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Research Article

An experimental study on release mechanism of iron and manganese from sediments to the water column in reservoirs

Buse VURAL[1], Şebnem ELÇI[1,*], Hatice Eser ÖKTEN[2]

[1] *Izmir Institute of Technology, Department of Civil Engineering, Izmir, Turkey*
[2] *Izmir Institute of Technology, Department of Environmental Engineering, Izmir, Turkey*

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ABSTRACT

Iron and manganese accumulation in drinking water reservoirs is a challenging issue and should be controlled 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. Also, 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 the water column in reservoirs and investigates methods to prevent this release. Effects of hypoxia, hypolimnetic aeration, alkalinity of water, and thermal stratification on iron and manganese concentrations were investigated through laboratory experiments. Experiments done simulating the water column showed that hypoxia caused more dissolution of ferrous iron when compared with that of manganese. Accordingly, aeration of the water column in hypoxic conditions lead to a significant decrease in ferrous iron concentrations (in our case reaching zero). However, manganese and total iron levels were not affected by the aeration of the water column. Alkalinity level of the water column was observed to have a great effect on the solubility of iron and manganese. Concentrations of total Fe and total Mn measured for acidic (pH = 5) conditions were considerably greater than concentrations measured at neutral conditions. As for alkaline (pH = 11) conditions, the opposite was observed with measured concentrations of total Fe and total Mn being lower than the ones measured for neutral conditions. Thermal stratification had an enhancing effect on the solubility of both iron and manganese ions. While aeration of the stratified water column slightly decreased the concentrations of Total Fe and Mn, it had a greater impact on decreasing Fe^{2+} concentrations.

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***Corresponding author.**
*E-mail address: sebnemelci@iyte.edu.tr

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INTRODUCTION

Behavior of metals in reservoirs is influenced by the composition of sediment bed, suspended sediment composition, and water chemistry, which controls the rate of adsorption and desorption of metals to and from sediments. Since a natural degradation process for eliminating the excess metals does not exist, they are often absorbed by the sediments. As a result of accumulation of metals in underlying sediments, concentration of metals in sediments may be much higher than the water column above it. In general, sediment composed of fine sand and silt have higher levels of adsorbed metals than quartz, feldspar, and detrital carbonate-rich sediments [1]. Metals also have a high affinity for humic acids and organic matter [2].

Iron and manganese are two similar elements that commonly exist in Earth's crust. Iron is the most widely found element together with manganese in water supplies. These two elements are found frequently in water systems that use groundwater. Water, infiltrating through soil or rock, may dissolve iron and manganese that are inherently present in the solid material. Moreover, iron pipes may leach and cause high concentrations of iron in water. On the other hand, surface water generally does not contain large amounts of iron or manganese. Considering the reservoirs, varying iron and manganese speciation may be observed in the water column. While Fe^{2+} and Mn^{2+} ions are mostly soluble in water, when enough oxygen is supplied, they are converted to insoluble Fe^{3+} and Mn^{4+} ions, precipitating towards sediments underlying the hypolimnetic water layer.

Thermal stratification generally occurs during summer months due to the heating of the upper layers of the water column. Once thermal stratification occurs, it is generally accompanied by a lack of oxygen in the hypolimnetic zone. Under anoxic conditions, iron and manganese are soluble in water and these soluble elements may accumulate in the hypolimnion. Moreover, organic residues tend to sink to hypolimnion and due to microbial degradation of these organic residues in sediments, remaining oxygen is depleted. Anoxic or anaerobic microbial degradation tends to change the pH of sediment and eventually of hypolimnion towards acidic conditions. It may lead to several adverse results such as failure of meeting the drinking water quality standards, aquatic problems such as fish kills, cloggings of the pipeline system, stains on fixtures and laundry, etc. Due to these adverse effects, water intake depth needs to be adjusted in drinking water reservoirs to minimize the iron and manganese concentrations along with suspended solids concentration.

Previous studies pointed out iron and manganese occuring naturally as oxidized, insoluble forms in bed sediments of thermally stratified reservoirs ([3], [4]). Conditions during stratification may lead to reductive dissolution of iron and manganese from sediments to the water column [5]. Although previous studies investigated effects of hypolimnetic aeration on the metal concentrations, the combined effect of pH, metal oxidation mechanisms and mixing in the water column and sediments at the reservoir scale still remains unknown.

As stated by other researchers [6], hypolimnetic aeration alone might not be sufficient to remove manganese from the water column. Since the abiotic oxidation rate of manganese is pH-dependent, lakes and reservoirs having slightly acidic conditions (pH 5.6 to 7.5) may experience critical manganese problems. In another study [7], authors investigated the impact of oxygenation on manganese concentrations and they found that soluble manganese 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^{2+} ions from the sediment. However, they stated that the diffusive flux of manganese from the sediment also increased in response to the oxygenation which contradicted their previous remarks.

Manganese preparation mechanisms with the perspective of adsorption onto suspended solids and microbial oxidation of Mn was studied in Lake Biwa [8]. Concentration of dissolved manganese, Mn^{2+}, decreased at $pH > 7$ by microbial oxidation in aerobic water samples maintained in the laboratory. In the end, it was observed that autoclaving, irradiation with ultraviolet light, filtration of water samples and the addition of NaN_3 prevented Mn^{2+} precipitation. Besides, in the suspended solid, the adsorption of Mn^{2+} was appreciable at $pH > 7$ and it reached equilibrium point within the minimum 30 minutes. When the Mn^{2+} oxidation rate was compared with Mn^{2+} adsorption rate, it was much slower. 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 be required for the Mn^{2+} precipitation mechanism process.

Oxygenation systems could decrease soluble manganese concentrations by increasing dissolved oxygen levels, subsequently causing manganese oxidation and adsorption to other particles, resulting in precipitation to the sediment ([4], [9]). These researchers also pointed out that oxygen dynamics and biogeochemical processes were variable at the sediment-water interface and thus changes in the sediment oxygen uptake rate might occur. In these studies, the influence of oxygenation on sediment-water fluxes of manganese was also unclear. 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.

World Health Organization (WHO) set the maximum allowable concentration limits for Fe and Mn as 0.3 mg/l and 0.1 mg/l, respectively. Iron deposits in various part of the brain were known to be related to risks for Alzheimer's disease [10]. Overconsumption of manganese also affects the brain, leading to increased movement abnormalities [11]. Removing Fe and Mn from water withdrawn from lakes or reservoirs by oxidation and filtration techniques is especially difficult and expensive, and thus in situ treatment is preferred in most cases. A common application for in-situ treatment is hypolimnetic aeration, which increases 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. When dissolved oxygen (DO) concentration increases in hypolimnion, oxidized iron and manganese species precipitate to bottom sediments. However, bottom sediments may release metals as a result of the combined effects of DO concentration, pH, and microbial activity, which need further research in order to elucidate the whole mechanism. In this paper, we aim to investigate the processes that control concentrations of Fe and Mn, facilitating the good management practices for drinking water supply reservoirs.

METHODOLOGY

Preparation of Iron and Manganese Solution

Iron and manganese solutions from ferrous chloride tetrahydrate ($FeCl_2.4H_2O$, Sigma Aldrich) and manganese (II) sulfate monohydrate ($MnSO_4.4H_2O$, Sigma Aldrich) were prepared for sediment spiking, respectively and were used as sources of Mn^{2+} and Fe^{2+}. In total, 12.18 grams of $MnSO_4.4H_2O$ and 10.68 grams of $FeCl_2.4H_2O$ were used to prepare a solution. Iron and manganese concentrations of the prepared solution were 3 g/L each.

Experimental Setup

Two identical glass water tanks (1 m × 0.4 m × 0.5 m), with 200 L capacity were used to examine the effects of hypoxia, aeration, alkalinity and thermal stratification on iron and manganese concentrations (Fig. 1). To simulate sediments in a water supply reservoir, sediment size composition observed in Tahtali Reservoir, Turkey was used as the reference. Thus, sediments consisting of 60 % sand and 40 % silt and clay were obtained by sieve analysis. For each experiment, a total of 1.2 kg sediment was distributed homogeneously to a container and then mixed with 300 mL of prepared stock solution to form a firm creamy paste. The contaminated sediment container was always placed at bottom of the tank slowly in order to avoid any unintended mixing.

Figure 1. Water tank used in experiments.

Dissolved oxygen (DO), pH, and temperature were monitored via a multimeter (HQ40D, Hach Lange). The multimeter was calibrated and the probes were rinsed with DI water and dried before and after each analysis. All samples were kept at +4 °C prior to analysis. All samples were analyzed using a spectrophotometer (UV-2600, Shimadzu) (Fig. 2). At the beginning of each analysis, the wavelength of the device was set to 265 nm for total Fe, 295 nm for Mn, and 255 nm for Fe^{2+}. Total Fe, Fe^{2+}, and Mn analyses were conducted following the spectrophotometric methods (Hach Lange) specified by the manufacturer (see DOC316.53.01053, DOC316.53.01049, DOC316.53.01058).

Experiments

Tap water was analyzed for total iron and manganese concentrations, which were 0.003 mg/l and 0.001 mg/L, respectively. Total Fe and Mn analyses for the bare sediment also showed negligible results (total Fe = 0.001 mg/l; Mn = 0.0015 mg/L). The release mechanism of Fe and Mn from sediments to the water column was investigated in a series of experiments grouped in three categories (Table 1).

For all experiments, the first sample was collected as soon as the contaminated sediment container was placed at the bottom of the tank (0 hour) and the rest of the samples were collected at 2, 6, 12, 24, 36, 48, 72 and 96 hours, while dissolved oxygen (DO), pH and temperature measurements were conducted simultaneously. Water samples were taken from 5 cm above the sediment surface.

The first experiment represented the reference case. The aim was to observe iron and manganese release from the sediments to the water column under normal conditions. In the rest of the experiments, the starting conditions were representing hypoxia. Following the filling of the water tank with tap water, *Elodea canadensis*, a common waterweed, which is known to consume high rates of oxygen in a short time, was used to create hypoxia in the water tank (Fig. 3). It is an aquatic plant native to most of North America, with average lengths between 20 and 30 cm. Its numerous overlapping, dark green, translucent, and minutely toothed leaves are about 1 cm long and 2–3 mm wide. It was selected for its ability to consume oxygen rapidly in the dark, simulating the depths of a reservoir. Hence, the water tank with waterweed was covered with black nylon to prevent sunlight and air diffusion to the tank. The tank stayed covered with black nylon for about 4 days until the DO level of 5 mg/l was reached. When the desired DO level was achieved, the nylon cover was removed from the tank. For experimental runs 3 and 7, aeration of 60 L/h was applied. In many reservoirs, aeration of the water column 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 and seventh experiments aimed to investigate how aeration in the hypolimnium affects the dissolution of Total Fe, Fe^{2+}, and Mn. As it was the case for the second experiment, hypoxia was maintained using Elodea plants. The purpose of the fourth experiment was to show how acidic water conditions affected iron and manganese solubility in the case of hypoxia. The tank was filled, and the plant was placed to create hypoxia in the tank. To reach a low level of pH, HCl was used. HCl solution was prepared and poured to the tank gradually to adjust the pH of water around 5. In the fifth experiment, to achieve alkaline water conditions, NaOH solution was added to the water tank slowly until the pH of water reached 11. The sixth and the seventh experiments aimed to investigate the effects of thermal stratification on the solubility of iron and manganese. Stratification in the water tank was achieved through an electric heater placed at the top of the tank. Electric heater was kept running until a temperature profile representing thermal stratification was obtained (Fig. 3). In experiment 6, after the

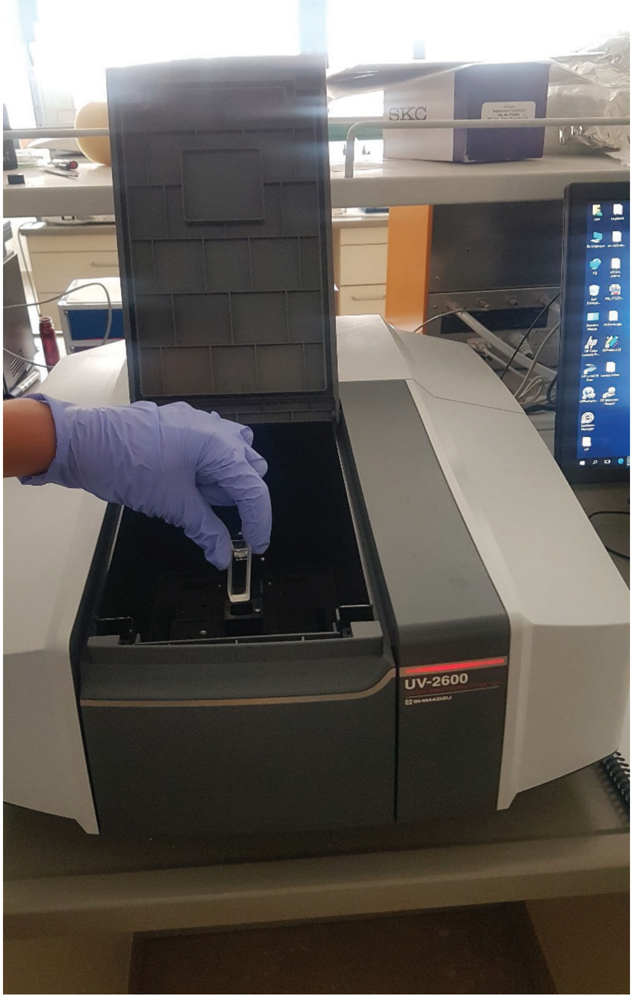


Figure 2. Insertion of the cell holder to the spectrophotometer.

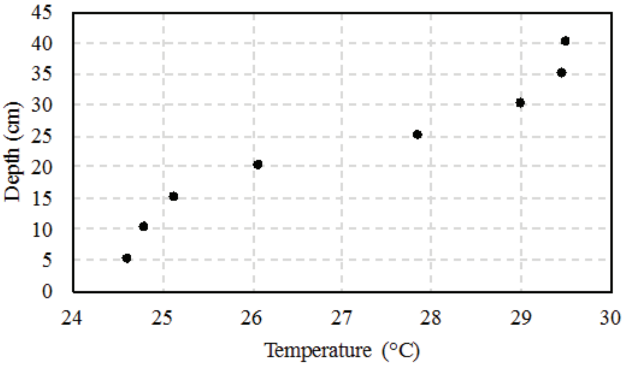


Figure 3. Vertical temperature profile obtained after heating of the water column.

Table 1. Summary of studied conditions

Experiment #	Oxygen level	Aeration rate (l/s)	pH	Stratified/Mixed	Oxygen level	Group #
1	Oxic	–	7	Mixed	Oxic	1
2	Hypoxia	–	7	Mixed	Hypoxia	
3	Hypoxia	60	7	Mixed	Hypoxia	
4	Hypoxia	–	5	Mixed	Hypoxia	2
5	Hypoxia	–	11	Mixed	Hypoxia	
6	Hypoxia	–	7	Stratified	Hypoxia	3
7	Hypoxia	60	7	Stratified	Hypoxia	

water column was stratified, the Elodea plant was used to achieve hypoxia and the water tank was covered with black nylon. When the DO reached around 5, the plant was removed and the polluted sediment was placed to the bottom of the tank. The seventh experiment simulated the case where aeration would be effective in a stratified reservoir experiencing hypoxia. Thus, this last experiment aimed to investigate how aeration affects the dissolution of Total Fe, Fe^{2+}, and Mn in the joint case of stratification and hypoxia.

RESULTS AND DISCUSSION

Representing the reference scenario, values of DO and pH stayed pretty much the same for 96 hours where temperature values slightly increased after 12 hours adjusting to ambient temperature in experiment 1 (Fig. 4a). Concentrations of Total Fe and Fe^{2+} increased in the first two hours, then both decreased slowly until the end of 96 hours (Fig. 4b). Manganese showed a different behavior than iron. While its concentration decreased sharply during the first two hours, it followed a smoother decrease for the following 48 hours. All three parameters stabilized after 60 hours.

In the second experiment, through prevention of photosynthesis, the plant was forced to consume the DO in the water column which was approximately 7.5 mg/l. The experiment started when DO concentration reached a value of 5 mg/l. During the second experiment, the temperature did not vary significantly and stayed around 24°C, and so did pH, fluctuating within the values of 7.5–8.2 as it was observed during the first experiment. Dissolved oxygen (DO), however, increased from its initial value of 5 mg/l to 7.8 mg/l (Fig. 4c). Created hypoxia in the water column caused more dissolution of Fe^{+2} in the water column (Fig. 4d). In fact, at the end of the second experiment, the concentration of Fe^{+2} in the water column doubled as compared to the first experiment. Created hypoxia caused more dissolution of manganese in water although this increase was trivial as compared to the increase of Fe^{2+}.

During experiment 3, the water column was aerated at a flow rate of 60 L/hr using an air diffuser designed for aquariums. As expected, aeration led to a faster increase of DO levels from 5 mg/l to 7.9 mg/l as compared to non-aeration cases (Fig. 4e). Aeration caused a significant decrease of Fe^{+2} concentration reaching zero. We believe aeration did not eliminate the formation of reduced Fe^{+2} instead pushed the oxic-anoxic boundary to the sediments. Total manganese and iron levels were not affected by the aeration of the water column when their levels were compared with the results of the second experiment where aeration was not applied (Fig. 4f). In contrast to iron, manganese oxidation kinetics are slower, and manganese persists in the water column longer after initiation of hypolimnetic aeration (Gantzer et al., 2009).

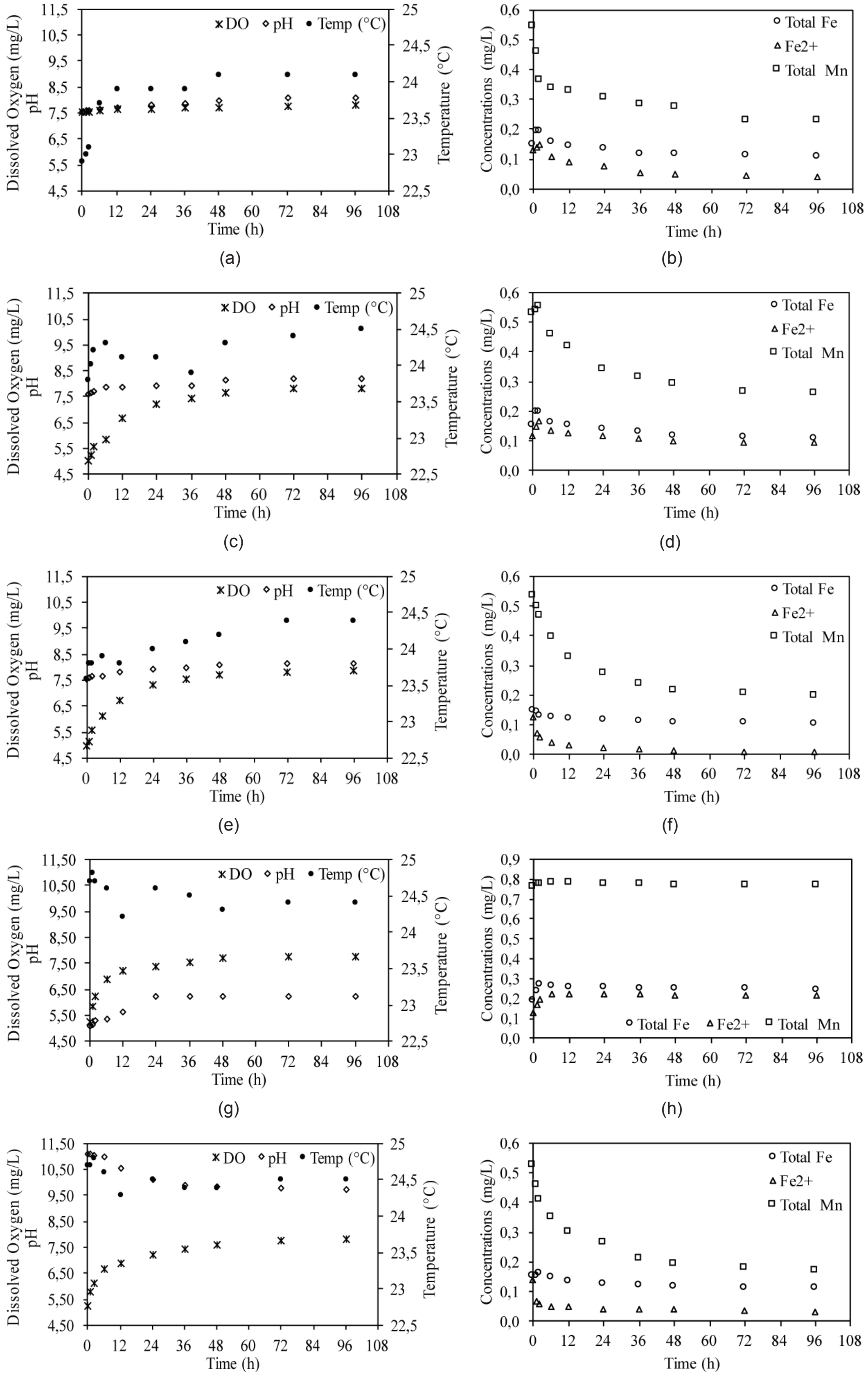
In experiment 4, the pH increased from 5 to 6 in 24 hours and then remained at 6 for the following 72 hours (Fig. 4g). An increase in DO concentration from 5 mg/l to 8 mg/l during the experiment was observed. There was no considerable change in water temperature. When the results of acidic water conditions (Fig. 4h) were compared with the results of neutral water conditions (Fig. 4d), concentrations of total Fe, Fe^{2+}, and total Mn in the acidic water were considerably greater than the neutral conditions. Manganese concentration in the water column reached to 0.770 mg/L at the end of the 96 hours where its counterpart for the neutral conditions was only 0.229 mg/L. Similarly, Fe^{2+} concentration in the water column reached 0.220 mg/L at the end of the 96 hours whereas it was 0.096 mg/L for the neutral conditions.

In experiment 5, the pH decreased from 11 to 10 in 24 hours and then remained around 10 for the following 72 hours (Fig. 4i). Also, as it was the case in the previous experiment, DO increased from 5 mg/l to 8 mg/l and no significant variation of temperature was observed. Total Fe, Fe^{2+} and total Mn concentrations showed a considerable decrease in alkaline water conditions (Fig. 4j). In fact, total Mn concentration decreased to 0.174 mg/L at the end of four days whereas this value was 0.770 mg/l for acidic and 0.261 mg/l for neutral conditions.

Variation of the water quality parameters during the sixth experiment is given in Figure 5a. The pH values fluctuated between 7 and 8. Temperature values also fluctuated around 29°C, higher than the previous experiment due to heating of the water column. DO concentrations increased from 5 mg/l to 7.5 mg/l during the experiment, as was the case in the previous experiments. The results showed that the solubility of both iron and manganese were significantly higher in stratified conditions as compared to the mixed water column (Fig. 5b). The values of total Fe, Fe^{2+}, and total Mn concentrations were 0.282 mg/l, 0.199 mg/l, and 0.781 mg/l at the end of the sixth experiment whereas at the end of the second experiment they were 0.112 mg/l, 0.096 mg/l, and 0.261 mg/l, respectively.

In the seventh experiment, pH values fluctuated between 7.5 and 8.1, temperature values were around 29°C due to heating of the water column, and DO concentrations increased from 5 to 7.6 (Fig. 5c). Results showed that the solubility of both iron and manganese were significantly higher in stratified conditions as compared to the mixed water column (Fig. 5d). Aeration of the water column had a slight effect on lowering the concentrations of total Fe, Fe^{2+} and total Mn.

Time variation of monitored total iron (Fig. 6a), ferrous ion (Fig. 6b), and total manganese (Fig. 6c) concentrations at the water column measured at 5 cm above the sediment



(a) (b)

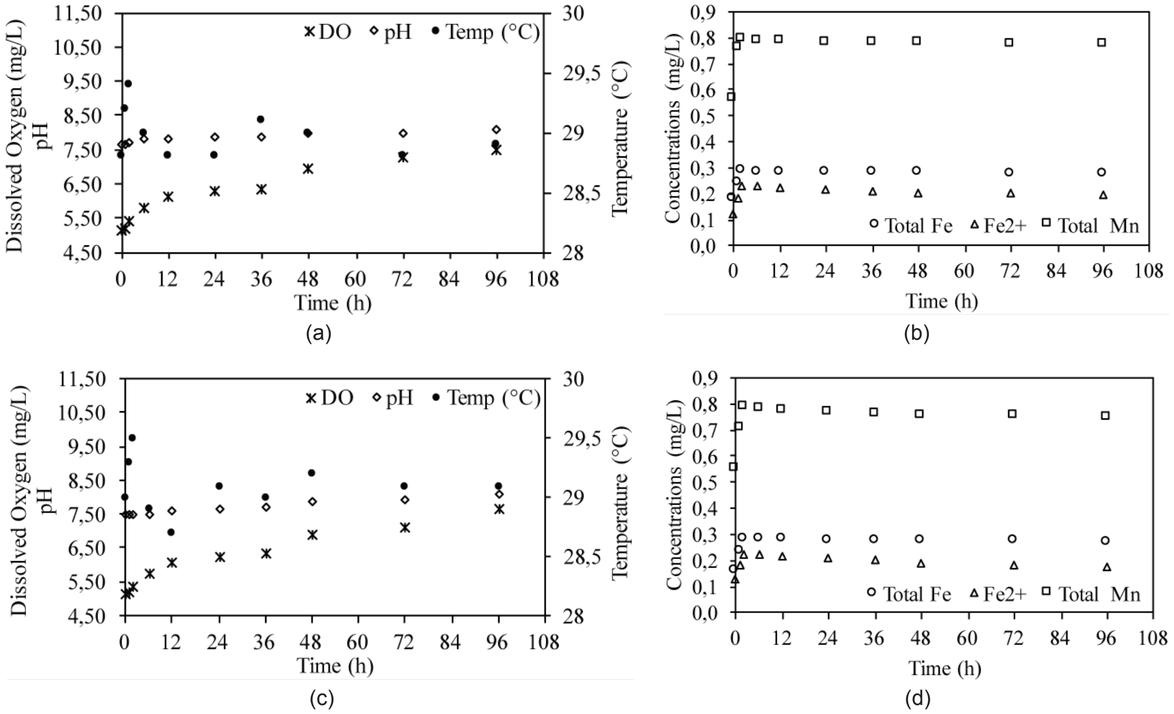
(c) (d)

(e) (f)

(g) (h)

(i) (j)

Figure 4. Variation of DO, pH, and temperature during the experimental runs 1 (a), 2 (c), 3 (e), 4 (g), 5 (i). Variation of Total Fe, Fe^{2+} and Total Mn in experimental runs 1 (b), 2 (d), 3 (f), 4 (h), 5 (j).



(a) (b)

(c) (d)

Figure 5. Variation of DO, pH, and temperature during the experimental runs 6 (a) and 7 (c). Variation of Total Fe, Fe^{2+} and Total Mn in experimental runs 6 (b) and 7 (d).

container was presented for all seven experiments. As stated by other researchers (Munger et al., 2016), hypolimnetic aeration alone might not be sufficient to remove manganese from the water column. Because the abiotic oxidation rate of manganese is pH-dependent, lakes and reservoirs might experience critical manganese problems due to slightly acidic conditions (pH 5.6 to 7.5). Increasing DO levels may decrease soluble Mn concentrations by facilitating manganese oxidation, adsorption to other particles and ultimately precipitation to the sediment ([4], [9]). Researchers also pointed out that oxygen dynamics and biogeochemical processes were variable at the sediment-water interface and thus changed 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. Even in oxic conditions, sediments may continue releasing elements as reported by other researchers ([4], [7]).

CONCLUSIONS

Present study investigated the release mechanism of iron and manganese from the sediments to the water column and was expected to serve as a guide for better management practices under the increasing stresses related to climate change and urbanization. The processes which control concentrations of iron and manganese become complicated when these stresses result in unfavorable conditions such as hypoxia and high acidity levels. Hypoxia, which occurs in reservoirs following nutrient-induced algae production and formation of thermally stratified layers, is observed in many reservoirs around the world. Reservoirs in Turkey, including the Tahtali Reservoir, are no exception since warming of the water bodies in summer is a common phenomenon and unfortunately nutrient inputs occur mostly due to agricultural activities. Thus, deterioration of water quality in water supply reservoirs is a current and crucial issue to tackle. Aeration, which is preferred as a water quality improvement method by many professionals around the world, is selected for this analysis and the release mechanisms of the iron and manganese were investigated under aeration of the water column. Finally, the acidity of the reservoirs that was highly affected by urbanization and its deteriorating effects was considered for the analysis. Release mechanisms of iron and manganese from the sediments to the water column were studied under different acidity conditions of the water column.

Main findings of this study were summarized as:

1) Hypoxia increased Fe^{+2} concentration in the water column. It resulted in more dissolution of manganese in the water column as well, however, this increase was trivial as compared to the increase of Fe^{2+}.
2) Aeration of the water column caused significant decrease of Fe^{+2} concentrations (in this case

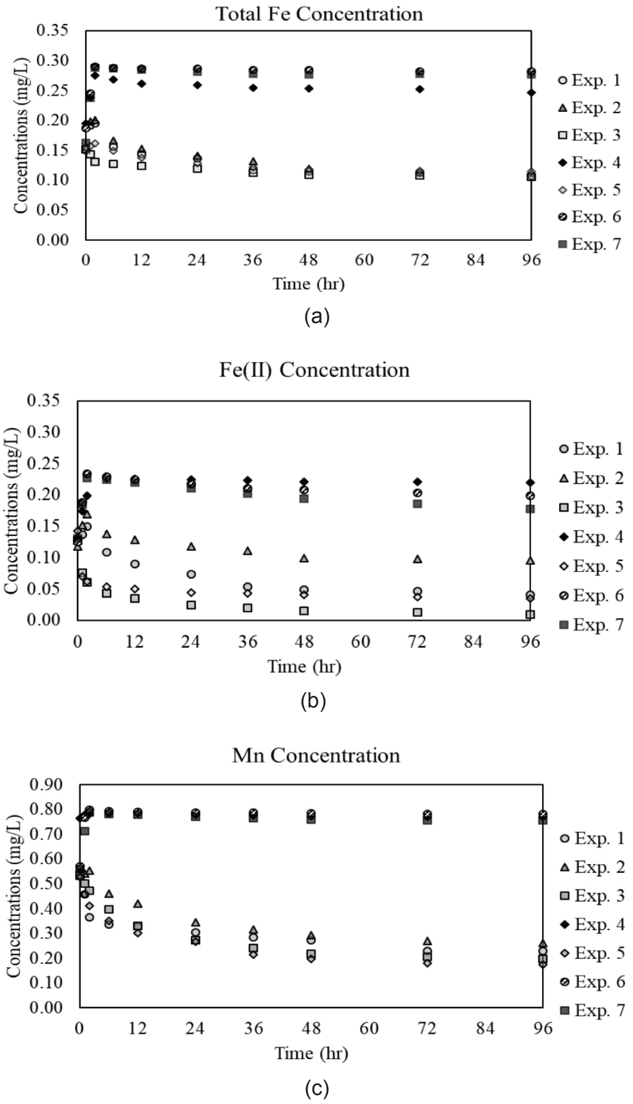


Figure 6. Comparison of total iron (a), ferrous iron (b), and total manganese (c) concentrations in seven different experiments.

reaching to zero). We believe aeration did not eliminate the formation of reduced Fe^{+2} instead pushed the oxic-anoxic boundary to the sediments. This is not the case for manganese and total iron levels were not affected by the aeration of the water column.

3) It was observed that acidity level of the water column had a great effect on the solubility of iron and manganese. When the results of acidic water conditions (pH = 5) were compared with the results of neutral water conditions (pH = 7), the concentrations of total Fe, Fe^{2+}, and total Mn in the acidic water were considerably greater than the neutral conditions. According to the results, all total Fe, Fe^{2+} and total Mn concentrations showed a considerable decrease in alkaline water conditions. Manganese concentration in the water column reached 0.770 mg/L at the end of the 96 hours where this value was observed as 0.229 mg/L for the neutral conditions. Similarly, Fe^{2+} concentration in the water column reached 0.220 mg/L at the end of the 96 hours where this value was observed as 0.096 mg/L for the neutral conditions. Alkaline water conditions (pH = 11) had an opposite impact on total Fe, Fe^{2+}, and total Mn concentrations, lowering the concentrations observed during the neutral water conditions.
4) Solubility of both iron and manganese increased in stratified conditions as compared to the mixed water column. Aeration of the stratified water column had a slight effect on lowering the concentrations of total Fe, Fe^{2+} and Mn.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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