Characteristics of water quality response to hypolimnetic anoxia in Daheiting Reservoir

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ABSTRACT

Anoxia is a common phenomenon at the bottom of large reservoirs during thermal stratification. In an anoxic environment, an increasing amount of reducing substances and nutrients are released and settle at the hypolimnion of the reservoir, leading to water quality deterioration and eutrophication. This work presents a case study on Daheiting Reservoir, a part of the Water Diversion Project from the Luanhe River to Tianjin City. With the monitored data of the water temperature and dissolved oxygen content in the reservoir, and based on the mechanism of redox reactions, the water quality response to the hypolimnetic anoxia in Daheiting Reservoir was systematically analyzed. It was found that the release of total phosphorus from the sediments in Daheiting Reservoir was a joint effect of the biological and chemical processes, and the redox reaction in the anoxic zone boosted release of phosphorus. Anoxia in the reservoir caused the ammonia nitrogen released from sediments in the reservoir to accumulate at the hypolimnion, which increased the concentration of ammonia nitrogen in the water. Anoxia in the reservoir led to an increase in the concentration of iron and manganese, which accounts for the major driving factor of release of iron and manganese.

Key words: anoxic zone, pollutant release, thermal stratification, water quality response

HIGHLIGHTS

• This paper describes in detail the formation and development process of the hypoxic zone of the reservoir, and clarifies the temporal and spatial changes of the hypoxic zone of the reservoir.
• This paper illustrates the accelerated release process of polluted sediments under hypoxic conditions, proves the relationship between hypoxia and deterioration of water quality.

1. INTRODUCTION

It is common to observe an anoxic zone at the hypolimnion of deep-water lakes or reservoirs during thermal stratification in summers (Zhang et al. 2015; Du et al. 2019). The depletion of oxygen in reservoirs (especially at the hypolimnion) has been an intensively-studied feature of the water environment in reservoirs (Mammarella et al. 2018). Though the water at the epilimnion in most reservoirs is fully oxidized, the water at the hypolimnion during thermal stratification will consume large quantities of oxygen due to decomposition of organic matter and oxygen consumption by substrates, leading to hypolimnetic anoxia in the reservoir (Parrl 2004; Steinsberger et al. 2020). Under hypoxic conditions, the release of nitrogen, phosphorus, organic matter, iron and manganese in the bottom sediments of lakes and reservoirs will accelerate, which will seriously affect the water quality of the bottom waters of lakes and reservoirs. When the water is short of oxygen, aquatic organisms rely on nitrates, hydroxides or oxides and sulfides of iron and manganese by sequence for respiration, which changes the biogeochemical cycle (Pena et al. 2010). As revealed in existing publications, when the hypolimnion is at an anoxic state during thermal stratification, an increasing amount of reducing substances (iron, manganese, sulfides for instance) and nutrients (nitrogen, phosphorus, etc.) will be released and settle at the hypolimnion, reducing the water quality and resulting in eutrophication (Mueller et al. 2012). Elci (2008) made a case study on the Tahtali Reservoir in Turkey, and found that the thermal stratification in the reservoir led to a sharp drop of dissolved oxygen (DO) at the hypolimnion and reduced the water quality there. Kraemer (Kraemer et al. 2015) indicated that thermal stratification would exacerbate oxygen depletion in the water, lead to a substantial change in the nutrient load, and hence reduce the productivity of the water body. Lee et al. (2010) explored the environmental factors of the thermal stratification and chemical stratification in a reservoir in South Korea and the seasonal change patterns of water quality stratification. He et al. (2014) studied the changes of DO in Tianmu
Lake in Jiangsu Province, China and its impact on the release of endogenous nitrogen, and found that hypolimnetic anoxia in the summer would lead to release of ammonia nitrogen from sediments to the bottom of the lake. Yang et al. (2018) analyzed the impact of DO on the release of nitrogen and phosphorus from sediments in Dianchi Lake, and found that the gradient of DO concentration was one of the driving factors that boosted release of ammonia nitrogen and phosphates from sediments. Xu et al. (1999) studied the vertical distribution pattern of iron and manganese in Aha Reservoir in Guiyang, Guizhou province, China with seasonal anoxia, and revealed the layered distribution of water temperatures along the vertical direction; they also found that high concentrations of iron and manganese occurred at the metalimnion and hypolimnion of the reservoir during thermal stratification, and thermal stratification was closely related to hypolimnetic anoxia, decline of pH scale, and secondary pollution induced by release of iron and manganese from sediments. Hu et al. (2019) explored the correlation between the DO in the water body and its physical influencing factors. These aforementioned works have revealed that anoxia during thermal stratification in reservoirs would lead to substantial releases of pollutants from sediments and worsen the water quality.

Large and medium-sized reservoirs, with large water depths, are very likely to see thermal stratification, during which the hypolimnion is often short of or even deprived of oxygen. Even though measures are taken to control non-point pollution or contamination from water inflow in reservoirs, hypolimnetic anoxia will still occur when sedimental pollutants settle and accumulate at the bottom of reservoir and consume oxygen (Wang et al. 2017). Besides, in reservoirs in China which serve to supply water, the water intake towers are principally located in areas prone to oxygen deficiency, which leads to safety problems in the supplied water. Thus, probing into the response of water quality to anoxia in reservoirs during thermal stratification is of great significance to ensure the safety of supplied water.

The present work made a case study on Daheiting Reservoir, the source reservoir for the water diversion project from the Luanhe River to Tianjin city. Specifically, with monitored data about the temperature and DO content of this reservoir, and based on the redox reactions in the water, the response of water quality to hypolimnetic anoxia in the reservoir was systematically analyzed, and the impacts of anoxia on the water quality were explored. This research will be able to more accurately and intuitively explain the effects of hypoxia on water quality and provide solutions to the problem of worsening water quality in reservoirs during thermal stratification.

2. STUDY AREA AND RESEARCH METHOD

2.1. Introduction to the study area

Daheiting Reservoir, located on the trunk stream of Luanhe River in Qianxi County, Tangshan City, Hebei, China, is a crucial part of the water diversion project from Luanhe River to Tianjin city. It is a Level II hydrological project in China, with a water storage capacity of 337 million m³ and a backwater reach about 23 km long. The maximum water depth in front of the dam is 28 m. Built in 1986, the reservoir receives water from Panjiakou Reservoir in the upper reach of Luanhe River, and supplies water for agriculture, industries and domestic uses in Tangshan, Tianjin and other downstream cities. From the 1980s to the late 1990s, the water quality in Daheiting Reservoir was good and reached the Level III standard (Tian 2018). With economic boom in the 2000s, however, the concentrations of pollutants in the reservoir grew, and wider adoption of cage culturing (The number of cage culture is 11,000, and the area of cage culture accounts for 11% of the total area of the reservoir) led to severe pollution of water and substrates in the reservoir (Wang et al. 2016). This situation was reversed later in 2016 when cage culturing was banned in Daheiting Reservoir (Wang et al. 2017), but pollutant sediments in the reservoir continued to cause anoxia in the reservoir during thermal stratification (Liu et al. 2019), which led to substantial releases of pollutants from the sediments and undermined the function of water supply.

2.2. Research method

To capture the changes in the water quality and DO in Daheiting Reservoir, the water quality was monitored throughout the reservoir. The data were monitored once every month for 12 times from August 2017 to November 2018 (except the freeze-up period that lasted from December to the next March), and the monitoring was performed from 10th to 25th every month. In the early stage (before June 2018), 13 monitoring sites were set up in front of the dam of Daheiting Reservoir, the central area of the reservoir, Panjiahe River Estuary at the tail of the reservoir, and the estuary of Sahe River. In the later stage (since June 2018), 35 monitoring sites that formed a network were deployed across the reservoir. The monitoring sites distributed evenly across the reservoir to obtain representative data. Figure 1 shows the distribution of specific monitoring sites in the reservoir. The portable YSI EXO1 water quality monitoring meter (YSI, U.S.) was used as the monitoring device. The monitoring
indicators in the present work include water temperature (−5 to 35 °C, ± 0.01 °C), dissolved oxygen content (0–50 mg/L), conductivity (0–50 ms/cm), pH scale (0–14), chlorophyll (0–400 μg/L), and redox potential (−999 to 999 mV).

To analyze the water quality in the hypolimnion at the front of the dam of the reservoir, monitored data of the content of nitrogen, phosphorus and manganese at the surface (0.5 m below the water surface), middle (Half depth), and bottom (0.5 m above the bottom) of the reservoir from 2017 (Jul to Sept) to 2018 (Apr to Aug) were obtained.

3. RESULTS AND DISCUSSION

3.1. Temporal evolution of the anoxic zone in Daheiting Reservoir

The DO concentrations in the hypolimnion at the front of the dam of Daheiting Reservoir presented significant changes over time. As Figure 2 shows, in August 2017, obvious thermal stratification occurred at the front of the dam of the reservoir, and the hypolimnion of the reservoir was anoxic, with a DO concentration lower than 2.0 mg/L (The hypoxia standard given by the EPA is that the dissolved oxygen concentration in the water is less than 2.0 mg/L). In September, the thermal stratification began to disappear, but water temperature still presented a layered structure; the supply of DO to the hypolimnion was blocked, and could not make up for the consumption of oxygen, and hence the hypolimnion remained anoxic. In October, the upper boundary of the DO mixed layer moved up substantially, and the lower boundary dropped to about 15.0 m below the water surface from 7.5 m to 10.0 m below the surface in August and September. In November, thermal stratification existed no longer, the oxygen-rich water at the epilimnion mixed with the oxygen-deficient water at the hypolimnion, and the oxygen stratification and anoxic zone began to disappear; at this time, the DO concentration at the epilimnion reached about 8.0 mg/L.

In April 2018, no dissolved oxygen stratification occurred at the front of the dam of the reservoir, and the DO concentration throughout the reservoir stayed at around 12.0 mg/L. In May, DO stratification began to merge: the difference of DO concentration between the epilimnion and hypolimnion increased to 3.0 mg/L, but the DO concentration in the oxygen-deficient layer stayed high at 9.0–10.0 mg/L, and no anoxia occurred at the oxygen-deficient layer. In June, vertical gradients of DO
3.2. Phosphorus in the water of Daheiting Reservoir and the anoxic zone

In the present work, monitored data of the total phosphorus (TP) from the epilimnion, metalimnion, and hypolimnion in the front of the dam of Daheiting Reservoir in 2017 as well as the data of TP and phosphates from these three layers in the front of the dam of the reservoir in 2018 (Figure 3) were employed to analyze the impact of the anoxic zone on the content of phosphorus in the water of Daheiting Reservoir.

According to the monitored data and the temporal evolution features of the anoxic zone in Daheiting Reservoir, when the thermal stratification and the anoxic zone occurred in 2017 in the reservoir, the concentration of TP in the reservoir presented a vertical distribution pattern: the TP concentration increased sharply from the epilimnion to the hypolimnion of the reservoir; during the thermal stratification period, the TP concentration on the epilimnion did not change much and stayed around 0.09 mg/L, but as the water depth and the DO content increased, the TP concentration rose as well, and in July, the TP concentration on the hypolimnion layer reached 0.25 mg/L, which was nearly three times that on the epilimnion layer. As Figure 3 shows, during the fully mixing period (April), the vertical distribution pattern of the TP concentration was not that obvious. In May, as the water temperature rose, activities of the microbes increased, which led to more release of TP at the bottom of the reservoir. At this time, the TP concentration began to present a vertical distribution pattern. In June and July, an anoxic zone began to merge at the bottom of the reservoir, and the concentration of TP continued to grow at the bottom due to the combined effects of biological and chemical processes, and reached 0.16 mg/L in July, which was four times the concentration on the epilimnion layer of the reservoir. In August, due to the flood discharge of the reservoir, the DO content at the bottom of the reservoir increased slightly, leading to a slight drop in the TP concentration. In 2018, the phosphates accounted for the major contributor to the TP concentration in the reservoir, and the changes in the concentration of phosphates mirrored the changes in the TP concentration throughout the year.

Phosphorus, a key element to life, exists in all nucleotides. In water bodies, phosphorus exists in two forms: inorganic phosphorus and organic phosphorus. The former includes phosphorus in an exchangeable and weak adsorption state, aluminum phosphate, iron-phosphorus, calcium-phosphorus, detrital phosphorus; the latter include phosphomonoester, phosphodiester, phosphatide, DNA and RNA. Iron-phosphorus is phosphorus combined with ferric oxides or ferric hydroxides, which is sensitive to the changes in the redox potential and is considered phosphorus easy to release. Aluminum phosphate is generated by bonding between the phosphate anions and aluminum oxides or hydroxides; because the aluminum hydroxides are not subject to the redox potential, aluminum phosphates are considered a form of phosphorus hard to utilize. Calcium-phosphorus involve insoluble phosphates like hydroxyapatites, fluorapatites and superphosphates. Calcium phosphorus is a stable
Figure 3 | Vertical distribution of phosphorus in Daheiting Reservoir. (a) Concentration of total phosphorus in Daheiting Reservoir in 2017. (b) Concentration of total phosphorus in Daheiting Reservoir in 2018. (c) Concentration of phosphates in Daheiting Reservoir in 2018.
state of phosphorus, hard to utilize and has little impact on eutrophication of the water body. The release of phosphorus is a bio-chemical process that fully engages biological organisms, and the biological process promotes the phosphorus release in the following three ways:

1) Biological processes directly boost release of phosphorus, for which the decomposition of microorganisms in water is a fine example: bacteria can, by decomposing cells or by releasing the soluble polyphosphates generated under aerobic conditions, release soluble reactive phosphorus in an anoxic context. In their research on the release of phosphorus from sediments in Wuli Lake of Taihu Lake, Yin et al. (1994) pointed out that microorganisms could transform or decompose organic phosphorus in the sediments into inorganic phosphorus, during which phosphates were released, insoluble phosphates were transformed into soluble ones and released to the water.

2) Biological processes affect release of phosphorus by affecting the iron ions. As shown in some studies, reduction of Fe\(^{3+}\) (which will be transformed into Fe\(^{2+}\)) is not fully controlled by the DO in water, because there is a film of stable organic matter on the surface of Fe\(^{3+}\) compounds, and common reduction reactions cannot reduce all Fe\(^{3+}\) ions into Fe\(^{2+}\) ions. The iron-reducing bacteria in water, however, can take Fe\(^{3+}\) as the electron acceptor for aerobic decomposition of organic matters, and reduce the Fe\(^{3+}\) into Fe\(^{2+}\). This biological process will enhance dissolution of Fe (OOH) and phosphorus polymers, and lead to release of phosphorus. Sun et al. (2006), in a case study on Taihu Lake, found that one way that biological processes boost the release of phosphorus was to increase the reduction of iron: in an anoxic context in water, the concentration of Fe\(^{2+}\) under the action of microbes is significantly higher than that without the action of microbes.

3) Biological processes affect the release of phosphorus by consuming DO in water. At the early stage of reaction in water, the DO is sufficient, and predominant heterophytes take DO as the receptor in aerobic oxidation reactions of organic matters, while biological processes in water will directly increase the consumption of oxygen. In this way, chemicals with weak oxidation properties (such as Fe\(^{3+}\)) take place of DO to obtain electrons from oxidized organic matters and undergo reduction, thereby promoting the release of phosphates.

As the monitored data show, the release of TP from sediments in Daheiting Reservoir is a joint result of biological and chemical processes. In August in 2017 and 2018, as the hypolimnetic anoxia exacerbated, the release of phosphorus increased due to the redox reactions, resulting in a rising concentration of TP in the water body. The rise of TP concentration in May 2018 reflects the impact of biological processes on the release of phosphorus: as the bottom water in the reservoir saw a high DO concentration in May, the redox reactions could not fully resolve the ferrophosphorus polymers in the sediments; the rising release of phosphorus at the bottom, in this case, was mainly caused by the decomposition effect of microbes in the reservoir.

In sum, the release of phosphorus in water is a result of joint effects of chemical and biological processes. Under aerobic conditions, the phosphorus element can be released by the action of microbes; under anoxic conditions, the release of phosphorus can be boosted by joint effects of chemical and biological processes. In deep-water reservoirs, anoxia is one of the necessary condition for the increasing release of phosphorus from sediments (Contaminant concentration in sediments is another important condition). In this logic, resolving the problem of anoxia is a fundamental measure to alleviate the release of phosphorus from sediments in reservoirs.

3.3. Response of the anoxic zone to the content of nitrogen in Daheiting Reservoir

In the present work, the monitored data of the ammonia nitrogen content in Daheiting Reservoir in 2017 and 2018 were employed to explore the impact of the anoxic zone on the content of nitrogen in the water of the reservoir (Figure 4).

As Figure 4 shows, during the thermal stratification and anoxic period in 2017, the concentration of ammonia nitrogen on the epilimnion layer of the reservoir showed little changes and stayed around 0.2 mg/L, and as the water depth increased, the concentration rose as well, reaching the maximum at the bottom of the reservoir. In July, the concentration of ammonia nitrogen on the hypolimnion layer reached 0.84 mg/L, which was 3.6 times that on the epilimnion layer. In September, as the thermal stratification alleviated, the difference in the concentration of ammonia nitrogen between the epilimnion layer and the hypolimnion layer narrowed. In 2018, during the water mixing period, the overall concentration of ammonia nitrogen in the reservoir was low and showed no obvious differences along the vertical direction; as the thermal stratification intensified and the content of DO at the bottom of the reservoir dropped, the concentration of ammonia nitrogen showed differences along the vertical direction; in June, the difference of concentration reached 0.6 mg/L, and the concentration of ammonia
nitrogen at the bottom of the reservoir was 4.4 times that on the surface. Later, in August, due to the flood discharge of the reservoir, the DO content at the bottom of the reservoir increased, and the vertical mixing of water grew as well, leading to a smaller difference in the content of ammonia nitrogen along the vertical direction of the reservoir.

Nitrogen presents two forms in water: inorganic nitrogen and organic nitrogen. The former includes soluble nitrogen gas (N₂), ammonia nitrogen (NH₄⁺-N), nitrate nitrogen (NO₃⁻-N), and nitrite nitrogen (NO₂⁻-N), and the latter includes amino acids, protein, nucleic acids, and humic acids. The nitrogen cycle refers to the transformation between organic nitrogen, ammonia nitrogen, nitrate nitrogen, nitrite nitrogen and nitrogen gas, and the main reaction processes include ammonification, nitrification, and denitrification.

(1) Ammonification

Ammonification refers to the transformation of organic nitrogen into inorganic ammonia nitrogen, a process realized through degradation and mineralization of organic matters by anaerobic and aerobic microbes. The degradable organic nitrogen in substrates undergo degradation and ammonification under the effect of heterotrophic microbes, and the produced ammonia nitrogen, after entering the interstitial water, enter the overlying water through diffusion.

(2) Nitrification

Nitrification refers to the transformation of NH₄⁺ into NO₃⁻ under oxidation catalyzed by microbes, from which the microbes obtain energy needed for metabolism. Nitrification is a biological process instead of a chemical oxidation process, and can be expressed as

\[
NH_4^+ + 2O_2 = NO_3^- + H_2O + 2H^+
\]

In fact, nitrification is completed by two steps: nitrosation and nitration, shown as below:

\[
NH_4^+ + \frac{1}{2}O_2 = NO_2^- + 2H^+ + H_2O
\]

\[
NO_2^- + \frac{1}{2}O_2 = NO_3^-
\]

According to the formulae, 4 mg DO is required to transform 1 mg NH₄⁺ into NO₃⁻. Therefore, nitrification will result in considerable DO consumption at the hypolimnion layer of the reservoir. As shown by the statistics of Lake Ontario in the 1980s, 40% of oxygen at the bottom of the lake was consumed by nitrification, and in the anoxic zone, ammonification led to a high content of NH₄⁺, and in an anoxic context, the nitrification stayed at the nitrosation stage.

(3) Denitrification

Denitrification refers to the dissimilatory reduction of oxynitrides (NO₃⁻ or NO₂⁻) catalyzed by microbes. Under denitrification, the oxynitrides first transform into gaseous nitrogen (NO or N₂O), and then into nitrogen gas (N₂), which escapes from

Figure 4 | Vertical distribution of nitrogen content in Daheiting Reservoir. (a) Concentration of ammonia nitrogen in Daheiting Reservoir in 2017. (b) Concentration of ammonia nitrogen in Daheiting Reservoir in 2018.
the nitrogen cycle in water and enters the atmosphere, leading to loss of the nitrogen element in water. Nitrification, in essence, provides the $\text{NO}_3^-$ or $\text{NO}_2^-$ as the electron acceptors for heterotrophic facultative anaerobes under oxygen-deficient conditions to fulfill relevant reactions.

Analyses above have revealed the crucial part that DO plays in the nitrogen cycle. A DO-rich environment can promote nitrification, and reduce the content of ammonia nitrogen in water; deficiency of oxygen in water, however, will limit nitrification and result in accumulation of ammonia nitrogen.

With many pollutant sediments at the bottom, Daheiting Reservoir saw a slight rise in the content of ammonia nitrogen (caused by ammonification) at the bottom even in months without thermal stratification. At this time, however, the water at the bottom of the reservoir was rich in DO, and nitrification occurred aside from ammonification, which transformed $\text{NH}_4^+$ produced in ammonification into $\text{NO}_3^-$ through catalysis by microbes. In this case, the overall content of ammonia nitrogen in the reservoir was low. As thermal stratification became increasingly obvious in the reservoir, the DO content at the bottom dropped sharply, and the nitrification was halted due to shortage of DO. The ammonification on the surface of sediments, however, continued (ammonification can take place regardless of presence of oxygen). As a result, the $\text{NH}_4^+$ is continued to be produced, but the nitrification action that would consume $\text{NH}_4^+$ halted, leading to an increasing concentration of ammonia nitrogen at the bottom of the reservoir. The rising concentration of ammonia nitrogen at the bottom of Daheiting Reservoir was attributable to the transformation of organic nitrogen in pollutant sediments, but it was anoxia that led to accumulation of ammonia nitrogen at the bottom and further increase of the concentration of ammonia nitrogen in the water of the reservoir.

### 3.4. Response of the anoxic zone to the content of iron and manganese in Daheiting Reservoir

In the present work, the monitored data of the concentrations of iron and manganese, together with the monitored DO concentration data in Daheiting Reservoir in 2018, were analyzed to explore the impact of the anoxic zone on the content of iron and manganese in the reservoir (Figures 5 and 6). As the figures show, substantial release of iron and manganese was observed in Daheiting reservoir during thermal stratification.

In the water rich in DO and without many soluble organic matters, $\text{Fe}^{3+}$ will generate large amounts of insoluble oxides or peroxides ($\text{FeOOH}$), which will accumulate at the bottom of the water body and generate a reddish-brown film coating the surface of sediments. This often happens in water rich in DO. When the microbes in water oxidize organic matters, the DO, manganese, nitrate and iron will be reduced as the terminal electron receptor of the reduction reaction in sequence by oxidability. When the manganese is taken as the electron receptor, the water body begins to enter an anoxic state.

For the iron element, when reducible sulfur is absent from the water, $\text{Fe}^{2+}$ is soluble in the anoxic context and can be diffused from sediments to the surface water. In the water mixing period when the thermal stratification ended, $\text{Fe}^{2+}$ will quickly be oxidized due to contacts with the DO on the epilimnion layer of the water body. The $\text{Fe}^{3+}$ produced by oxidation will generate $\text{FeOOH}$ polymers and fall onto the bottom of the lake or reservoir, waiting to be dissolved when the anoxic zone occurs again. A high concentration of iron in the anoxic zone on the hypolimnion layer is a typical feature of eutrophic reservoirs or lakes, and the dissolution of FeOOHP polymers in anoxic conditions leads to a high concentration of phosphorus in the

![Figure 5](http://iwaponline.com/wst/article-pdf/doi/10.2166/wst.2021.491/962386/wst2021491.pdf)  
Figure 5 | Vertical distribution of iron and manganese in Daheiting Reservoir. (a) concentration of iron at the bottom of Daheiting Reservoir in 2018. (b) concentration of manganese at the bottom of Daheiting Reservoir in 2018.
water. The release of iron that accompanies oxidization of organic matters in anaerobic conditions is as follows:

\[(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 212Fe_2O_3 + 848H^+ \rightarrow 424Fe^{2+} + 106CO_2 + 16NH_3 + H_3PO_4 + 530H_2O\]

In the case of manganese, manganese oxides (Mn\(^{4+}\) for instance) can be reduced with redox potentials higher than Fe\(^{3+}\) and SO\(^2^-\), i.e., when the redox potential drops, manganese undergoes reduction by taking part in the redox reaction as the terminal electron receptor ahead of iron and sulphate, while the iron stays in the insoluble FeOOH state. As the DO concentration rises in the water, the soluble Mn\(^{2+}\) falls to the bottom of the reservoir in the form of flocculent hydroxides of Mn\(^{4+}\).

The release of manganese from oxidation of organic matters in anoxic conditions can be described as follows:

\[(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 236MnO_2 + 472H^+ \rightarrow 236Mn^{2+} + 106CO_2 + 8N_2 + H_3PO_4 + 366H_2O\]

As shown in Figure 5, the concentration of iron and manganese on the hypolimnion layer of the reservoir was higher than on the epilimnion layer during the oxygen-deficient period, which indicates that the DO at the bottom of the reservoir was not sufficient to support decomposition of organic matters, and the iron and manganese sediments in the substrates began to undergo redox reactions and transform from the sedimental state into the soluble state. As Figure 6 shows, the iron and manganese occurred only when the hypolimnion was in a low-oxygen or oxygen-deficient state, the concentration of iron and manganese was negatively correlated to the DO concentration, which means that DO deficiency on the hypolimnion layer of the reservoir was the major contributor to the increasing concentration of iron and manganese in water. Besides, according to the pattern of TP release mentioned earlier, the reduction of Fe caused by anoxia led to dissolution of the polymers comprised of Fe(OOH) floccule and phosphorus, and increased the concentrations of iron, TP and phosphates in water.

Analyses above have revealed the direct correlation between the content of iron and manganese and the DO content in the water: in oxygen-rich water, iron and manganese settle at the bottom of the water as sediments; in oxygen-deficient water, the iron and manganese elements transform into soluble sediments and reduce the water quality. DO is the major factor that affects the content of iron and manganese in water.

4. CONCLUSIONS

(1) The paper made a case study on Daheiting Reservoir, the source reservoir for the water diversion project from the Luanhe River to Tianjin city. Specifically, with monitored data about the temperature and DO content of this reservoir, and based on the redox reactions in the water, the response of water quality to hypolimnetic anoxia in the reservoir was systematically analyzed, and the impacts of anoxia on the water quality were explored. The major findings are as follows.

(2) The release of TP from sediments in Daheiting Reservoir is a result of joint effects of biological and chemical processes; the redox reaction during the anoxic period boosted the release of phosphorus in the water, which, together with the biological processes, reduced the water quality in the reservoir; the increasing content of ammonia nitrogen at the bottom of Daheiting Reservoir was mainly caused by the release of transformed organic nitrogen from pollutant sediments; the
anoxia of the reservoir, however, led to deposition of the released ammonia nitrogen at the bottom of the reservoir, which further increased the concentration of ammonia nitrogen in the water; the anoxia in Daheiting Reservoir promoted the transformation of iron and manganese elements from the sedimental state into the soluble state, which led to an increasing concentration of iron and manganese as well as a rising concentration of TP and phosphates in the water, and this is the major driving contributor to the release of iron and manganese elements.

(3) The anoxia process at the deep-water region of Daheiting Reservoir throughout the year was the major contributor to the temporal changes of water quality in the reservoir. Multiple factors in the water present complicated correlations: under a highly eutrophic condition, decomposition of organic matters consume DO considerably. During the thermal stratification, the DO on the hypolimnion layer was not efficiently supplied and was thus quickly depleted, transforming the water from an oxidation state to a reduction state. In this case, anoxia at the bottom of the reservoir further reduced the water quality. In an anoxic context, chemicals with weak oxidation properties served as the electron receptors for redox reactions, which changed the properties of these chemicals, increased the concentration of iron, manganese and phosphorus in the water; meanwhile, anoxia led the nitrification reactions to a halt, and the sediments, due to the effect of ammonification, generate ammonia nitrogen that will settle at the bottom of the reservoir.

(4) Anoxia is the root cause for release of pollutants in the reservoir. Anoxia is a result of high eutrophication, and the driving force to deterioration of the water quality. Therefore, such measures as artificial oxygenation which could restrain anoxia are effective measures to improve the water quality at the bottom of the reservoir during thermal stratification.

(5) Despite the findings, there is, however, room for improvement and further research. This work is based on monitored data for merely two years, but the release of pollutants from the reservoir sediments is a long-term process. Therefore, in future studies, it is necessary to probe into the patterns and characteristics of the pollutant release based on continuous monitoring for a longer period of time.

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DATA AVAILABILITY STATEMENT
All relevant data are included in the paper or its Supplementary Information.

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