Study on the Migration of Manganese in the Hyporheic Zone of a Reservoir

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Abstract: In order to study the laws of the spatial change of manganese in hyporheic zone, this paper takes Reservoir A as the actual research object, and analyzes the migration and change mechanism of manganese in the hyporheic zone by means of field sampling and data collection. The results show that the manganese content in the hyporheic zone of Reservoir A is changed rapidly after impoundment, and a new hyporheic zone is formed. When the hyporheic zone is closer to the surface water of the reservoir, the manganese content will stabilize faster. In the vertical direction, the hyporheic zone has a de-oxidation effect on manganese. The de-oxidation effects on manganese during wet period and dry period are 19.2% and 13.7% respectively. Within the hyporheic zone, the change of manganese content decreases gradually; while outside the hyporheic zone, the change of manganese contents increases gradually from the top to the bottom.

1. Introduction
The hyporheic zone is the lower edge of the riparian zone, where surface water and ground water interact with each other. The horizontal distribution and vertical distribution of hyporheic zone present unique characteristics. It helps purify the water body by filtering the pollutants in groundwater as well as replenishing groundwater\cite{1-2}. Therefore, combined regulation of underground water and surface water is a common mode of water resource utilization\cite{3-5}. As a large-scale impoundment and flood detention reservoir, Reservoir A is an important controlling project on the main stream of Liaohe River, with a total storage capacity of 185 million cubic meters\cite{6}. It uses an integrated surface water and groundwater regulation mode for water supply, with an average daily water supply of 100,000 m$^3$/d, which plays an important role in the replenishment of water resources in surrounding areas\cite{7}. The water of Reservoir A comes from Liaohe River. The manganese content in the groundwater of Reservoir A is seriously exceeding the standard because taking water from nearby river strengthens the hydraulic linkage between the surface water and groundwater and a large amount of ammonia nitrogen enters the groundwater. The change of the manganese content in the hyporheic zone is unclear\cite{8}. Therefore, a detailed study on the manganese migration law in the hyporheic zone of the reservoir area will help Reservoir A to regulate and store floods, improve the quality of groundwater in the reservoir, and provide reference and guidance for related water body research.

2. General introduction to Reservoir A
The construction of the main part of Reservoir A started in 2003, the main construction of the barrage and floodgate was completed in 2015, and it started to impound water in 2009. Due to the serious pollution of surface water in some areas, reservoir water usually comes from the groundwater on the riverbank, but the content of manganese in the groundwater is relatively high and will cause problems such as blockage of water wells and easy rusting of pipelines\cite{9}. The reservoir usually takes water from
nearby river and then the water is treated through water plants. In addition, manganese is greatly affected by the environment, and the temperature, salt content and dissolved oxygen in the groundwater will affect the manganese content and chemical reactions\cite{10-11}. Therefore, studying the migration law of manganese in the hyporheic zone can provide guidance for groundwater protection and development. The soil in Reservoir A is weakly alkaline, and the following chemical reactions occur in the groundwater:

\[ M_{n}^{2+} + HCO_{3}^{-} = M_{n}CO_{3(s)} + H^{+} \]

The impoundment of the reservoir has a great impact on groundwater. The area of Reservoir A is wide and the submerge range of the reservoir area reaches 50.41 km\(^2\). As a flood detention reservoir, Reservoir A is not deep, but it is large in area. The landform of the reservoir area is mostly floodplains and terraces, the upper part is small and medium sand layer and partly is coarse sand layer, which has a good water permeability, and thus surface water can well replenish groundwater. Since there is a great difference between surface water and groundwater, and they are sensitive to manganese change, thus hyporheic zone is suitable for studying the migration law of manganese element.

3. Influence of reservoir impoundment on manganese change

3.1. Spatial distribution of iron and manganese before impoundment

3.1.1. Select research scope

As a large-scale plain reservoir for flood regulation, storage and detention, Reservoir A has an impact on a large area. For this reason, the area from the gate of the reservoir to the water resource is selected as a monitoring area in the horizontal direction, and the area from Liaohe River to the outside of the reservoir dam is selected as the monitoring area in the vertical direction. The good water permeability of the soil in the reservoir area and taking water from nearby river have strengthened the connection between groundwater and surface water. According to monitoring, the depth of the groundwater level is about 10 meters, and the hyporheic zone is 15 meters below the ground elevation, which can be selected as the study objective.

3.1.2. Select monitoring section

Select two monitoring point groups to detect the manganese content in the hyporheic zone near the reservoir and the Liaohe River, and in the shallow groundwater outside the reservoir area. Figure 1 shows the distribution of groundwater monitoring points.

![Figure 1 Monitoring points of Reservoir A](image1)

3.1.3. Data processing

According to the groundwater monitoring experiment data of A reservoir, compare the hydrological data over the years to analyze the iron and manganese content of each monitoring point.

Surfer software is used to calculate the difference value of the data and the distribution and content of manganese in the hyporheic zone of Reservoir A are shown in Figure 2\cite{12}, wherein the solid line represents iron ions, and the dotted line represents manganese ions.
Figure 2 Manganese content of groundwater before impoundment

Figure 2 shows that surface water can well replenish shallow groundwater, and its replenishment becomes less gradually with the increase of the distance from the river. The spatial distribution of groundwater in Reservoir A is ring-shaped, the manganese content inside the reservoir is high and decreases gradually outward. The closer it is to the river, the lower the manganese content in the groundwater. The concentration of manganese ions in the shallow groundwater of the Reservoir A is quite different before impoundment, with a concentration between 2.5 mg/L and 0.5 mg/L. The manganese content in the shallow groundwater of the reservoir gradually increases from the highest point outward. The decreasing rate of manganese concentration from the reservoir to the south slows down gradually because Liaohe River replenishes the groundwater and dilutes the manganese, reducing the content of manganese. In addition, the dissolved oxygen content in the groundwater is relatively small, and the dissolved oxygen content in the surface water is high, which means that the manganese ions oxidize and precipitate as Liaohe River replenishes the groundwater of Reservoir A, and thus the manganese content of the groundwater decreases.

3.2. The change of manganese content after impoundment

3.2.1. Select research scope

According to the previous division of the hyporheic zone of the reservoir, almost the entire part of the reservoir area is hyporheic zone and the vertical depth is 5 meters from the earth's surface. So, the research area is the entire reservoir area with a depth of 5 meters from the earth's surface.

3.2.2. Select monitoring data

Reservoir A started operation in 2009, and the dry and wet periods of the reservoir are April and August respectively. Therefore, the average manganese concentration in shallow groundwater from 2009 to 2017 is used as the monitoring data.

3.2.3. Change of manganese concentration after impoundment

Based on the monitored data of the water in the hyporheic zone of Reservoir A, the changes of iron and manganese contents at different well sites are shown in Figure 3.

Figure 3 The change of manganese concentration in the groundwater of Well 3

As Figure 3 shows, the manganese content in the groundwater of Reservoir A is high before impoundment, reaching 2.5 mg/L. At the initial impoundment, the manganese content in the hyporheic zone quickly drops to 1.5 mg/L in 2009, about 3/5 of the original content, and then gradually stabilizes after reaching 0.5 mg/L. This is because Well 3 is very close to the reservoir (less than 50 meters), the
surface water directly replenishes the groundwater at the initial impoundment, diluting the manganese in the groundwater and reducing its concentration. When a new hyporheic zone is formed, the water content is relatively stable, the replenishment effect of surface water on the hyporheic zone is small, and the manganese concentration in groundwater decreases slowly. It shows that the manganese concentration in the hyporheic zone within 50 meters from the river is 0.25 mg/L, and the manganese concentration gradually stabilizes after the reservoir is filled for 3 or 4 years.

Figure 4 The changes of the manganese contents in Well 10 and Well 11
As Figure 4 shows, when the reservoir starts storing water, the manganese content in Well 11 first decreases to 0.7 mg/L, and then remains stable at around 0.7 mg/L. The change of manganese concentration in Well 10 is similar to that in Well 11, its manganese content first decreases from 0.42 mg/L to 0.3 mg/L, slowly increases to 0.32 mg/L and then remains stable. The reason for the change is that after the reservoir starts storing water, the groundwater environment is changed within the range of 50–100 meters due to the dilution of surface water, but the change is less than the groundwater within 50 meters area. It shows that within the range of 50–100 meters from the reservoir water, the surface water of Reservoir A has little effect on the manganese in the hyporheic zone, and manganese content is mainly affected by evaporation, precipitation and other factors.

Figure 5 The changes of the manganese contents in Well 5 and Well 7
As Figure 5 shows, before Reservoir A is filled, the manganese concentration in Well 5 is 1.57 mg/L and the manganese concentration in Well 7 was 0.87 mg/L. After the reservoir starts storing water, the manganese concentration in groundwater of Well 5 changed rapidly, reducing to 0.68 mg/L in 2009 and finally stabilizing at 0.6 mg/L. The manganese concentration in Well 7 drops from 0.87 mg/L to 0.71 mg/L after Reservoir A begins filling, it falls to 0.6 from 2009 to 2012 mg/L, and ultimately stabilizes at about 0.6 mg/L. It shows that within the range of 200–500 meters, the surface water of the reservoir has a strong replenishment effect on the groundwater. When the concentration of manganese in the hyporheic zone stabilizes at 0.6 mg/L, the hyporheic zone can regulate the manganese in the groundwater to a certain extent, keeping the manganese at an equal concentration.
As shown in Figure 6, within a range of 500~1000 meters from the surface water of the reservoir, the impoundment of the reservoir has little effect on the manganese concentration of the groundwater. The manganese content in Well 2 changed little at the initial impoundment, and then it increased gradually to 1.81 mg/L. The reason is that on the one hand, it is far from the surface water of the reservoir, on the other hand, the manganese is relatively insensitive to the environment, indicating that the concentration of manganese in the groundwater at this location is mainly affected by climate and other factors, and the impact of reservoir impoundment on it is relatively small. Well 13 is closer to the hyporheic zone, and the basic manganese content is rather low. After the reservoir starts filling, the change of manganese concentration is small and it stabilizes at around 0.55 mg/L. The basic manganese content in Well 15 before impoundment is high, combining with the hydraulic linkage between the impoundment and hyporheic zone, its manganese concentration decreases from 1.05 mg/L gradually and remained at the level of 0.68 mg/L after 2013, which indicates that hyporheic zone has a great impact on the manganese concentration at this position, and the manganese concentration decreases gradually with the increase of its distance from Liaohe River.

Within a range of 500~1000 meters from the surface water of Reservoir A, the impact of reservoir impoundment on groundwater weakens, reservoir impoundment strengthens the hydraulic relationship between Liaohe River and the groundwater and increases the scope of hyporheic zone.

In summary, in the horizontal direction, the impact of the reservoir impoundment is within 1 km from the surface water of the reservoir. After the reservoir is impounded, the groundwater environment in the submerged area will soon be changed and a new hyporheic zone will be formed. As the distance from the surface water increases, the hydraulic relationship between the surface water of the reservoir and the hyporheic zone weakens gradually, and the manganese content in the hyporheic zone increases with the increase of the distance from the reservoir. After the reservoir is filled, the manganese concentration in the groundwater stabilizes after about 4 years. During the impoundment process, as the reservoir is close to Liaohe River, a hydraulic relationship between the reservoir and Liaohe River is established and the scope of the hyporheic zone expands.

4. Vertical transformation of manganese in the underflow layer

In this paper, the water and soil of Well 2 during the wet period are used as the object to study the vertical transformation of manganese in the hyporheic zone.

4.1. Experimental materials and equipment

The experimental device used in this paper is a Perspex column, with sampling holes, a filter screen and a water valve at the top of the column. The sampling holes are connected with Perspex to collect water samples, and a latex tube is added as an outlet for water samples. To avoid clogging the water outlets, a quartz gravel layer of 5 cm thick is laid on the bottom of the column, and a layer of glass cellulose is added on it.

4.2. Experiment results and analysis

During the experiment, measure the manganese concentration of different depth sections, the graph of manganese concentrations at 20 cm position and 40 cm positions is shown as follows [13].
Figure 7 Manganese concentration change at 20 cm position during dry period

As Figure 7 shows, in the first 5 days of the experiment, the manganese content of the soil at the position 20 cm from the earth surface is stable, with a concentration of 1.3 mg/L. From day 5 to day 11, the manganese concentration decreases from 1.3 mg/L to 1.25 mg/L. From day 11 to day 23, the manganese concentration remains stable. This is because when manganese begins to migrate, the water in the soil column penetrates faster, the water sample collected in the first 5 days are original water, and thus the manganese concentration is relatively stable. After the 7th day, the water content in lower layer of the soil column rises, and the water in the middle layer is saturated, causing the penetrating rate to slow down, the oxidizing salts in the soil are dissolved, the manganese is oxidized, and the manganese concentration decreases gradually. After the 11th day, water penetrates into the soil completely and the flow rate stabilizes, and the manganese concentration remains stable.

Figure 8 Manganese concentration change at 20 cm position during wet period

As shown in Figure 8, the manganese concentration decreases rapidly from day 1 to day 7, decreasing from 1.8 mg/L to 1.75 mg/L and reaching 1.74 mg/L. Compared with that during dry period, a sufficient reaction occurs and the change of manganese concentration is great. The main reason is that the temperature in wet period is high, the content of dissolved oxygen is high, the contents of salt and organic materials are high, and thus the manganese in the water is easily oxidized.

Figure 9 Manganese concentration change at 40 cm position during dry period
As figure 9 shows, in day 13, the manganese concentration of the water sample collected from the soil 50 cm deep from the surface is 1.12 mg/L, which is much smaller than the initial concentration. From day 13 to day 19, the manganese content decreases rapidly and stabilizes at 1 mg/L. It is because the initial iron concentration at this position is low and the oxidation rate is slow; in addition, the water content in the soil column is high, water flows slowly, and the dissolution of salt is slow, and water flows out stably.

Figure 10 Manganese concentration change after day 23 during dry period

Figure 10 shows that when the experiment is stable and water has penetrated from the surface to the bottom of the soil column, the concentration of manganese decreases in the vertical direction, reducing from 1.24 mg/L to 1.01 mg/L. It is because in a natural penetrating process and under alkaline condition, the oxidation saline materials such as nitrates and microbes in the soil promote the oxidation reaction of manganese.

Figure 11 Manganese concentration change after day 23 during wet period

Figure 11 shows that after the experiment is stable and water has penetrated from the surface to the bottom of the soil column, the manganese concentration change during wet period is greater than that during dry period, reducing from 1.75 mg/L to 1.51 mg/L, and presents a decreasing trend. It is because the temperature and dissolved oxygen content during wet period are high, which promotes the oxidation reaction of manganese.

In summary, the change law of manganese content in the hyporheic zone of Reservoir A in the vertical direction is: in the hyporheic zone, the manganese concentration decreases with the increase of depth due to the penetration of surface water and the oxidation effect of microbes. However, as the depth increases, the penetrating rate of surface water slows, oxygen and microbes become less and their oxidation effect weakens, and thus the change of the manganese concentration slows.

5. Conclusions

The spatial migration of manganese in the hyporheic zone helps us learn the changing trend of manganese in the hyporheic zone at different depth, and provides guidance and reference for the protection and development of groundwater resources as well as biogeochemistry in the river area.

(1) In the horizontal direction, when the hyporheic zone of Reservoir A is close to the surface water, the replenishing effect of the surface water is strong, and the manganese concentration is low. As the distance from the surface water increases, the manganese concentration increases gradually.
(2) After the reservoir fills, the structure of the shallow groundwater is changed, and a new hyporheic zone is formed for about 1 year. The closer is the hyporheic zone to the surface water, the faster is the formation and stabilization of the new hyporheic zone, and the impacting range of reservoir impoundment on manganese concentration is around 1 km. As the distance from the surface water exceeds 1 km, the replenishing effect of evaporation and rainfall on shallow surface water is greater than the replenishing effect of surface water.

(3) The vertical migration of manganese in the reservoir area shows that when the groundwater with high manganese concentration penetrates into the hyporheic zone of Reservoir A, the manganese concentration decreases with the increase of penetrating depth under the oxidation effect of microbes, and the removal capacity of manganese in the hyporheic zone during dry period and wet period are 19.2% and 13.7% respectively. As the basic manganese content in the groundwater of Reservoir A is high, in the vertical direction, the manganese concentration in the hyporheic zone decreases gradually, and the manganese concentration outside the hyporheic zone increases gradually.

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