heater. | Contaminated Sediments, Clean Water with Hypoxia in Neutral Water Condition (pH=7). Aeration applied at a rate of 60 L/s of air discharge. Water column is stratified with a heater. |
| The tank is deoxygenated using the same plant. Then soil samples contaminated with a 500 mL of stock solution with a concentration of 3 g/L of both Mn$^{2+}$ and Fe$^{2+}$ are placed after the tank has filled with water. The system is heated gradually. | First, the hypoxia condition is occurred using the elodea plant. Then contaminated soil samples with the same stock solution are placed. The system both gradually heated and aerated with a rate of 60 L/h. |

As it has been also understood from the tables, the experiments were grouped within themselves, Group #1, Group #2 and Group #3.

## 2.6.1. Group #1

The experiments performed under Group #1 aimed to observe releases mechanism of iron and manganese from sediment to water under neutral water conditions where both hypolimnion and aeration was utilized.

### 2.6.1.1. Experiment #1

Experiment #1 can be defined as a base experiment for the other experiments and represents the simplest case. The aim of this part is to observe iron and manganese release from the sediment to the water column. The very first step of the study is to prepare a stock solution with a concentration of 3 g/L of both $Mn^{2+}$ and $Fe^{2+}$.

The water tank (Figure 2.11), was filled with 200 liters tap water. The tap water iron and manganese concentration were also analyzed before the experiment. The result for iron is 0.003 mg/L and manganese is 0.001 mg/L. It shows the concentration of these two elements is quite few and so it is not worth considering. Because of that, it is supposed that the tap water has not contained iron or manganese.

Iron and manganese stock solution was prepared in the laboratory and then mixed with 1.2 kilograms of clean sediment. Then sediment container has been placed at the bottom of the tank. The container is placed slowly to avoid the sediments mixing with the water. It is noted that clean sediment means iron and manganese elements in the sediment are too low to be considered.

The location for sampling at the water column was determined and marked prior to the experiments on the front of the tank as 5 cm above the top-level of sediment container to observe the concentrations of the iron and manganese.

During the experiments, the first water sample was taken just after the container was placed at the bottom of the tank and it was taken from 5 cm above the sediment container upper point and this sampling was considered as time zero sample. The second one was taken an hour after the container placed at the bottom. The rest of the 3rd, 4th, 5th, 6th,7th, 8th, 9th, and 10th samples were taken at times 2, 6, 12, 24, 36, 48, 72 and 96 hours, respectively. At this time the water quality parameters including temperature, pH and dissolved oxygen that is expected to affect the concentration of iron and manganese were measured while the samples were being collected.

All specimens were preserved at the ideal refrigerator temperature. The sediments in the tank were removed out of the tank then the tank was emptied and cleaned. All the collected data were then analyzed using the spectrophotometer.

### 2.6.1.2. Experiment #2

Low concentration of dissolved oxygen conditions is a problem in reservoirs or lakes, especially during the summer season. It causes releasing of some soluble heavy metal from the sediment to the water and affects aquatic life directly. To prevent negative effects such as fish kills and improve the water quality, dissolved oxygen must be successfully injected into the bottom layer of reservoirs or lakes.

Experiment #2 aimed to investigate how total iron (Fe), ferrous ion ($Fe^{2+}$) and manganese (Mn) behave in case the system has not enough oxygen. The only difference between the first and the second experiments is the creation of the hypolimnetic conditions in the second experiment.

Again the clean water tank was filled with tap water. Next, the elodea plant, which is known the consume high rates of oxygen in a short time, was used to create hypoxia in the water tank. The elodea plant (Figure 2.4) was placed to the tank bottom then the tank was covered with black nylon to prevent air diffusion to the tank (Figure2.14). Thus the process of photosynthesis of elodea in the tank was prevented and the oxygen production was blocked. The tank stayed covered with black nylon for about 4 days until dissolved oxygen levels of 5 m/l were reached.

When the desired DO levels were achieved, the nylon cover was removed from the tank. The sediment container that was contaminated with 3 g/L Fe and Mn stock solution was then placed to the bottom of the water tank. The first sample was taken right after the sediments were placed corresponding to time zero measurement. All other samples were collected at 2, 6, 12, 24, 36, 48, 72 and 96 hours, respectively. At these times the water quality parameters including temperature, pH and dissolved oxygen were also measured while the samples were being collected.

All specimens were preserved at the ideal refrigerator temperature. The sediments in the tank were removed out of the tank then the tank was emptied and cleaned. All the collected were then analyzed using the spectrophotometer.

Figure 2.14. Water Tank Covered with Black Nylon

### 2.6.1.3. Experiment #3

As it is stated above low dissolved oxygen concentrations can cause negative effects on water quality. To improve water quality, aeration of the water body is a common practice in many reservoirs. However, in most cases, aeration is done without investigation of water quality parameters in advance.

Aeration is a well-known method that specially used for the treatment of huge water bodies from high elements or minerals. Especially in many reservoirs, the aeration system is accepted as the sole solution for improving the water quality for better management strategies. It can increase dissolved oxygen while preserving thermal stratification in water bodies.

The third experiment aimed at investigation of how aeration effects the dissolution of Total Fe, $Fe^{2+}$ and Mn in the hypolimnetic water layer. However, aeration was applied to the system very carefully to keep air diffusion at the nominal level (Figure 2.15). The water column was aerated at a flow rate of 60 L/hr (Figure 2.16). If air diffusion is too high, iron and manganese can not oxidize because of insufficient air. On the other hand, in case water flow is too low, water can saturate with dissolved oxygen and it leads to corrosive water in the system. This type of water can cause lead and copper level increase at the taps.

Figure 2.15. Aerator

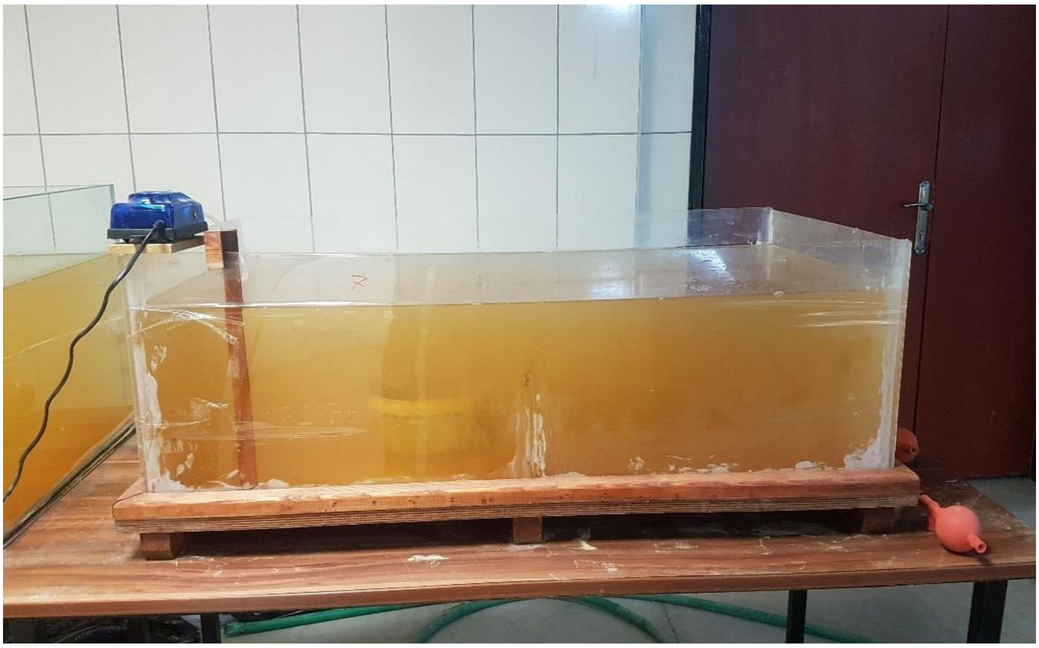


Figure 2.16 Applying Air with Aerator

A concentration of 3 g/L Fe and Mn stock solution was prepared. Then 200 liters tap water was filled to the tank. Similar to the other experiments, 1.2 kilograms of sediment was mixed with stock solution and then placed to the bottom of the tank slowly to avoid the sediments in the container to mix with the water column.

Following the placement of the containers with the contaminated sediments, the first water sample was collected from 5 cm above the sediment container upper point and marked as time zero.

All other samples were collected at 2, 6, 12, 24, 36, 48, 72 and 96 hours, respectively At these times the water quality parameters including temperature, pH and dissolved oxygen were also measured while the samples were being collected.

All specimens were preserved at the ideal refrigerator temperature. The sediments in the tank were removed out of the tank then the tank was emptied and cleaned. All the collected were then analyzed using the spectrophotometer.

### 2.6.2. Group #2

Investigation of release rates of iron and manganese from sediments to the water column with respect to different acidity levels of the water conditions were aimed at the fourth and fifth experiments. For this group of experiments, experiments were performed under hypoxia conditions created by the oxygen consumption of the elodea plant.

#### 2.6.2.1. Experiment #4

Under neutral water conditions, iron and manganese dissolve in water. According to previous studies, the water solubility of most iron and manganese compounds increases at acidic water. Additionally, the response of these compounds also depends upon the pH of water a scale used to specify how acidic or basic a water-based solution is. The reaction rate is slower under acidic water than under basic water conditions.

The purpose of the next experiment, Experiment #4 was to show how acidic water conditions affect iron and manganese solubility in case of hypoxia. The tank was filled, and the elodea plant was used to create hypoxia in the tank. When the DO level was reached around 5, the elodea was removed from the tank.

To reach the low level of pH, HCl was utilized (Figure 2.17). The solution of HCl was prepared and poured to the tank gradually to reach the pH of the water around 5.

Following the creation of hypoxia in the water tank via elodea plant, solution of HCI was poured to tank and so, pH was decreased around 5. Then sediment container, contaminated with a concentration of 3 g/L Fe and Mn stock solution was placed to the bottom of the tank, slowly. As always, just after the placement completed, the first water sample was taken from 5 cm above the sediment container upper point and this sample represented data for time zero.

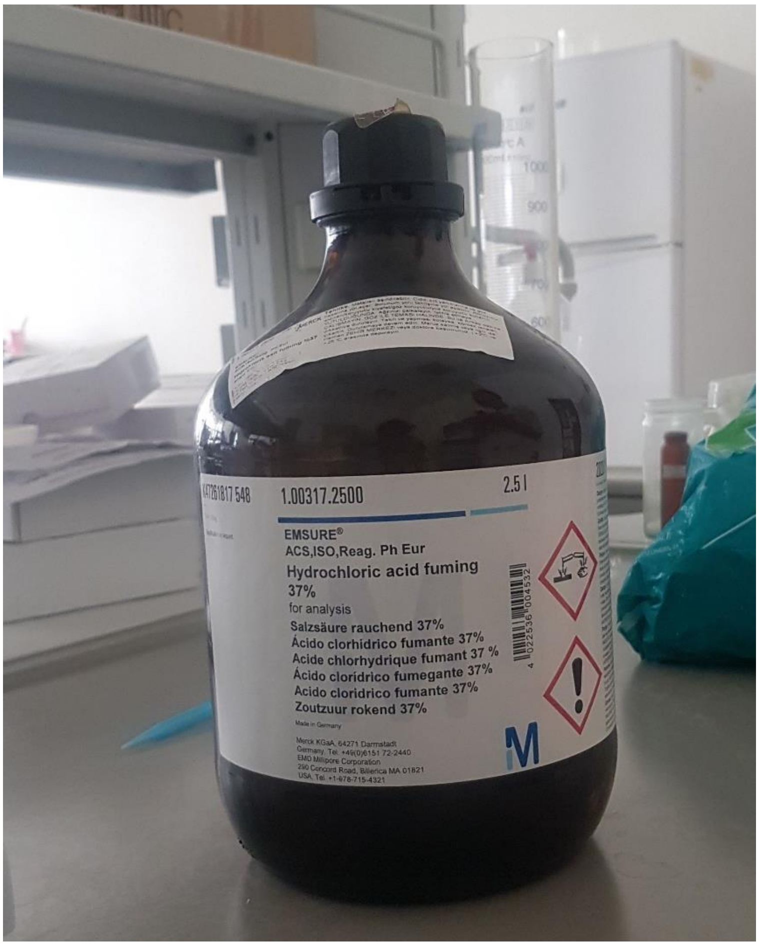


Figure 2.17. HCl Solution to Decrease Water pH

All other samples were collected at 2, 6, 12, 24, 36, 48, 72 and 96 hours, respectively. At these times the water quality parameters including temperature, pH and dissolved oxygen were also measured while the samples were being collected.

All specimens were preserved at the ideal refrigerator temperature. The sediments in the tank were removed out of the tank then the tank was emptied and cleaned. All the collected were then analyzed using the spectrophotometer.

### 2.6.2.2. Experiment# 5

Previous studies (Munger et al., 2016) showed that well-oxygenated conditions prevent or reduce soluble iron concentration accumulation in the hypolimnion of stratified reservoirs. However, there is no evidence for this kind of effect for manganese, soluble manganese still accumulated acidic to neutral (pH 5.6 to 7.5) hypolimnion.

The fifth experiment investigated the effect of basic (alkaline) conditions of water on iron and manganese concentrations. In order to increase water pH to an approximate value of 11, the NaOH solution was prepared before the tank was filled (Figure 2.18). Then the tank was filled, and the elodea plant placed to create hypoxia in the tank. When the DO level reached around 5, the elodea was removed from the tank. Then, the prepared NaOH solution was poured slowly until the tank reached pH 11.  After that, the tank was mixed slowly to prevent aeration.

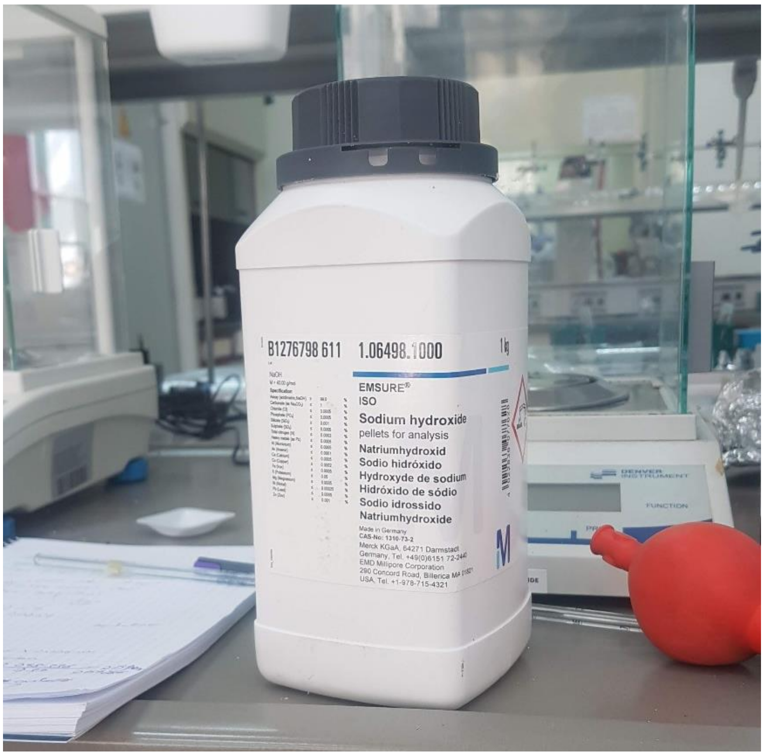


Figure 2.18 NaOH Used to Increase Water pH

A concentration of 3 g/L Fe and Mn stock solution was prepared. 1.2kilogram sediment was mixed with stock solution and then placed to the bottom of the tank slowly to avoid the sediments mixing with the water column.

Following the placement of the containers with the contaminated sediments, the first water sample was collected from 5 cm above the sediment container upper point and marked as time zero.

All other samples were collected at 2, 6, 12, 24, 36, 48, 72 and 96 hours, respectively. At these times, the water quality parameters including temperature, pH and dissolved oxygen were also measured while the samples were being collected.

All specimens were preserved at the ideal refrigerator temperature. The sediments in the tank were removed out of the tank then the tank was emptied and cleaned. All the collected were then analyzed using the spectrophotometer.

### 2.6.3. Group #3

The next experiments, Experiments #6 and Experiment #7 were performed to simulate stratified reservoirs. As observed in many reservoirs all around the world, dissolved oxygen concentrations are reduced in hypolimnion due to prevention of the vertical mixing by the thermocline. The main purpose of the experiments performed under this group is to analyze and investigate the behaviour of soluble iron and manganese concentrations exposed to thermal stratification with and without applied aeration during the experiments.

#### 2.6.3.1. Experiment #6

Dissolved oxygen concentrations decrease in the hypolimnion due to the lack of vertical mixing in the water column. Having this in mind, it is observed how stratification effects iron and manganese concentrations.

Thermal stratification is a process of changing the temperature at different depths in the lake. This natural process is based on the change in water's density with the temperature that develops two discrete layers of water: warm and cold. Temperature changes are another important parameter affecting the dissolution capacity of minerals in the water.

The main purpose of the sixth experiment is to investigate thermal stratification effects on soluble iron and manganese concentrations.

The stratification in the water tank was achieved by exposing the water column to a heater placed within the tank walls. The heater placed with a slope above the tank was kept until the following temperature profile was obtained (Figure 2.19). The vertical temperature profile according to depth is shown in Figure 2.20.

Before the water column was stratified, elodea plant was placed to the tank to reduce the oxygen in the tank and the tank was covered with black nylon. When the DO reached around 5, the plant removed and the sediment mixed with the specified concentration of the stock solution was placed to the bottom of the tank. Then the system was heated gradually.

Figure 2.19. Heater on Water Tank

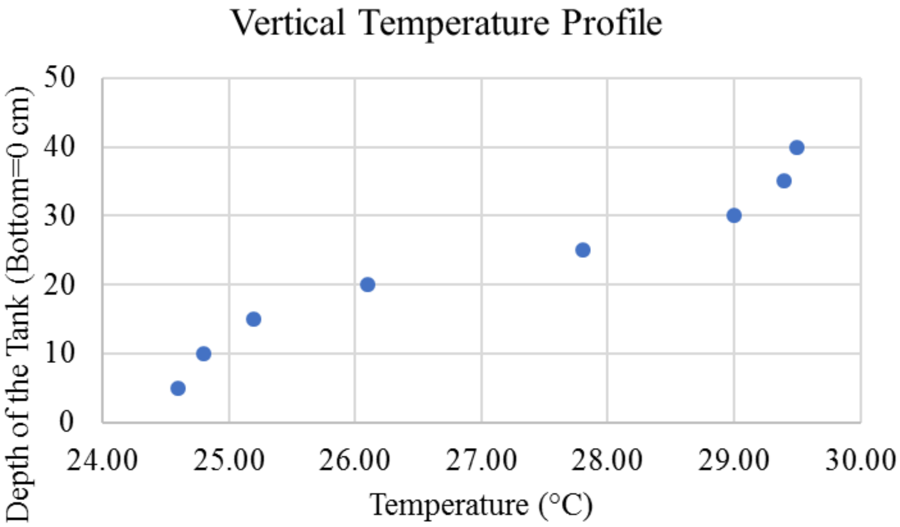


Figure 2.20. Vertical Temperature Profile

Following the placement of the container with the contaminated sediments, the first water sample was collected from 5 cm above the sediment container upper point and marked as time zero.

All other samples were collected at 2, 6, 12, 24, 36, 48, 72 and 96 hours, respectively. At these times, the water quality parameters including temperature, pH and dissolved oxygen were also measured while the samples were being collected.

All specimens were preserved at the ideal refrigerator temperature. The sediments in the tank were removed out of the tank then the tank was emptied and cleaned. All the collected were then analyzed using the spectrophotometer.

### 2.6.3.2. Experiment #7

As it is stated in Experiment #6, high temperature causes decreasing of dissolved oxygen concentration in water. In this part, it is aimed to observe temperature and aeration effect together on concentration changes of iron and manganese.

A heater was placed with the same slope then aerator hose was fixed to the top of the tank (Figure 2.21). While the performing of experiment, aerator and heater worked at the same time and duration.

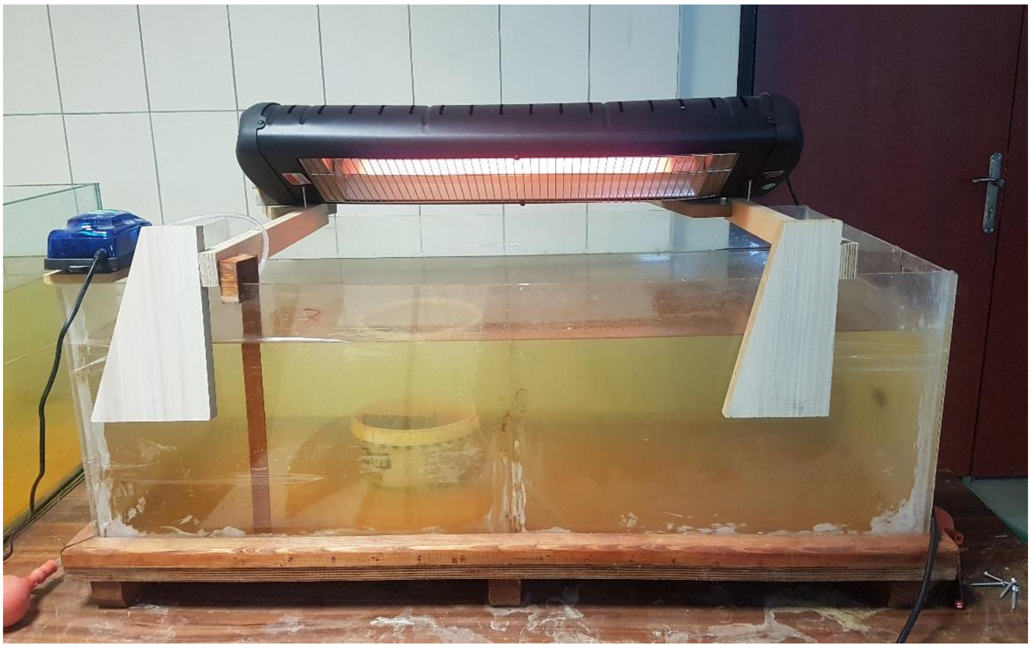


Figure 2.21. Heat and Aeration Applying Together to the Tank

Experiment #7 is the combination of aeration (Experiment #3) and stratification (Experiment #6). As it is known, hypolimnetic aeration applies to the water system to prevent hypolimnetic anoxia. Also, aeration is a well-known method that specially used for the treatment of huge water bodies from high elements or minerals. The aeration system is accepted in many reservoirs as the sole solution for improving the water quality for better management strategies. It can increase dissolved oxygen while preserving thermal stratification in the water body. Additionally, thermal stratification is a process of changing the temperature at different depths in the lake. This natural process is based on the change in water's density with the temperature that develops two discrete layers of water: warm and cold.

Experiment #7 purposed to investigate how aeration effects the dissolution of Total Fe, $Fe^{2+}$ and Mn in case of stratification and the hypoxia together. For that purpose, first, the heater was installed to the top of the tank. Then aerator was also placed to the bottom of the tank. To prevent disturbing stratification aeration is applied at the surface of the water. Moreover, aeration was applied to the system very carefully to keep water flow at the nominal level. If water flow is too high, iron and manganese can not oxidize because of insufficient air. On the other hand, in case water flow is too low, water can saturate with dissolved oxygen and it leads to corrosive water in the system.

Stock solution with a concentration of 3 g/L Fe and Mn was prepared and mixed with the sediment. Elodea plant placed to the tank filled with tap water to create hypoxia in the tank. In case the DO level reached around 5, the elodea was removed from the tank. Then, the sediment container placed to the bottom of the tank. The first sample just is taken after the sediment placement to the tank from 5 cm above the sediment container upper point and marked as time zero. Before taking all other samples, the tank was heated and aerated together, for half an hour. The rest of the 2nd, 3rd, 4th, 5th, 6th,7th, 8th, 9th, and 10th samples were taken 1,2, 6, 12, 24, 36, 48, 72 and 96 hours later than the first one, respectively. Water quality parameters, temperature, pH and dissolved oxygen were measured while the samples were taken. In the end, the tank was emptied. Then all the samples were analyzed at the spectrophotometer. As a note that, all specimens were preserved at the ideal refrigerator temperature.

# CHAPTER 3

# RESULTS

## 3.1. Results of the Experiments

Totally seven different experiments were performed by changing only one parameter for comparison purposes. Two water tanks with the same capacity of 200 liters were used. Concentration of 3 g/L Fe and Mn were used to contaminate 1.2 kilograms of sediment samples at each experiment. It is noted that sediment size distribution of the Tahtalı Reservoir was simulated for this study.

In all experiments, firstly, the water tank was filled with 200 liters tap water then sediment contaminated with a concentration of 3 g/L Fe and Mn was placed to the tank's bottom quite slowly to prevent mixing with water. The critical point was analyzing tap water's Fe and Mn concentration before performing experiments. Experiment results indicated that iron and manganese concentrations of tap water were insignificant.

In the Experiment #1, 3 g/L Fe and Mn stock solution was prepared before filling the tank with 200 liters of tap water. 1.2 kilogram sediment was mixed with stock solution then placed to the bottom of the tank slowly to avoid the sediments released from the containers. Just after placement completed, the first sample was taken from 5 cm above the sediment container upper point and marked as time zero. The second specimen was taken one hour later than the first one. The rest of the 3rd, 4th, 5th, 6th,7th, 8th, 9th, and 10th samples were taken 2, 6, 12, 24, 36, 48, 72 and 96 hours later than the first one, respectively. At the same time, the quality parameters of water, temperature, pH and dissolved oxygen that effects highly change of concentration of two elements were measured while the samples were taken. All specimens were preserved at the ideal refrigerator temperature. The sediments in the tank were got out of the tank then the tank was emptied.

Then samples were analyzed in the spectrophotometer. According to results, shown in the below figures (Figure 3.1 and Figure 3.2), Total Fe and $Fe^{2+}$ were increased in the first two hours, then both were decreased slowly till the end of 96 hours. Manganese showed different behavior than the others. While the first two hours it was sharply decreased, it followed smooth decreased till the end. According to Figure 3.3, dissolved oxygen and pH followed a smooth path in the whole experiment while the temperature was showed a small increase.

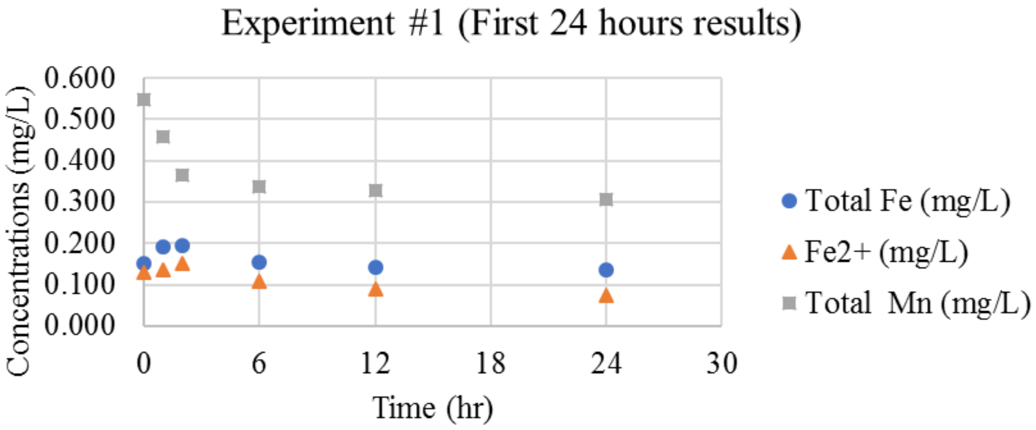


Figure 3.1. Variation of Iron and Manganese Concentrations for the First Experiment During the First 24 Hours

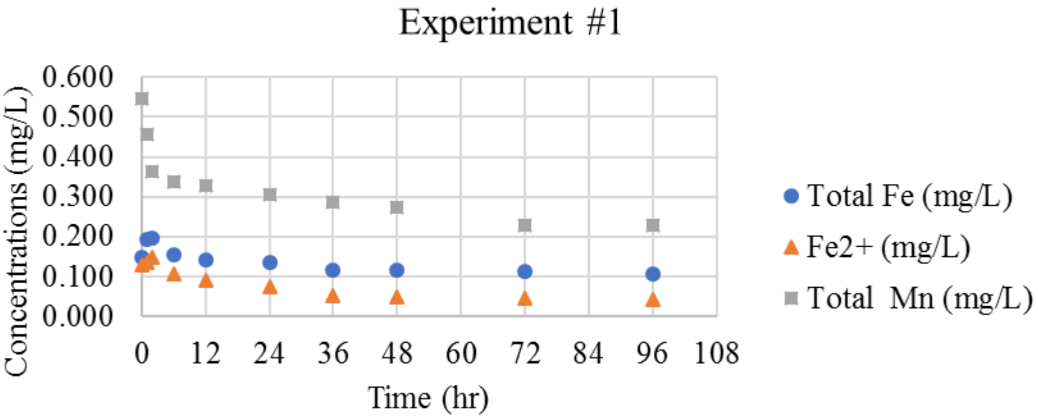


Figure 3.2. Variation of Iron and Manganese Concentrations for the First Experiment

As it is known, hypoxia (lack of oxygen) significantly affects the solubility of minerals in the water. Experiment #2 aimed to investigate how Total Fe, $Fe^{2+}$ and Mn behave in case the system has not enough oxygen. The only difference between Experiment #1 and Experiment #2 is creating the hypolimnetic condition in Experiment #2. To create hypoxia in the water tank elodea plant, which is popular with high oxygen consumption, was used. The elodea plant was placed to the tank bottom then the tank covered with black nylon to prevent air diffusion to the tank. Thus, it was blocked to photosynthesis of elodea in the tank.

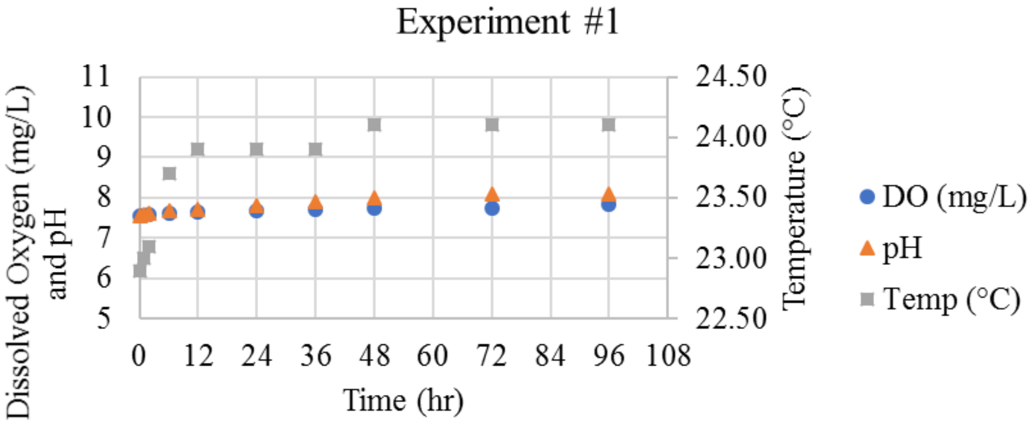


Figure 3.3. Variation of DO, pH and Temperature for the First Experiment Figure

The rest of experiment steps is same with Experiment #1. The clean water tank was filled with tap water. The sediment container had contaminated with 3 g/L Fe and Mn stock solution was placed to the bottom of the water tank. The first sample was taken just after the tank contaminated. All other samples were taken 2, 6, 12, 24, 36, 48, 72 and 96 hours later than the first one, respectively. Moreover, quality parameters of water, which are temperature, pH and dissolved oxygen, were observed together with taking of the samples. The samples were kept at the ideal refrigerator temperature.

According to the results analyzed in the spectrophotometer, the figures were drawn. The results (Figure 3.4 and Figure 3.5) showed that hypoxia in the tank was led to dissolve more $Fe^{+2}$ in the water. Moreover, the Figure 3.4 showed the amount of dissolved Total Fe increased but not as much as $Fe^{2+}$. When dissolved Mn concentration compared between the Experiment #1 and Experiment #2, a hypolimnetic condition caused more dissolution of Mn in water. The Figure 3.6 were followed so similar paths with Experiment #1.

Dissolved oxygen and pH followed a smooth path in the whole experiment while the temperature was showing a small increase. According to Figure 3.6, the temperature did not vary greatly and was around 24 ° C, as the first experiment. pH showed a similarly smooth path in around 8-9. Dissolved oxygen (DO) increased from about 4 to 9.

Hypolimnetic aeration installs into the reservoir in order to prevent hypolimnetic anoxia. Aeration is a well-known method that specially used for the treatment of huge water bodies from high elements or minerals. Especially in many reservoirs, the aeration system is accepted as the sole solution for improving the water quality for better management strategies. It can increase dissolved oxygen while preserving thermal stratification in water bodies.

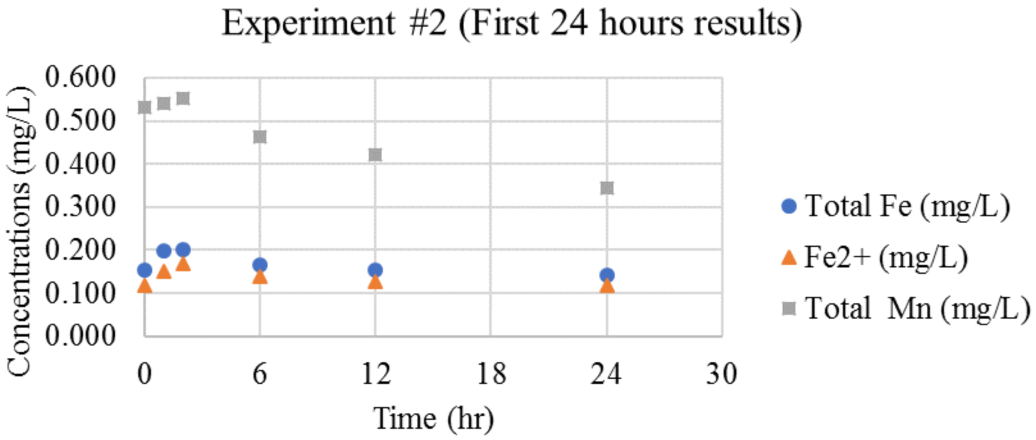


Figure 3.4. Variation of Iron and Manganese Concentrations for the Second Experiment During the First 24 Hours

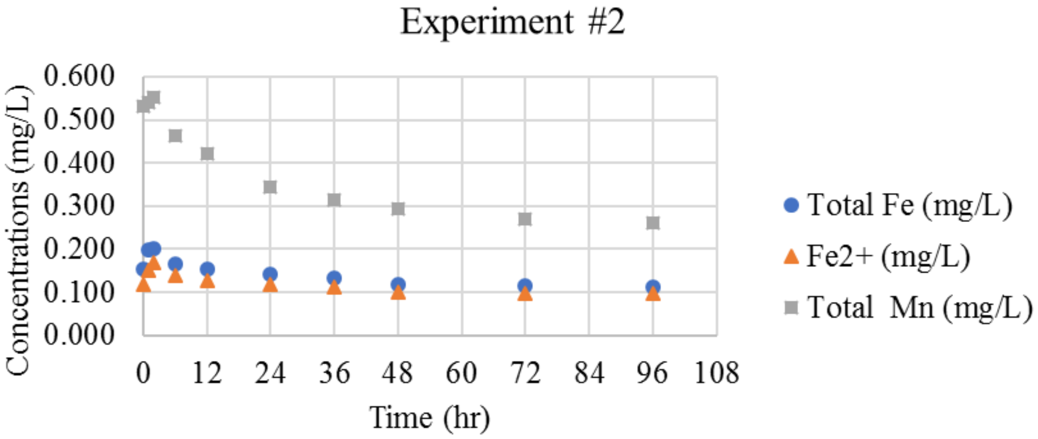


Figure 3.5. Variation of Iron and Manganese Concentrations for the Second Experiment

Experiment #3 purposed to investigate how aeration in the hypolimnetic condition effects the dissolution of Total Fe, Fe2+ and Mn. However, aeration was applied to the system very carefully to keep water flow at the nominal level. If water flow is too high, iron and manganese can not oxidize because of insufficient air. On the other hand, in case water flow is too low, water can saturate with dissolved oxygen and it leads to corrosive water in the system. This type of water can cause lead and copper level increase at the taps.

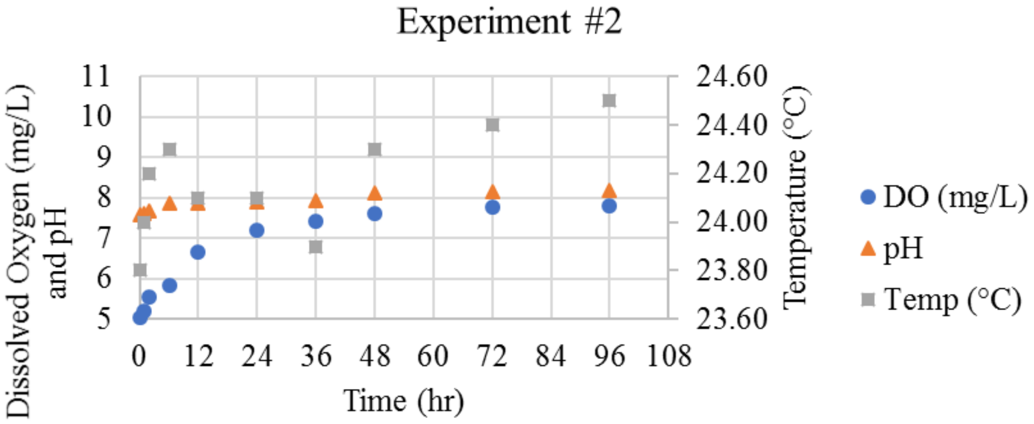


Figure 3.6. Variation of DO, Ph and Temperature for the Second Experiment Figure

Before the tank was filled, a concentration of 3 g/L Fe and Mn stock solution was prepared Then 200 liters tap water was filling the tank. As the same with other experiments, one point two-kilogram sediment was mixed with stock solution then placed to the bottom of the tank slowly to avoid the sediments released from the containers. When the placement completed, the first sample was taken from 5 cm above the sediment container upper point and marked as time zero. The second specimen was taken one hour later than the first one. The rest of the 3rd, 4th, 5th, 6th,7th, 8th, 9th, and 10th samples were taken 2, 6, 12, 24, 36, 48, 72 and 96 hours later than the first one, respectively. As always, the quality parameters of water, temperature, pH and dissolved oxygen that effects highly change of concentration of two elements were measured while the samples were taken. All specimens were preserved at the ideal refrigerator temperature. In the end, the sediments in the tank were got out of the tank then the tank was emptied. Then all the samples were analyzed at the same spectrophotometer. According to results, no major change was observed on the Figure 3.7 and Figure 3.8. However, unlike Experiment #1 and Experiment #2, the first two hours of Total Fe and Fe2+ concentrations decreased and continued similarly until the end of 96 hours.

According to Figure 3.9, the temperature did not vary greatly and was around 24°C, similar to the first two experiments. pH showed a similarly smooth path in around 9. Dissolved oxygen (DO) increased from about 4 to 9.

Iron and manganese dissolve under neutral water conditions. The water solubility of most of iron and manganese compounds increase at acidic water. Moreover, aeration reaction rate depends upon water pH. The reaction rate is slower under acidic water than under alkalic water conditions. The water quality condition for example temperature and pH at the Experiment #1, Experiment #2 and Experiment #3 generally similar with each other. According to studies done before, it was noticed that a low level of water pH causes more iron and manganese dissolution.

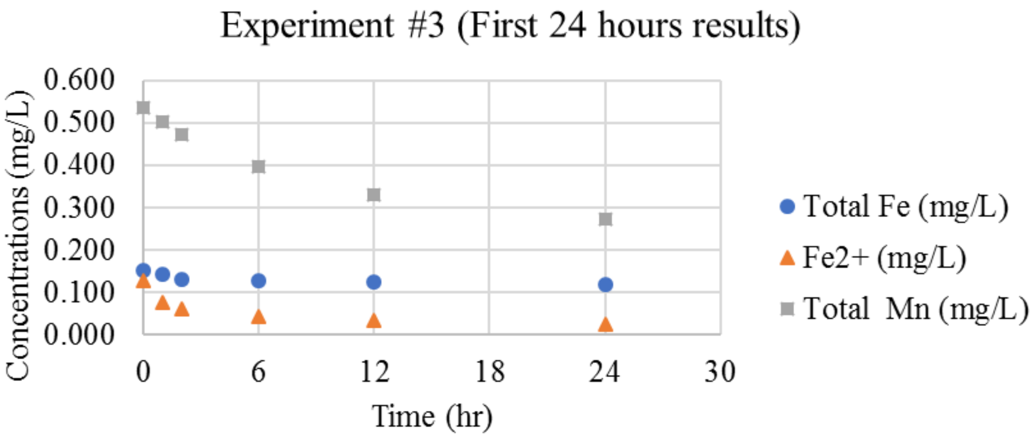


Figure 3.7. Variation of Iron and Manganese Concentrations for the Third Experiment During The First 24 Hours

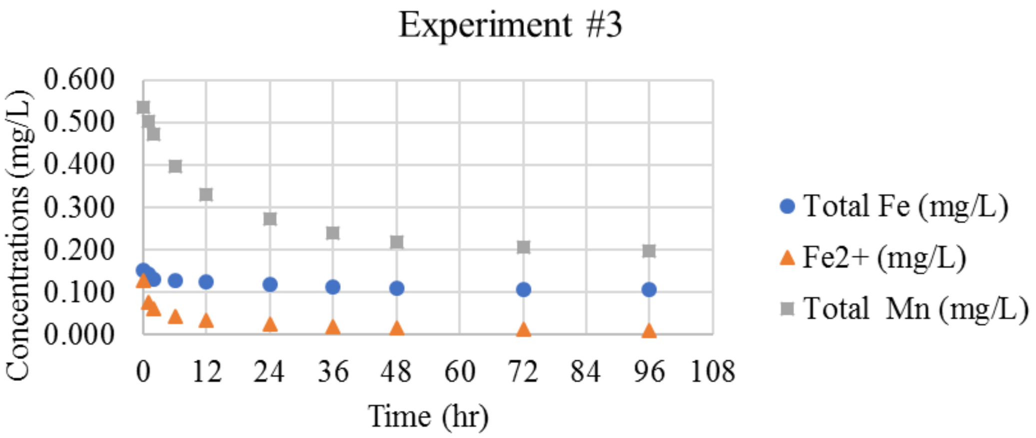


Figure 3.8. Variation of Iron and Manganese Concentrations for the Third Experiment

Experiment #4 aimed to show how acidic water conditions affect iron and manganese solubility in case of hypoxia. The tank was filled, and the elodea plant placed to create hypoxia in the tank. When the DO level reached around 5, the elodea was removed from the tank. To reach the low level of pH, HCl was used. The solution of HCl was prepared and poured to the tank gradually to reach the pH of the water around 5.

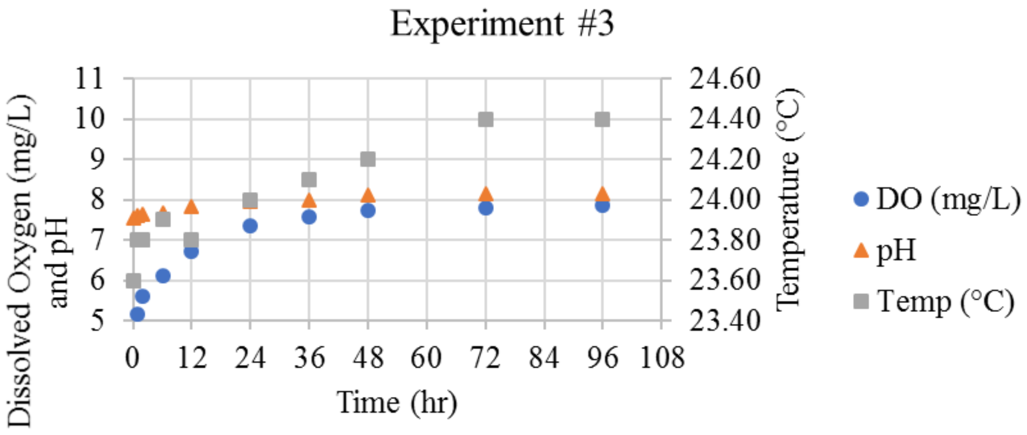


Figure 3.9. Variation of DO, pH and Temperature for the Third Experiment Figure

Elodea plant was used to reduce the DO rate and create hypoxia in the filled tank. Then the sediment container, contaminated with a concentration of 3 g/L Fe and Mn stock solution was placed to the bottom of the tank, slowly. As always, just after the placement completed, the first sample was taken from 5 cm above the sediment container upper point and marked as time zero. The rest of the 2nd, 3rd, 4th, 5th, 6th,7th, 8th, 9th, and 10th samples were taken 1,2, 6, 12, 24, 36, 48, 72 and 96 hours later than the first one, respectively. The quality parameters of water, temperature, pH and dissolved oxygen were measured while the samples were taken. All specimens were preserved at the ideal refrigerator temperature. In the end, the tank was emptied. Then all the samples were analyzed at the spectrophotometer.

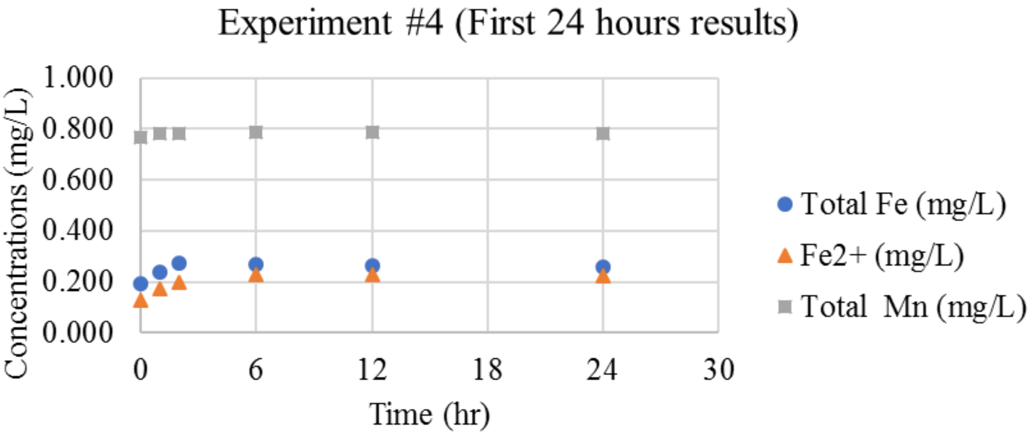


Figure 3.10. Variation of Iron and Manganese Concentrations for the Fourth Experiment During the First 24 Hours

The results in Figure 3.10 and Figure 3.11 show that acidic water highly affected the solubility of iron and manganese. When Experiment #1 and Experiment #4 is compared, the concentration of Total Fe, $Fe^{2+}$ and Mn in the acidic water was considerably greater than Experiment #1.

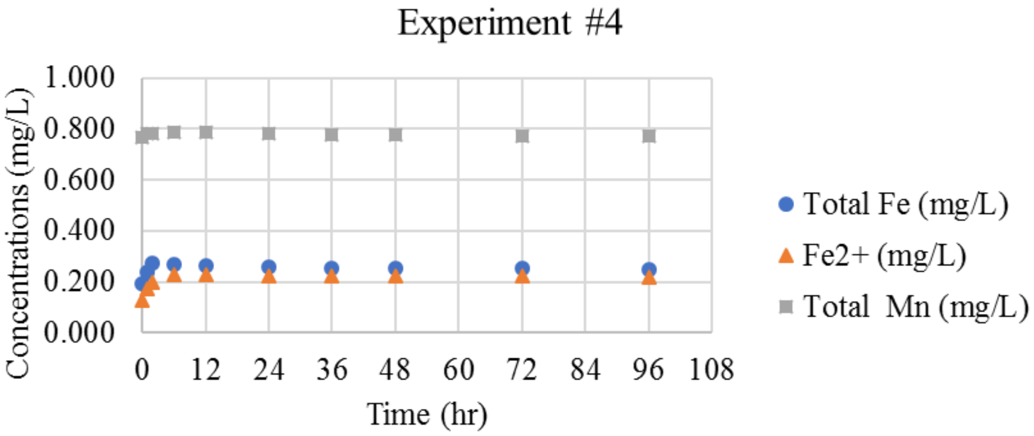


Figure 3.11. Variation of Iron and Manganese Concentrations for the Fourth Experiment

According to Figure 3.12, pH was around 5 then it increased to 6 at the end. As well, DO increase from 5 to 7. There is no considerable change in temperature.

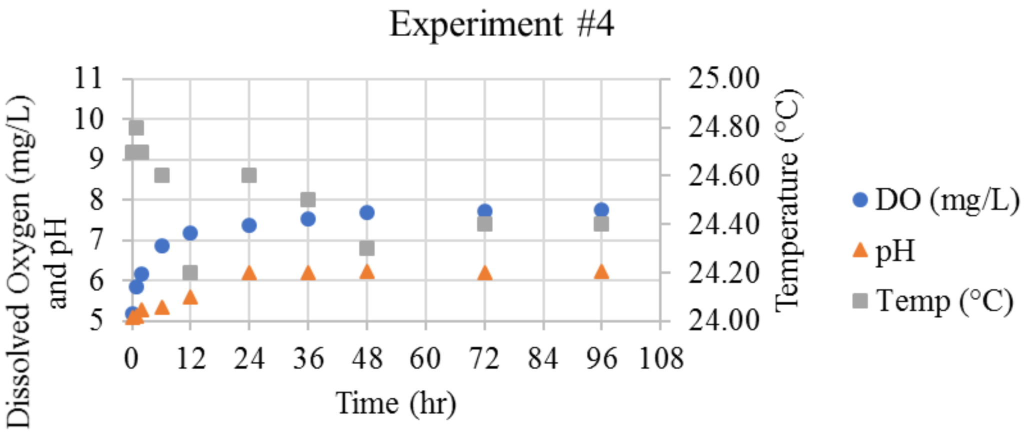


Figure 3.12. Variation of DO, pH and Temperature for the Third Experiment Figure

As stated above, water pH plays a significant role in the oxidation of iron and manganese. Moreover, a low level of water pH causes more iron and manganese dissolution. The ideal water pH range is 7.5 to 8.0 for the oxidation of iron according to Mazzei Technical Bulletin No. 2. However, water pH should be at least 9.5 for the manganese. Oxidation of manganese is quite slow below this pH level.

To increase water pH to around 11, the NaOH solution was prepared before the tank filled. Then the tank was filled, and the elodea plant placed to create hypoxia in the tank. When the DO level reached around 5, the elodea was removed from the tank. Then, the prepared NaOH solution was poured slowly until the tank reached pH 11. After that, the tank was mixed slowly to prevent aeration.

A concentration of 3 g/L Fe and Mn stock solution was prepared. One point two-kilogram sediment was mixed with stock solution then placed to the bottom of the tank slowly to avoid the sediments released from the containers. When the placement completed, the first sample was taken from 5 cm above the sediment. All other samples were taken 2, 6, 12, 24, 36, 48, 72 and 96 hours later than the first one, respectively. As always, the quality parameters of water, temperature, pH and dissolved oxygen that effects highly change of concentration of two minerals were measured while the samples were taken. The samples were preserved at the ideal refrigerator temperature. In the end, the sediment in the tank was got out of the tank then the tank was emptied. Then all the samples were analyzed at the spectrophotometer.

According to results, no major change is observed for Total Fe and Fe2+ according to Figure 3.13 and Figure 3.14. However, unlike all other experiments, Mn concentration shows a considerable decrease in alkaline water conditions.

Water quality parameters Figure 3.15 shows that pH decreased around 11 to 9. Also, DO increased from 5 to 8. The temperature level still around 24, according to Figure 3.15.

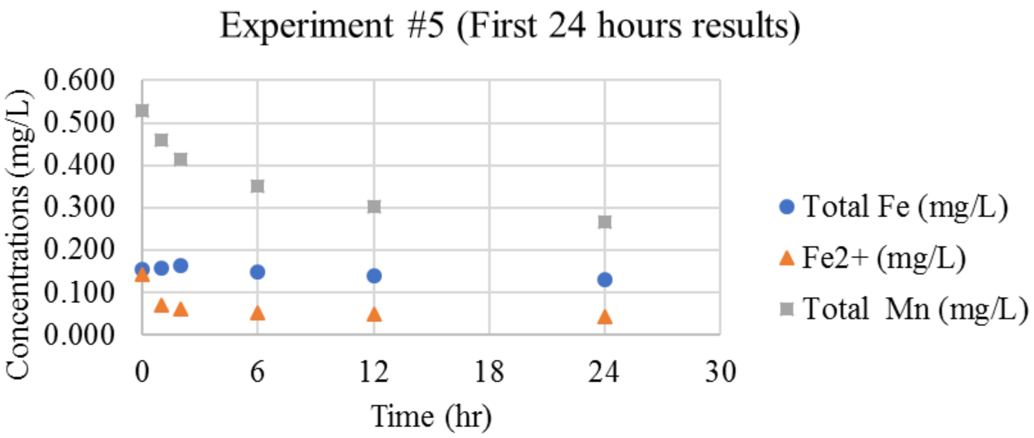


Figure 3.13. Variation of Iron and Manganese Concentrations for the Fifth Experiment During the First 24 Hours

Thermal stratification is a process of changing the temperature at different depths in the lake. This natural process is based on the change in water's density with the temperature that develops two discrete layers of water: warm and cold. Temperature changes are another important parameter affecting the dissolution capacity of minerals in the water.

Moreover, oxygen concentration reduces while the temperature increases. The main purpose of the Experiment #6 is to analyze and investigate thermal stratification effects on soluble iron and manganese concentration.

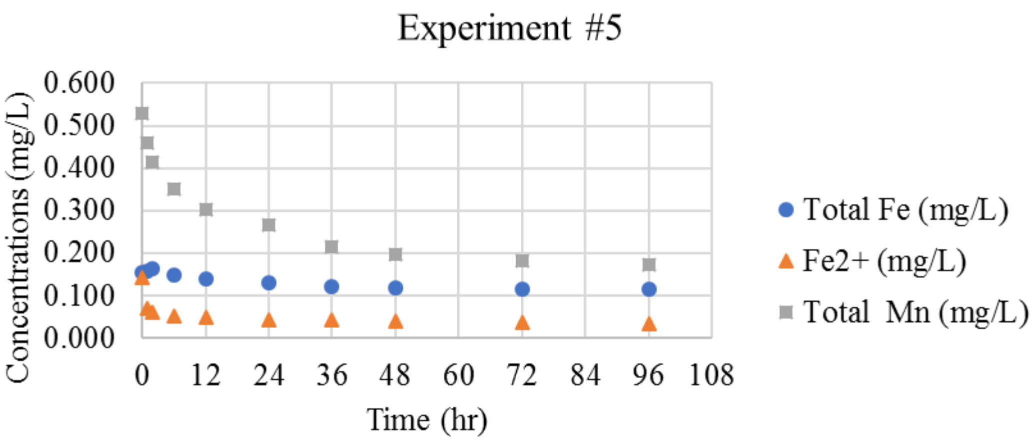


Figure 3.14. Variation of Iron And Manganese Concentrations for the Fifth Experiment

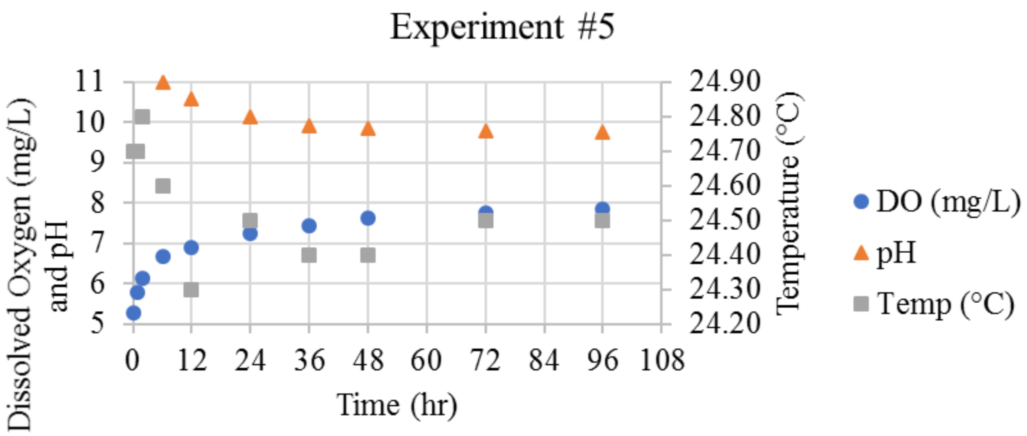


Figure 3.15. Variation of DO, pH and Temperature for the Fifth Experiment Figure

To create stratification on the water body, a heater was installed at the top of the water tank. A concentration of 3 g/L Fe and Mn stock solution was prepared and mixed with the sediment. Then the tank was filled with tap water and the elodea plant placed to the tank to create hypoxia in the tank. When the DO level reached around 5, the elodea was removed from the tank. Then, the sediment container placed to the bottom of the tank. The first sample just is taken after the sediment placement to the tank from 5 cm above the sediment container upper point and marked as time zero. Before taking all other samples, the tank was heated for half an hour. The rest of the 2nd, 3rd, 4th, 5th, 6th,7th, 8th, 9th, and 10th samples were taken 1,2, 6, 12, 24, 36, 48, 72 and 96 hours later than the first one, respectively. The quality parameters of water, temperature, pH and dissolved oxygen were measured while the samples were taken. All specimens were preserved at the ideal refrigerator temperature. In the end, the tank was emptied. Then all the samples were analyzed at the spectrophotometer.

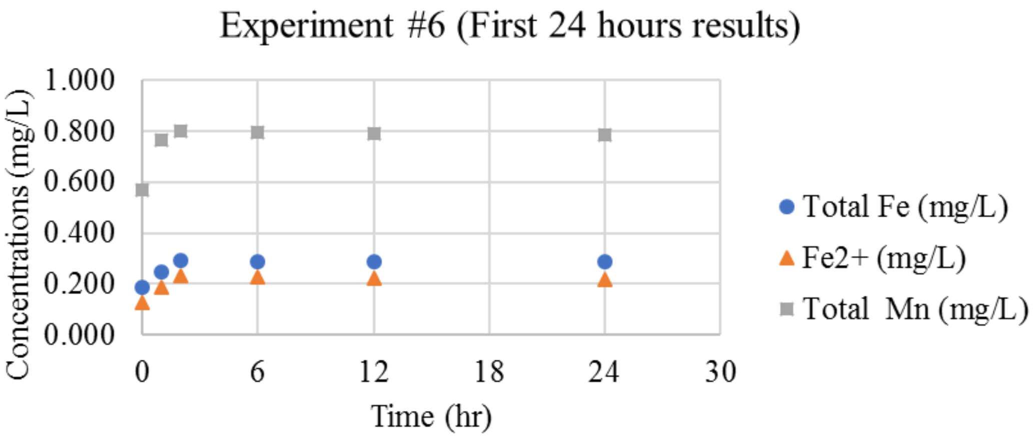


Figure 3.16. Variation of Iron and Manganese Concentrations for the Sixth Experiment During the First 24 Hours

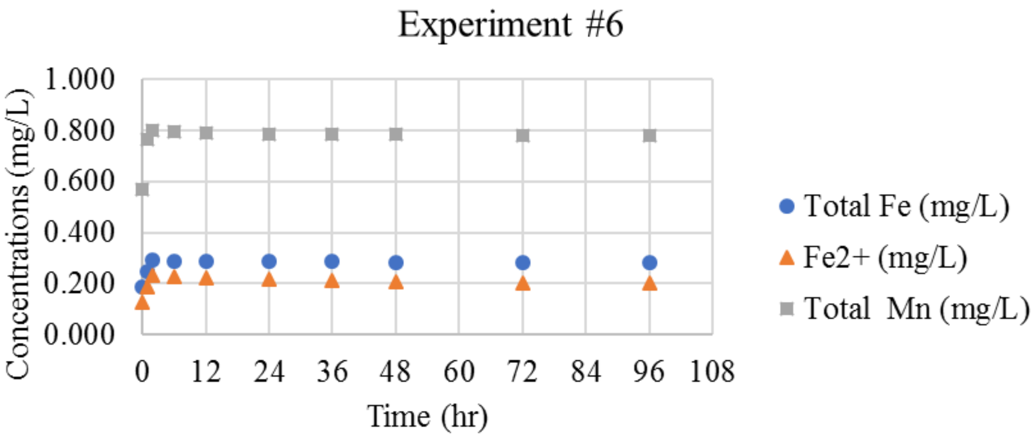


Figure 3.17. Variation of Iron And Manganese Concentrations for the Sixth Experiment

The results in Figure 3.16 and Figure 3.17 show that high temperature, means stratification on the water body, considerably affected the solubility of iron and manganese. When Experiment #1, Experiment #4, and Experiment #6 are compared, the concentration of Total Fe and Mn is very high in case of stratification.

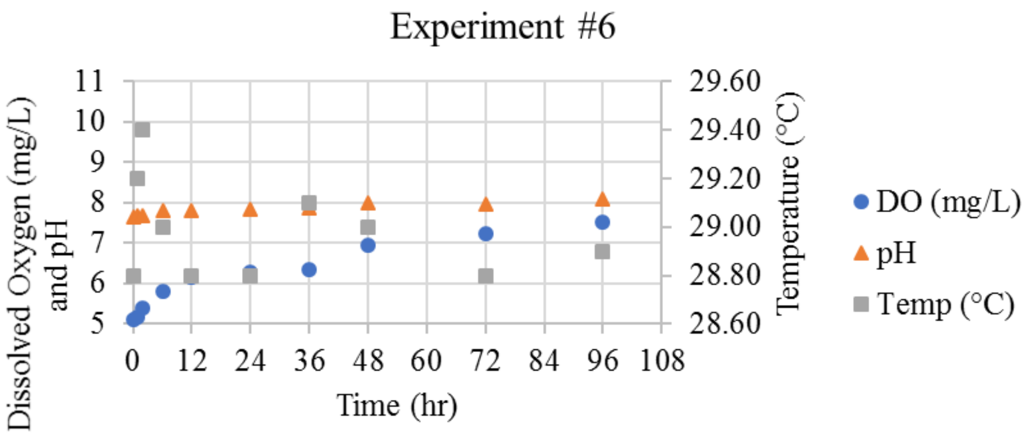


Figure 3.18. Variation of DO, pH and Temperature for the Sixth Experiment Figure

According to Figure 3.18, the pH level is around 7 to 8. As well, DO increase from 5 to 7. The temperature is high because of applying heat to the system. It is around 29°C.

Experiment #7 is the combination of aeration (Experiment #3) and stratification (Experiment #6). As it is known, hypolimnetic aeration applies to the water system to prevent hypolimnetic anoxia. Also, aeration is a well-known method that specially used for the treatment of huge water bodies from high elements or minerals. The aeration system is accepted in many reservoirs as the sole solution for improving the water quality for better management strategies.  can It increases dissolved oxygen while preserving thermal stratification in the water column. Additionally, thermal stratification is a process of changing the temperature at different depths in the lake. This natural process is based on the change in water's density with the temperature that develops two discrete layers of water: warm and cold.

Experiment #7 purposed to investigate how aeration effects the dissolution of Total Fe, Fe2+ and Mn in case of stratification and the hypoxia together. For that purpose, first, the heater was installed to the top of the tank. Then aerator was also placed to the bottom of the tank. To prevent disturbing stratification aeration is applied at the surface of the water. Moreover, aeration was applied to the system very carefully to keep water flow at the nominal level. If water flow is too high, iron and manganese can not oxidize because of insufficient air. On the other hand, in case water flow is too low, water can saturate with dissolved oxygen and it leads to corrosive water in the system.

Stock solution with a concentration of 3 g/L Fe and Mn was prepared and mixed with the sediment. Elodea plant placed to the tank filled with tap water to create hypoxia in the tank. In case the DO level reached around 5, the elodea was removed from the tank. Then, the sediment container placed to the bottom of the tank. The first sample just is taken after the sediment placement to the tank from 5 cm above the sediment container upper point and marked as time zero. Before taking all other samples, the tank was heated and aerated together, for half an hour. The rest of the 2nd, 3rd, 4th, 5th, 6th,7th, 8th, 9th, and 10th samples were taken 1, 2, 6, 12, 24, 36, 48, 72 and 96 hours later than the first one, respectively. Water quality parameters, temperature, pH and dissolved oxygen were measured while the samples were taken. In the end, the tank was emptied. Then all the samples were analyzed at the spectrophotometer. As a note that, all specimens were preserved at the ideal refrigerator temperature.

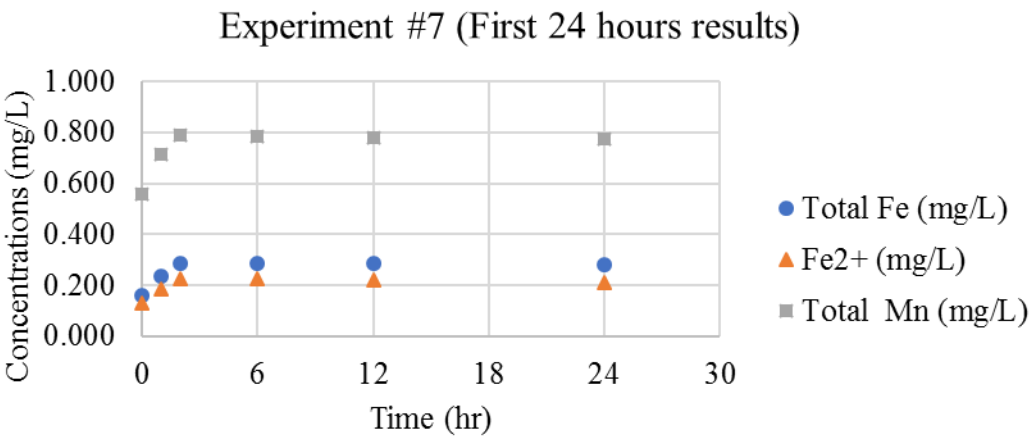


Figure 3.19. Variation of Iron And Manganese Concentrations for the Seventh Experiment During the First 24 Hours

The results in Figure 3.19 and Figure 3.20 show that high temperature together with aeration affected the solubility of iron and manganese. When Experiment #6 and Experiment #7 are compared, the concentration of Total Fe, Fe2+ and Mn in Experiment #7 is less than Experiment #6. It means aeration helps oxidation of iron and manganese minerals.

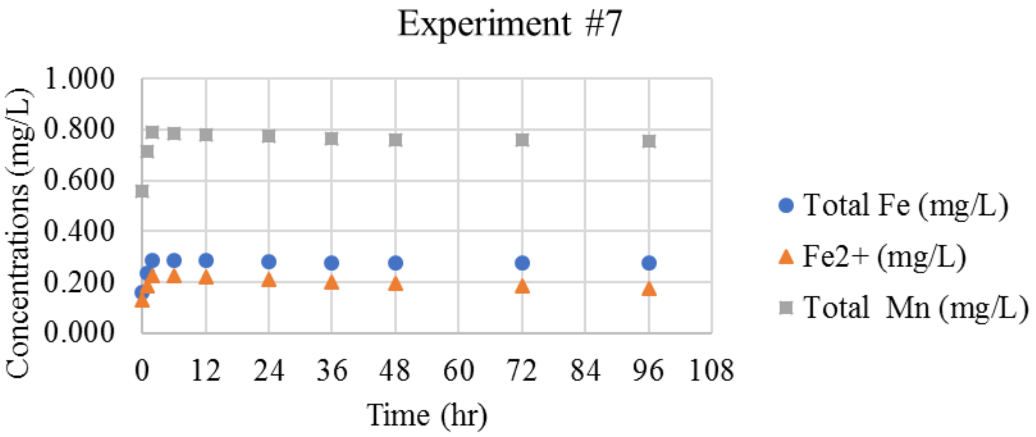


Figure 3.20. Variation of Iron and Manganese Concentrations for the Seventh Experiment

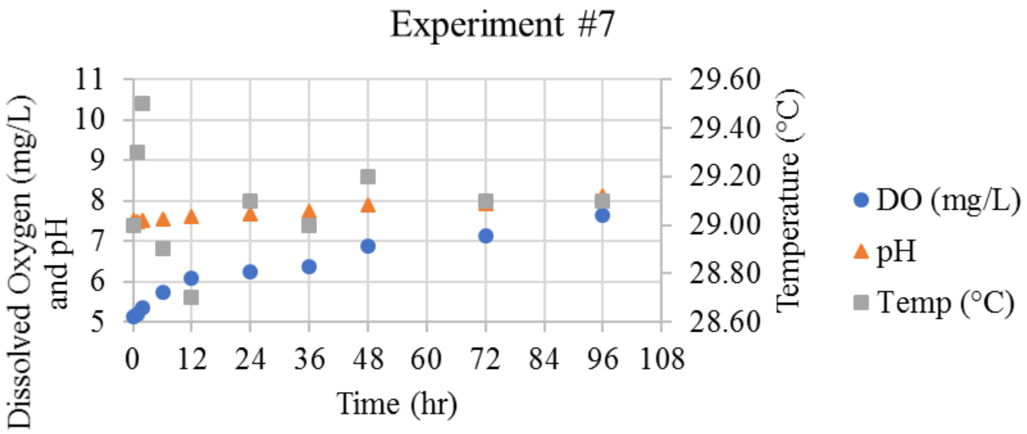


Figure 3.21. Variation of DO, pH and Temperature for the Seventh Experiment Figure

According to Figure 3.21, pH level is around 7. As well, DO increase from 5 to 7. The temperature is nearly same with Experiment #6 and it is high because of applying heat to the system. It is around 29°C.

## 3.2. Comparison Graphs Derived from Experiments

### 3.2.1. Total Iron (Fe) Concentration

Figure 3.22 and Figure 3.23 presents the total iron (Fe) concentrations at the water column measured 5 cm above the sediment container as obtained from Shimadzu UV-2600 Spectrophotometer analysis.

Time variation of monitored total iron (Fe) concentrations at the water column is presented for seven consecutive experiments Figure 3.23, for four days.

At the beginning of the first experiment, Fe concentration was 0.150 mg/L. It increased first to 0.195 mg/L in two hours then decreased to the value of 0.108 mg/L during the next four days.

The second experiment was started 4 days after the start of the first experiment in the other tank to create hypoxia in the water column. As can be seen from the results of the second experiment, the concentration of 0.153 mg/L total iron (Fe) was observed at time zero and the final concentration at the end of the fourth day was 0.112 mg/L. The peak point was observed at a value of 0.201 mg/Lat the end of the second hour.

The third experiment aimed to show aeration effects together with hypoxia. This experiment was started following the first two experiments completed. The concentration of 0.153 mg/L for total iron (Fe) was observed at time zero and decreased to 0.106 mg/L at the end of the fourth day. No increase in total iron (Fe) concentration was observed during the whole experiment.

The monitored value of Total iron (Fe) concentration at the beginning of the fourth experiment (in the condition of low pH), was 0.195 mg/L and it increased to 0.275 mg/L at the end of the second hour. and decreased to 0.247 mg/L at the end of the fourth day.

In the fifth experiment that observed the alkaline condition, the total iron (Fe) concentration value monitored initially at time zero was 0.155 mg/L, while the peak concentration observed was 0.162 mg/L at the end of the second hour. It decreased to 0.115 mg/L at the end of four days.

The initial recorded value of total iron (Fe) concentration at time zero was 0.187 mg/L in the sixth experiment for the case of contaminated sediments, clean water with hypoxia in neutral water condition. It increased to 0.290 mg/L at the end of the second hour and decreased to 0.282 at the end of the experiment.

The initial recorded value of total iron (Fe) concentration at time zero was with 0.163 mg/L for the seventh experiment, which considered the release of contaminated sediments to the clean, neutral water column with hypoxia, aerated at 60 l/h and stratified with a heater. the value of total iron (Fe) concentration increased to 0.288 mg/L at the end of the second hour and decreased to the value of 0.276 mg/L at the end of the experiment. Moreover, the tap water total iron concentration is 0.003 mg/L.

According to Figure 3.22 and Figure 3.23 below, in case of high temperature (Experiment #6 and Experiment #7) high elements dissolution capacity of water increased. These experiments demonstrate the summer season situation at the water structures. Moreover, acidic water (Experiment #4) caused dissolving of high elements while basic water (Experiment #5) helped to transform and precipitate of elements to the ground of water. When the first three parts compared, hypoxia with aeration (Experiment #3) gave the best desirable results for Total Fe.

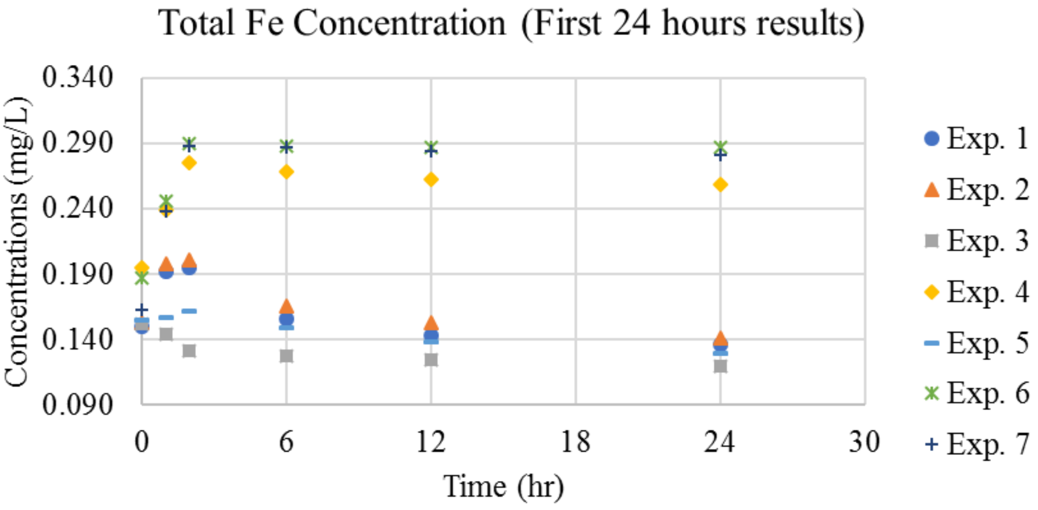


Figure 3.22. Total Fe Concentration First 24 Hours Results

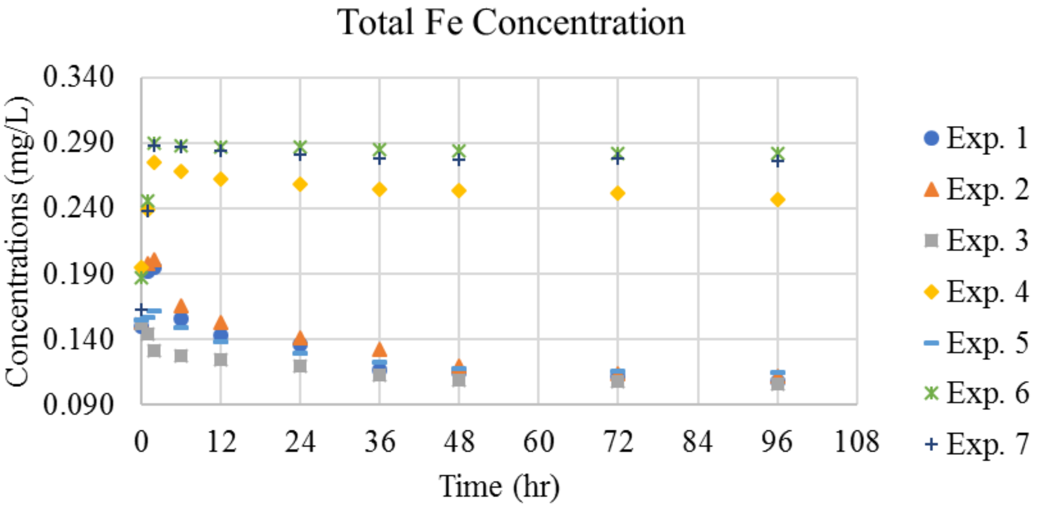


Figure 3.23. Total Fe Concentration All Results

### 3.2.2. Ferrous Ion ($Fe^{2+}$) Concentration

Time variation of monitored ferrous ion ($Fe^{2+}$) concentrations at the water column measured at 5 cm above the sediment container is presented for seven experiments in Figure 3.24 and Figure 3.25.

At the beginning of the first experiment, $Fe^{2+}$ concentration was 0.130 mg/L. It increased first to 0.150 mg/L in two hours then decreased to the value of 0.041 mg/L during the next four days.

The second experiment was started 4 days after the start of the first experiment in the other tank to create hypoxia in the water column. As can be seen from the results of the second experiment, the concentration of 0.118 mg/L ferrous ion ($Fe^{2+}$) was observed at time zero and the final concentration at the end of the fourth day was 0.096 mg/L. The peak point was observed at a value of 0.169 mg/Lat the end of the second hour.

The third experiment aimed to show aeration effects together with hypoxia. This experiment was started following the first two experiments completed. The concentration of 0.127 mg/L for ferrous ion ($Fe^{2+}$) was observed at time zero and decreased to 0.009 mg/L at the end of the fourth day. No increase in ferrous ion ($Fe^{2+}$) concentration was observed during the whole experiment.

The monitored value of ferrous ion ($Fe^{2+}$) concentration at the beginning of the fourth experiment (in the condition of low pH), was 0.128 mg/L and increased to 0.220 mg/L at the end of the fourth day. The peak point was observed at a value of 0.227 mg/Lat the end of the sixth hour.

In the fifth experiment that observed the alkaline condition, the ferrous ion ($Fe^{2+}$) concentration value monitored initially at time zero was 0.142 mg/L and decreased to 0.035 mg/L at the end of four days.

The initial recorded value of ferrous ion ($Fe^{2+}$) concentration at time zero was 0.125 mg/L in the sixth experiment for the case of contaminated sediments, clean water with hypoxia in neutral water condition. It increased to 0.234 mg/L at the end of the second hour and decreased to 0.199 at the end of the experiment.

The initial recorded value of ferrous ion ($Fe^{2+}$) concentration at time zero was with 0.131 mg/L for the seventh experiment, which considered the release of contaminated sediments to the clean, neutral water column with hypoxia, aerated at 60 l/h and stratified with a heater. the value of ferrous ion ($Fe^{2+}$) concentration increased to 0.227 mg/L at the end of the second hour and decreased to the value of 0.178 mg/L at the end of the experiment.

When all results of ferrous ion ($Fe^{2+}$) discussed, hypoxia with aeration (Experiment #3) gave the best desirable results for ferrous ion ($Fe^{2+}$). Again, high temperature, it means stratification, (Experiment #6 and Experiment #7) caused more dissolution of elements. However acidic water (Experiment #4) more affected the $Fe^{2+}$ dissolution than high temperature.

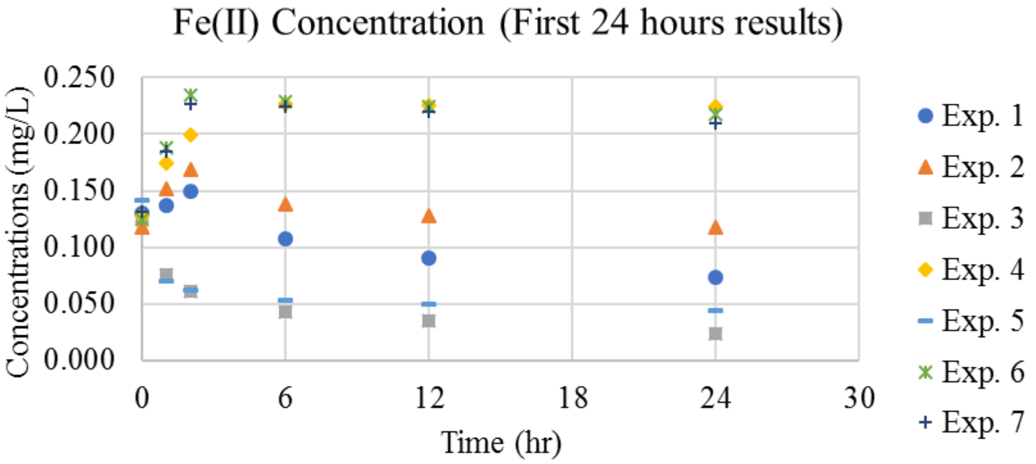


Figure 3.24. $Fe^{2+}$ Concentration First 24 Hours Results

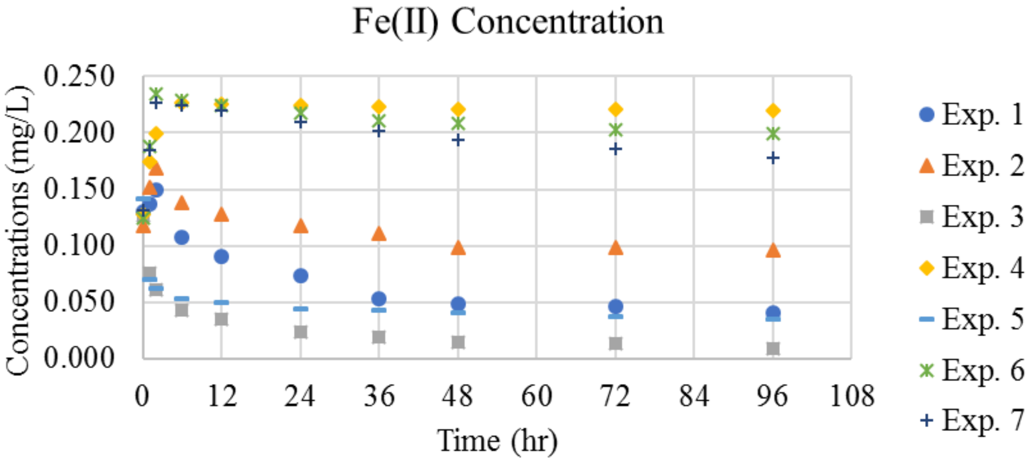


Figure 3.25. $Fe^{2+}$ Concentration All Results

### 3.2.3. Manganese (Mn) Concentration

The Figure 3.26 and Figure 3.27 show concentration and time variation of manganese (Mn) at the water column. Samples were collected at 5 cm above the sediment container. The same spectrophotometer was used in all experiment analysis.

At the beginning of the first experiment, manganese (Mn) concentration was 0.546 mg/L and then decreased to the value of 0.229 mg/L during the next four days.

The second experiment was started 4 days after the start of the first experiment in the other tank to create hypoxia in the water column. As can be seen from the results of the second experiment, the concentration of 0.532 mg/L manganese (Mn) was observed at time zero and the final concentration at the end of the fourth day was 0.553 mg/L. The peak point was observed at a value of 0.261 mg/Lat the end of the second hour.

The third experiment aimed to show aeration effects together with hypoxia. This experiment was started following the first two experiments completed. The concentration of 0.535 mg/L for manganese (Mn) was observed at time zero and decreased to 0.198 mg/L at the end of the fourth day. No increase in manganese (Mn) concentration was observed during the whole experiment.

The monitored value of manganese (Mn) concentration at the beginning of the fourth experiment (in the condition of low pH), was 0.765 mg/L and increased to 0.770 mg/L at the end of the fourth day. The peak point was observed at a value of 0.785 mg/Lat the end of the sixth hour.

In the fifth experiment that observed the alkaline condition, the manganese (Mn) concentration value monitored initially at time zero was 0.528 mg/L and decreased to 0.174 mg/L at the end of four days.

The initial recorded value of manganese (Mn) concentration at time zero was 0.570 mg/L in the sixth experiment for the case of contaminated sediments, clean water with hypoxia in neutral water condition. It increased to 0.801 mg/L at the end of the second hour and decreased to 0.781 at the end of the experiment.

The initial recorded value of manganese (Mn) concentration at time zero was with 0.558 mg/L for the seventh experiment, which considered the release of contaminated sediments to the clean, neutral water column with hypoxia, aerated at 60 l/h and stratified with a heater. the value of manganese (Mn) concentration increased to 0.789 mg/L at the end of the second hour and decreased to the value of 0.755 mg/L at the end of the experiment. Moreover, the tap water total manganese concentration is 0.001 mg/L.

Figure 3.26 and Figure 3.27 showed alkaline water conditions (Experiment #5) that gave the best desirable results for manganese (Mn). Acidic water (Experiment #5), and stratification (Experiment #6) and aeration with stratification (Experiment #7) gave similar results. All three are undesirable situations for Mn.

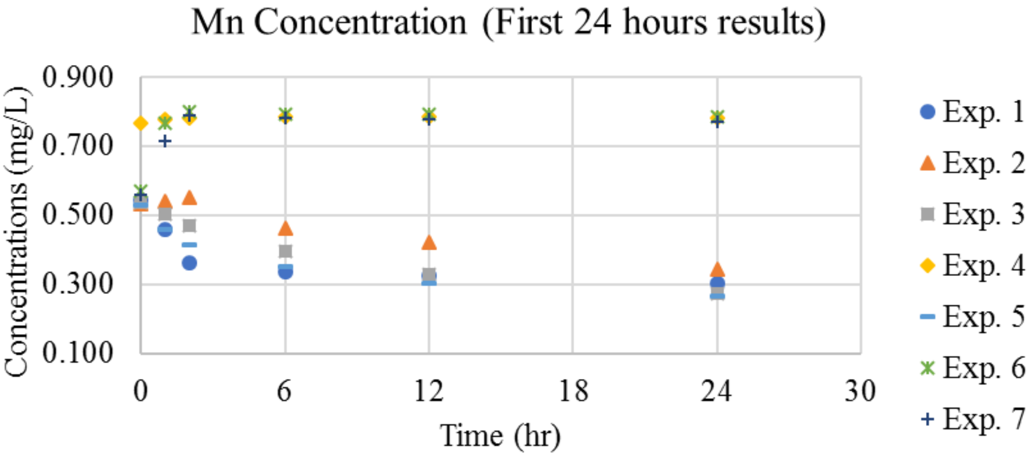


Figure 3.26. Mn Concentration First 24 Hours Results

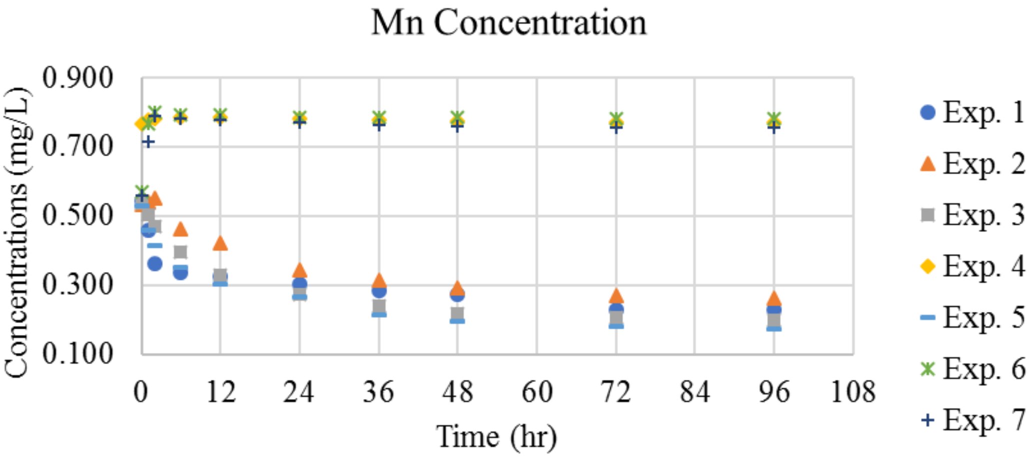


Figure 3.27. Mn Concentration All Results

# CHAPTER 4

# CONCLUSION

The release mechanism of iron and manganese from the sediments to the water column under different water acidity, aeration and stratified water conditions was investigated by experiments in this study. Several factors such as the effect of aeration, the acidity condition of water and the stratification level of the water column were decided upon to investigate, based on the results obtained from the literature and the primary experiments conducted during this study. Mainly results of seven experiments including the effects of these factors were discussed. In all experiments, monitoring of water sampling was conducted for 4 days and at 0, 1, 2, 6, 12, 24, 36, 48, 72 and 96 hours after the initiation of the experiment.

At the beginning of the experiments, soil and tap water used in the experiments were sampled and analyzed for iron and manganese concentrations. The values obtained from the spectrophotometer were 0.003 mg/L iron and 0.001 mg/L manganese for tap water and 0.001 mg/L iron and 0.0015 mg/L manganese for sediment respectively which considered to be negligible.

First experiment can be considered as the base experiments where neutral condition of water with no aeration or stratification is utilized and all the other experiments are compared with this one. In this experiment, the soil sample was contaminated with a 500 mL of stock solution with a concentration of 3 g/L both $Mn^{2+}$ and $Fe^{2+}$ while the water was free of iron and manganese elements.

The purpose of the second experiment was to simulate the reduced dissolved oxygen conditions in the water column likewise many stratified reservoirs in the world experiencing hypoxia in the bottom layer, hypolimnion. In order to investigate the effects of hypoxia on the release of iron and manganese from the sediments to the water column, the second experiment was set up. Hence the main difference between the first and second experiment is the creation of hypoxia in the water column. To achieve this, the elodea plant was placed in the middle of the full water tank to reduce the oxygen concentration in the water column intentionally. After the water in the tank reached the desired levels of dissolved oxygen, soil sample that was already contaminated with a 500 mL of stock solution with a concentration of 3 g/L both $Mn^{2+}$ and $Fe^{2+}$ was placed in the tank.

The third experiment in the study aimed to investigated effects of aeration on iron and manganese concentrations in the water column which was already experiencing hypoxia. For this purpose, the dissolved oxygen concentration values in the water tank were reduced by the help of the elodea plant as in the second experiment. The same stock solution was used to contaminate the soil sample. However, in this experiment water column was aerated for half an hour with the rate of 60 L/h, at certain intervals.

The fourth and fifth experiments aimed to investigate the effect of acidity condition of the water column on the release of iron and manganese from the sediments to the water column. In the fourth experiment, as in the previous cases, the elodea plant was utilized to reduce the dissolved oxygen concentrations to the desired levels. Then, the specified amount of hydrochloric acid (HCl) was used to maintain acidic conditions in the water column water. The pH level of the water column was set to 5 for this experiment. The contaminated soil sample with the same concentration of the stock solution was placed to the bottom of the tank.

In the fifth experiment, as in the previous cases, the elodea plant was utilized to reduce the dissolved oxygen concentrations to the desired levels. Then, the specified amount of sodium hydroxide (NaOH) was used to maintain basic conditions in the water. The pH level of the water column was set to 11 for this experiment. The contaminated soil sample with the same concentration of the stock solution was placed to the bottom of the tank.

The sixth experiment investigated the release of iron and manganese from the sediments to the water column under thermally stratified water conditions. Stratification was achieved by the help of a heater which gradually heated the water column where reduced dissolved oxygen concentration values were already maintained using elodea plant. The contaminated soil sample with the same concentration of the stock solution was placed to the bottom of the tank.

The seventh and last experiment investigated the effect of aeration on the release of iron and manganese from the sediments to the water column under thermally stratified water conditions. As in the previous experiment, stratification was achieved by the help of a heater which gradually heated the water column where reduced dissolved oxygen concentration values were already maintained using elodea plant. Following the placement of the contaminated soil sample with the same concentration of stock solution to the bottom of the tank, the water column was aerated at a rate of 60 L/h.

Once the sampling was completed for each experiment, water samples were taken to the lab for measurement of concentration using spectrophotometry method.

The initial recorded value of total iron (Fe) concentration at time zero was 0.150 mg/L in the first experiment. It increased first to 0.195 mg/L in two hours then decreased to the value of 0.108 mg/L during the next four days.

The second experiment (in the condition of contaminated sediments, clean water and aeration)was started 4 days after the start of the first experiment in the other tank to create hypoxia in the water column. As can be seen from the results of the second experiment, the concentration of 0.153 mg/L total iron (Fe) was observed at time zero and the final concentration at the end of the fourth day was 0.112 mg/L. The peak point was observed at a value of 0.201 mg/Lat the end of the second hour.

The third experiment was started following the first two experiments completed. This experiment aimed to show aeration effects together with hypoxia. The concentration of 0.152 mg/L for total iron (Fe) was observed at time zero and decreased to 0.106 mg/L at the end of the fourth day. No increase in total iron (Fe) concentration was observed during the whole experiment.

The initial monitored value of Total iron (Fe) concentration at the beginning of the fourth experiment (in the condition of low pH), was 0.195 mg/L and it increased to 0.275 mg/L at the end of the second hour. and decreased to 0.247 mg/L at the end of the fourth day.

The fifth experiment aimed to show alkaline water condition effects together with hypoxia. The total iron (Fe) concentration value monitored initially at time zero was 0.155 mg/L, while the peak concentration observed was 0.162 mg/L at the end of the second hour. It decreased to 0.115 mg/L at the end of four days.

In the sixth experiment, the initial recorded value of total iron (Fe) concentration at time zero was 0.187 mg/L for the case of contaminated sediments, clean water with hypoxia in neutral water condition. It increased to 0.290 mg/L at the end of the second hour and decreased to 0.282 at the end of the experiment.

The initial recorded value of total iron (Fe) concentration at time zero was with 0.163 mg/L for the seventh experiment, which considered the release of contaminated sediments to the clean, neutral water column with hypoxia, aerated at 60 l/h and stratified with a heater. the value of total iron (Fe) concentration increased to 0.288 mg/L at the end of the second hour and decreased to the value of 0.276 mg/L at the end of the experiment

Experiment #6 and Experiment #7 demonstrate the summer season situation at the water structures. The results show that in case of high temperature high elements dissolution capacity of water increased. In addition, acidic water (Experiment #4) caused dissolving of high elements while basic water (Experiment #5) helped to transform and precipitate of elements to the ground of water. When the first three parts compared, hypoxia with aeration (Experiment #3) gave the best desirable results for Total Fe.

In the first experiment, the initial recorded $Fe^{2+}$ concentration was 0.130 mg/L. It increased first to 0.150 mg/L in two hours then decreased to the value of 0.041 mg/L during the next four days.

The second aimed to show contaminated sediments clean water effects together with hypoxia. This experiment was started 4 days after the start of the first experiment in the other tank to create hypoxia in the water column. As can be seen from the results of the second experiment, the concentration of 0.118 mg/L ferrous ion ($Fe^{2+}$) was observed at time zero and the final concentration at the end of the fourth day was 0.096 mg/L. The peak point was observed at a value of 0.169 mg/Lat the end of the second hour.

The third experiment was started following the first two experiments completed. This experiment aimed to show aeration effects together with hypoxia. The concentration of 0.127 mg/L for ferrous ion ($Fe^{2+}$) was observed at time zero and decreased to 0.009 mg/L at the end of the fourth day. No increase in ferrous ion ($Fe^{2+}$) concentration was observed during the whole experiment.

The monitored value of ferrous ion ($Fe^{2+}$) concentration at the beginning of the fourth experiment (in the condition of low pH), was 0.128 mg/L and increased to 0.220 mg/L at the end of the fourth day. The peak point was observed at a value of 0.227 mg/Lat the end of the sixth hour.

The initial recorded value of ferrous ion ($Fe^{2+}$) concentration at time zero was 0.142 mg/L in the fifth experiment. It decreased to 0.035 mg/L at the end of four days.

The monitored value of ferrous ion ($Fe^{2+}$) concentration at time zero was 0.125 mg/L in the sixth experiment for the case of contaminated sediments, clean water with hypoxia in neutral water condition. It increased to 0.234 mg/L at the end of the second hour and decreased to 0.199 at the end of the experiment.

The initial recorded value of ferrous ion ($Fe^{2+}$) concentration at time zero was with 0.131 mg/L for the seventh experiment, which considered the release of contaminated sediments to the clean, neutral water column with hypoxia, aerated at 60 l/h and stratified with a heater. the value of ferrous ion ($Fe^{2+}$) concentration increased to 0.227 mg/L at the end of the second hour and decreased to the value of 0.178 mg/L at the end of the experiment.

Hypoxia with aeration (Experiment #3) gave the best desirable results for ferrous ion ($Fe^{2+}$) when all results of ferrous ion ($Fe^{2+}$) discussed. Again, high temperature, it means stratification, (Experiment #6 and Experiment #7) caused more dissolution of elements. However acidic water (Experiment #4) more affected the $Fe^{2+}$ dissolution than high temperature.

The Figure 3.26 and Figure 3.27 show concentration and time variation of manganese (Mn) at the water column.

At the beginning of the first experiment, manganese (Mn) concentration was 0.546 mg/L and then decreased to the value of 0.229 mg/L during the next four days.

The second experiment was started 4 days after the start of the first experiment in the other tank to create hypoxia in the water column. As can be seen from the results of the second experiment, the concentration of 0.532 mg/L manganese (Mn) was observed at time zero and the final concentration at the end of the fourth day was 0.553 mg/L. The peak point was observed at a value of 0.261 mg/Lat the end of the second hour.

The third experiment aimed to show aeration effects together with hypoxia. This experiment was started following the first two experiments completed. The concentration of 0.535 mg/L for manganese (Mn) was observed at time zero and decreased to 0.198 mg/L at the end of the fourth day. No increase in manganese (Mn) concentration was observed during the whole experiment.

The monitored value of manganese (Mn) concentration at the beginning of the fourth experiment (in the condition of low pH), was 0.765 mg/L and increased to 0.770 mg/L at the end of the fourth day. The peak point was observed at a value of 0.785 mg/Lat the end of the sixth hour.

In the fifth experiment that observed the alkaline condition, the manganese (Mn) concentration value monitored initially at time zero was 0.528 mg/L and decreased to 0.174 mg/L at the end of four days.

The initial recorded value of manganese (Mn) concentration at time zero was 0.570 mg/L in the sixth experiment for the case of contaminated sediments, clean water with hypoxia in neutral water condition. It increased to 0.801 mg/L at the end of the second hour and decreased to 0.781 at the end of the experiment.

The initial recorded value of manganese (Mn) concentration at time zero was with 0.558 mg/L for the seventh experiment, which considered the release of contaminated sediments to the clean, neutral water column with hypoxia, aerated at 60 l/h and stratified with a heater. the value of manganese (Mn) concentration increased to 0.789 mg/L at the end of the second hour and decreased to the value of 0.755 mg/L at the end of the experiment.

The results in Figure 3.26 and Figure 3.27 show that alkaline water conditions (Experiment #5) that gave the best desirable results for manganese (Mn). Acidic water (Experiment #5), and stratification (Experiment #6) and aeration with stratification (Experiment #7) gave similar results. All three are undesirable situations for Mn.

Group #1 experiment results show that aeration considerably affects the releasing of elements from sediment to water. When the acidic and alkaline water conditions compared, it is clearly observed that releases of total iron (Fe), ferrous ion ($Fe^{2+}$) and manganese (Mn) are low in case of high pH. Temperature is also one of the most important water quality parameters that affect the solubility of water. Group #3 experiment results proved that aeration in case of high temperature and hypoxia (Experiment #7) is a preferred method compared to no aeration (Experiment #6).

When the all experiment results compared, total iron (Fe) and ferrous ion ($Fe^{2+}$) concentrations in the water column decreased in time in case of aeration application in hypoxia (Experiment #3), it was also the case for manganese (Mn) concentrations. However, in alkaline water conditions (Experiment #5), the concentration of dissolved Mn in water is less than the aeration condition (Experiment #3). This is an indication that iron and manganese react differently under different water conditions.

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