The Influence of Bottom Sediment Redox State on Water Quality Dynamics under Long-term Anoxic Conditions in an Organically Polluted Reservoir

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Abstract: This study involved regular observations for four years in the reservoir, in which overabundant organic matter was prominent due to humic acid, to evaluate the water quality dynamic near the bottom during long-term anoxic periods. Based on the temporal changes of dissolved oxygen, nitrate-nitrogen, ammonia-nitrogen, phosphate-phosphorus, sulfide, total iron ions and sulfate, this study focused specifically on the influence of the redox state of the sediment surface during the early stage of thermal stratification on the anaerobic biochemical reactions. As a result, nitrate-nitrogen started to decrease to zero due to denitrification as soon as the anoxic state occurred, and then both ammonia-nitrogen and phosphate-phosphorus increased linearly with time due to iron reduction after nitrate-nitrogen had decreased to zero. Sulfide began to increase linearly due to sulfate reduction as soon as nitrate-nitrogen disappeared. Also, the initial redox state of sediment impacted on the change characteristics of phosphate-phosphorus, ammonia-nitrogen and sulfide in the points of increasing timings, duration and rates. It was concluded that our results would provide important finding about the mechanisms of aqueous environmental deterioration due to organic pollution as well as beneficial information for the modification of water quality prediction model.

Keywords: Thermal stratification; Anoxic water; Anaerobic degradation; Nutrient release; Sulfide generation

1 Introduction

One of the most aquatic environmental issues, occurring in a closed water body with an overabundance of organic matter, is the occurrence of anoxia due to thermal stratification during the warm season. This state leads to the depletion of oxygen and nutrients in the bottom sediment including nitrogen and phosphorus, and thus the death of aquatic organisms, which then accelerates eutrophication. Moreover, the production of hydro sulfide and the accumulation of sludge, such as metal sulfides and undecomposed organic matter in the bottom mud, are toxicities and damage the aquatic biosphere. These environmental problems are closely related to biochemical reactions under anaerobic states, including iron reduction and sulfate (SO$_4^{2-}$) reduction. For example, the iron reduction reaction leads to elution of phosphate-phosphorus from bottom sediment and SO$_4^{2-}$ reduction causes hydrogen sulfide generation. Thus, it is necessary to investigate biochemical water quality dynamics that are affected by anaerobic microorganisms to understand the mechanisms of aquatic environmental degradation that are associate with organic pollution. The basic knowledge obtained from this study could be useful in the management of water resources, especially in the conservation and restoration of organically polluted water bodies.

However, quantitative estimation of the water quality dynamics in the hypolimnion near the bottom bed from a biochemical perspective has rarely been conducted in actual water bodies. There have been a few studies that evaluated the increase of phosphate-phosphorus (PO$_4^{3-}$), ammonium-nitrogen (NH$_4^-$N), and sulfide near the bottom sediment in a strongly reductive state because of the long-term anoxia. For example, (Nishioka et al., 2016) carried out laboratory experiments to explain the impact of the bottom material on the biochemical characteristics of water quality dynamics under anaerobic conditions. In addition, Oniki et al. (2017) built experiments with beaker-scale water quality monitoring to clarify the temporal changes of NH$_4^-$N, PO$_4^{3-}$, and sulfide over time in relation to the initial nitrate-nitrogen (NO$_3^-$N) at early anoxic state. The study revealed that these variations with linear regression and nonlinear regression models were dependent on the initial NO$_3^-$N concentrations. Furthermore, Thach et al. (2017) focused on the impacts of the oxidative/reductive state of the sediment surface and the high/low levels of dissolved organic carbon on water quality characteristics in the bottom water by applying beaker-scale water quality monitoring under anaerobic conditions. The results suggest that high DOC concentrations and oxidative states of the sediment surface promoted the release of PO$_4^{3-}$ as well as the production of sulfide because these conditions accelerated iron reduction and SO$_4^{2-}$ reduction by increasing the respiratory substrates for anaerobic microorganisms. These findings from limited studies above might provide essential information for the investigation of water quality dynamics under an anaerobic state in closed water bodies.

In this study, we conducted the environmental analysis in a closed water body where thermal stratification was formed with two layers of the epilimnion and hypolimnion. The major objective of the study is to quantitatively estimate water quality dynamics from the viewpoint of anaero-
bic respiration through the observed profiles of seasonal changes in water quality above the bottom sediment where anoxic water could be kept for a long time. We carried out weekly field observations of vertical time-series data for water quality in the reservoir, where advanced levels of organic matter from humic acid was recorded during the warm season of April to November in 2014, 2015, 2016, and 2017. The study especially considered the seasonal variations of NO₃-N, NH₄-N, PO₄-P, sulfide, total iron ions, and SO₄²⁻ ions around the bottom sediment under long-term anaerobic states. The water quality analysis of these concentrations due to denitrification, iron reduction, and SO₄²⁻ reduction was focused on three points under the anoxic state: the correlations between these water quality parameters, the timing of increase or decrease of these parameters, and the rates of these variations. Furthermore, we focused on the differences in the redox state of the sediment surface between 2014-2015 and 2016-2017 at the time when DO above the bottom mud started to decrease to zero due to thermal stratification. By comparing the profiles for 4 years, the influence of oxidative/reductive bottom mud on water quality dynamics DO, NO₃-N, NH₄-N, PO₄-P, and sulfide was studied here with a particular interest in anaerobic respiration.

2 Field Observations of Water Quality
2.1 Study area
The target water body is a regulating reservoir on the Ito Campus of Kyushu University, Japan with water surface area of ca. 19,300 m², pondage of ca. 63,000 m³, and maximum water depth of ca. 8 m (Figure 1). This reservoir, located in the deforestation area, was created for rainfall storage. At present, the water level is maintained at a high level because the reservoir functions as a source of irrigation water to the downstream paddy fields. During rainfall, a large amount of water flows into the reservoir through two box culverts from the catchment area and the stored water is discharged simultaneously from the spillway.

The logged wood chips yielded at the time when the forested area had developed into the campus, are covered with the developed land including the neighborhood of the targeted reservoir. As a result, excessive levels of dissolved organic matter from the humified wood chips flow into the pond through two box culverts during rainfall and high inflow of humic acid causes a dark reddish-brown color in the water. In addition, earth and sand used in the campus construction flow into the reservoir through box culverts during heavy rainfall resulting in turbid water. The insufficient underwater light caused by dissolved and particulate matter leads to thermal stratification from summer to autumn, resulting in the formation of the hypolimnion with the decline of DO levels. Anoxic water could occur in depths > 2 m by strong thermal stratification in summer and the anoxification above the bottom bed could be maintained over six months (Harada et al., 2014; Nguyen et al., 2015). The thermal stratification would also cause seasonal increases in ammonium, phosphate, and sulfide levels in the hypolimnion and deposition of mud at the bottom (Nguyen et al., 2015).

2.2 Regular observation of water quality
The vertical profiles of water quality were observed weekly at the center of the target reservoir from April to December in 2014, 2015, 2016 and 2017. The observation period corresponded to the season when the water temperature had a non-uniform distribution in the vertical direction and the anoxic water occurred above the bottom bed. Measurements of DO, water temperature, and oxidation-reduction potential (ORP) were recorded at 0.5 m intervals from the water surface to just above the bottom sediment using the multi-parameter water quality meter (Model 6920, YSI Nanotech).

Also, water samples collected at 1 m intervals were analyzed for NO₃-N, NH₄-N, PO₄-P, sulfate ion (SO₄²⁻), sulfide, total iron ion (TFe), total organic carbon (TOC), dissolved organic carbon (DOC), and ultraviolet light absorption at the 254 nm wavelength (E254). TFe is defined as the sum of ferrous ion (Fe²⁺) and ferric ion (Fe³⁺) and regarded as a water quality parameter related to the anaerobic biochemical reaction of phosphate elution due to iron reduction. Both SO₄²⁻ and sulfide were analyzed to quantitatively estimate the sulfate reduction under the strong reductive state. E254 was used as an indicator of humic acid and other dissolved organic matter. The analytical methods can be summarized as follows: (a) both NO₃-N and SO₄²⁻ were analyzed using an ion chromatograph (DX-320, Dionex); (b) PO₄-P and TFe were analyzed using the ascorbic acid reduction-molybdenum blue method and the 2,4,6-tris (2-pyridyl)-1,3,5-triazine method, respectively, with a DR5000 (HACH) spectrophotometer; (c) sulfide was measured as S²⁻ ion using DR5000 based on the ethylene blue method and the analysis included ions liberated from hydrogen sulfide, hydrogen sulfide ions, and soluble metal sulfides (including iron sulfide) because of the presence of sulfuric acid; (d) NH₄-N was determined using a coulometric titration-type ammonia nitrogen meter (AT-2000, Central Kagaku Corp); (e) TOC and DOC were measured using a TOC analyzer (Sievers 900, GE Analytical Instruments) based on a wet ultraviolet oxidation reaction and selective membrane conductometric technology; and (f) E254 was measured using DR5000.

In addition, samples from the bottom sediment were collected using an Ekman grab in conjunction with weekly water quality observations to measure the chemi-
cal-physical characteristics of the bottom mud. The redox state of the bottom sediment surface could be recognized through its color, which could be useful in estimating the water quality dynamics depending on the aerobic/anaerobic state above the bottom bed.

3 Results and Discussion of Water Quality Observations

3.1 Seasonal characteristics of vertical profiles

The observed results of seasonal changes in the vertical profile of water quality parameters including water temperature, DO, ORP, NH$_4$-N, NO$_3$-N, PO$_4$-P, and sulfide in 2014, 2015, 2016, and 2017 are displayed in Figures 2, 3, 4, and 5.

Considering seasonal changes in water temperature, similarities can be found in the depth data over four years. Thermal stratification started to occur in April because of a significant difference in temperature between the water surface and bottom water layer (temperature deviations of up to 10°C) with its structure consisting of an epilimnion, thermocline, and hypolimnion. From April to August, the water temperature gradient increased so that a stable thermocline could be found at 2-4 m. In mid-September, as radiative cooling at water surface occurred significantly, the formation of a mixing layer of constant water temperature due to the settling of cold water is clear. The development of this layer reached a depth of 5 m in October and the two-layered stratification with a clear thermocline could not be recorded in November. Until mid-November, thermal

Figure 2: Seasonal changes in the vertical profiles of water quality items in 2014

Figure 3: Seasonal changes in the vertical profiles of water quality items in 2015
Stratification was weakened because vertical circulation reached all water depth zones and the water temperature displayed uniform distribution.

Destratification occurred in early November in 2014, in December in both 2015 and 2016, and in mid-November in 2017. Comparing profiles between four years, the duration of vertical stratification in 2017 and 2016 was longer by about one month compared with those in 2014 and 2015. It could be because the influence of fall warming reduced thermal convection caused by water surface cooling that suppresses the development of a mixing layer from September to November.

Next, the vertical profiles of DO showed a significant difference between 4 years in the spring season. The development of anoxia was observed in mid-April in 2016 and in early April in 2017 around the bottom sediment, while it was not confirmed until mid-April in 2014 and May in 2015. The hypolimnion was in an anoxic condition at depths ≥ 6~7 m until June in all 4 years, and the vertical profile of DO exhibited a similar distribution to water temperature with a three-layer structure: an upper layer with a high level of DO concentration, even reaching a saturated state, a transition zone where DO decreased to a low level, and a hypoxic zone above bottom sediment where DO was nearly zero. In August, hypoxia developed at ≥ 3 m due to the formation of a strong thermal stratification because of a
large deviation in temperature (up to 20°C) between the water surface and the bottom water. Accompanying the enlargement of a mixing layer in the fall, aerobic zones reached to ≤ 4 m depth in October and ≤ 6 m depth in early November. Therefore, when the DO concentration improved across all water depth zones, thermal stratification had disappeared through the development of vertical circulation in November or December. In 2014, the anaerobic state occurred in mid-April until mid-November when the disappearance of this state due to destratification was observed. This period of anaerobic state near the bottom sediment existed from May to December in 2015, from April to December in 2016, and from April to mid-November in 2017. This means that the anaerobic state above the bottom mud in 2016 and 2017 lasted about one month longer than that in 2014 and 2015. This is an important feature when evaluating the water quality dynamics under anaerobic conditions.

The vertical profile of ORP showed seasonal fluctuations in all 4 years at depths of > 6 m in the hypolimnion where a hypoxic state existed. A reductive state of ORP was recorded at the bottom water at the same time when DO reached zero. ORP decreased quickly to about -200 mV and this strong reductive state was maintained until the disappearance of thermal stratification. Except for the bottom depth, there was a time lag of one month between the timing points of DO = 0 and ORP < 0. For example, anoxia occurred in May 2014 at a depth of 7 m, but ORP was decreased to a negative value in August. In 2015 at the same water depth of 7 m, an anoxic state was reached in mid-June, but ORP reaching < 0 was in August. In 2016, although an anoxic state was confirmed at ≥ 3 m in August, ORP was still at an oxidative state at depths of 3-5 m. Like in 2016, a time lag between ORP < 0 and DO = 0 was also found in 2017. Anoxic state occurred in June at a water depth of 6 m, but ORP < 0 just was observed at this depth in August. In addition, the points at which a strong reductive state of ORP (from -200 mV to -100 mV) was kept at ≥ 6 m until November in 2014 and 2017, and late-November in 2015 and 2016, could be considered as an essential feature of the reservoir water environment.

NH₄-N, PO₄-P, and sulfide exhibited uniform concentration distribution and there were no seasonal changes of these concentrations at depths ≤ 6 m. In addition, these inorganic ions displayed seasonal increases at a water depth of 7 m and the bottom water. The vertical profile showed a maximum concentration at the bottom water, indicating that the increases in NH₄-N, PO₄-P, and sulfide were a result of the interaction between the water quality and the sediment with long-term anoxia and strong reduction caused through anaerobic biochemical reactions. Thus, elution of NH₄-N and PO₄-P from the bottom mud were seen as a result of organic matter decomposition by anaerobic microorganisms at the bottom sediment while sulfide was produced by SO₄²⁻ reduction in the water column above the bottom. Moreover, the increase in the concentrations of NH₄-N, PO₄-P, and sulfide just above the sediment surface could lead to an increase in their concentrations at a water depth of 7 m because of substance transportation upward by molecular diffusion. Regarding NO₃-N, after its concentration decreased gradually over time from the spring to the summer, NO₃-N was at a very low level during the summer time at all depths. Considering this variation from the viewpoint of the nitrogen cycle in water bodies, nutrient intake by algal activity through photosynthesis and reduction of nitrate ions by denitrification can be attributed to biochemical processes associated with the decline in NO₃-N. The first process depends on sufficient underwater light, while the second process occurs under anaerobic states. As a result, the decrease in NO₃-N from the spring to the summer is regarded as due to different biochemical processes depending upon the water depth, in which NO₃-N decreased by photosynthesis in the epilimnion and denitrification in the hypolimnion. Furthermore, the seasonal changes of inorganic nitrogen in the epilimnion indicate that NO₃-N declined to zero after the spring, while NH₄-N did not show a remarkable decreasing trend like NO₃-N over the stratification period. This suggests that phytoplankton might consume NO₃-N preferentially than NH₄-N in the intake of inorganic nitrogen for photosynthesis.

As long-term anoxia existed above the bottom water due to thermal stratification from the spring to the fall, the sediment was kept in a strong reductive state, recognizable by its gray color. However, the disappearance of anoxia due to the development of a mixing layer across all water depth zones could result in a recovery from the anaerobic state to the aerobic state even near the bottom water. Consequently, the sediment surface formed a reddish-brown in color oxidation layer in the spring, a sign of the change of reductive to oxidative state. This state of the sediment was observed in April 2014 and late-April 2015 (Figure 6). However, in 2016 and 2017, the sediment was in a reductive state represented by a gray color at the start of April, and there was no evidence of an oxidation layer in the sediment (Figure 6). The reasons leading to such a difference in the states of sediment surface might be due to duration of the anaerobic state above the sediment. First, the timing points of destratification in 2015 and 2016 was later than in an average year because the anoxia above the bottom bed lasted until December. And second, the hypoxic state in 2016 and 2017 was earlier than in an average year because the thermal
stratification was recorded in late March 2016 and 2017. Thus, the length of exposure time of the reductive sediment to the aerated water from December 2015 to March 2016 and December 2016 to March 2017 were shorter compared to an average year. As a result, an oxidation layer did not form in the spring 2016 and 2017 at the sediment surface, but a reductive state was still maintained. Such a difference in the redox state of sediment surface among 4 years might be responsible for the water quality dynamics in the hypolimnion from the spring to the fall. Thus, the impacts of long-term thermal stratification on closed water bodies could be evaluated by comparing the results of water quality monitoring between 4 years.

### 3.2 Biochemical dynamics of water quality near the bottom

As shown in Figure 7, the seasonal variations in the vertical profiles of water quality items indicated a decline in DO and NO₃-N and an increase in NH₄-N, PO₄-P, and sulfide.

![Figure 7: Field observations of DO, NO₃-N, NH₄-N, PO₄-P, sulfide, SO₄²-, TFe, DOC, and E254 near the bottom in 2014, 2015, 2016 and 2017.](image)

*Figure 7: Field observations of DO, NO₃-N, NH₄-N, PO₄-P, sulfide, SO₄²-, TFe, DOC, and E254 near the bottom in 2014, 2015, 2016 and 2017. S is the slope of the linear line*
concentrations near the bottom sediment. These temporal changes, caused by biochemical reactions under anaerobic conditions, and the numerical analysis of these processes need a quantitative evaluation of water quality dynamics, focusing on the relationship between water quality parameters.

In a previous study (Thach et al., 2017), we conducted beaker-scale water quality monitoring to examine the increases of NH$_4$-N, PO$_4$-P, and sulfide as well as the decline of NO$_3$-N under anaerobic conditions. The important findings could be summarized in the following points: (1) NO$_3$-N decreased to zero through denitrification, and elution of NH$_4$-N due to decomposition of organic matter began immediately when DO began to decrease, (2) the increase in PO$_4$-P due to iron reduction occurred right after DO reached zero, and (3) sulfide began to increase dramatically because of SO$_4^{2-}$ reduction when NO$_3$-N was exhausted. The results also revealed that biochemical reactions under anaerobic condition occurred, beginning with the highest oxidation potential compounds in the order of denitrification, iron reduction, and SO$_4^{2-}$ reduction. The initial concentration of NO$_3$-N and the initial redox state of the sediment surface influenced both the rates and starting points of increases in PO$_4$-P, NH$_4$-N, and sulfide under anaerobic states. These temporal increases were modeled by a linear regression equation with high initial NO$_3$-N concentrations and similar logarithmic curves to when initial NO$_3$-N concentration was low. Moreover, the rate of increase under high initial NO$_3$-N conditions was lower than the rate during the sudden growth under low initial NO$_3$-N conditions. There were no significant differences in the dynamic properties of NO$_3$-N and NH$_4$-N between initial oxidative and reductive states of the bottom sediment in terms of the rates of decline of NO$_3$-N and increase of NH$_4$-N, as well as in the timings of the start of the NO$_3$-N decrease and the NH$_4$-N increase. However, the initially oxidative sediment delayed the elution of PO$_4$-P and sulfide generation, and stimulated the rates of temporal changes of these concentrations. Based on these findings, the seasonal changes in NO$_3$-N, NH$_4$-N, PO$_4$-P and sulfide above the bottom mud were statistically estimated through field observations in the actual water body and the impacts of the difference in redox state at the bottom sediment surface between 2014, 2015, 2016, and 2017 on these changes in water quality over time were considered.

The results indicated that DO concentration was zero in late April of 2014, May of 2015, mid-April of 2016, and April of 2017. DO began to increase because of the disappearance of thermal stratification until mid-November of 2014, in December of 2015 and 2016, and in late-November of 2017. Following the decline in DO, ORP started to decrease approximately the time when DO was zero, and it reached a strong reductive state of about -200 mV in early June over four years. In 2014 and 2015, the sediment surface changed from an oxidative state with a dark-brown color to a reductive state with a gray color at the time when ORP decreased to the strongest reductive state. NO$_3$-N started to decrease in early April 2014, in early June 2015, and in mid-April 2016. In 2017 at the start of field observation, NO$_3$-N was at a low concentration in early April. NO$_3$-N decreased one month later than the time of DO = 0 in 2015, while NO$_3$-N in 2014 and 2016 decreased at the same time as DO decreased to zero. As NO$_3$-N decreased at the time of DO = 0, this decrease was caused by denitrification occurring under anaerobic conditions. In addition, NO$_3$-N exhibited a linear decline as a result of denitrification, but the rates of change in 2014 and 2015 were lower than that observed in 2016 (Figure 7). These rates of decline are 0.0048 mg/L/d, 0.0046 mg/L/d, and 0.0060 mg/L/d for 2014, 2015, and 2016, respectively. As initial levels of NO$_3$-N were almost the same (0.4 mg/L) with a starting anaerobic state, the lower rates of decline in NO$_3$-N mean that the required time for completion of denitrification in 2014 and 2015 was longer than in 2016. In particular, it took approximately 3 months from April to July to finish denitrification in 2014 when DO decreased to nearly zero. In 2015 after DO reached zero (one month), NO$_3$-N decreased from June to August (2 months), meaning that it took about 3 months to reduce NO$_3$-N to zero when DO was zero. In 2016, denitrification occurred from May to July (2 months). The low rates of decline in NO$_3$-N under anaerobic conditions might be because the oxidative state of the sediment surface in 2014 and 2015 inhibited the activation of anaerobic denitrifying bacteria. As a result, the denitrification was delayed one month in 2015 or slowed down the rate of the denitrification reaction in 2014. While in 2016 and 2017, as the sediment surface was in a reductive state at the time when DO decreased, denitrifying bacteria were promoted and NO$_3$-N denitrification promptly occurred. The difference between four years regarding the duration and the rates of decrease in NO$_3$-N under anaerobic conditions had a strong impact on the water quality dynamics caused by biochemical reduction reactions after denitrification.

Next, we examined the dynamics of PO$_4$-P and TFe because of the change in NO$_3$-N with time. Both TFe and PO$_4$-P started to increase quickly when denitrification had finished under anaerobic conditions. As the increase in Fe$^{3+}$ cannot occur under anaerobic conditions, the increase in TFe was considered a result of the elution of Fe$^{2+}$. The concentration of Fe$^{2+}$ increased with the reduction of the ferric ion at the bottom sediment. The starting point of the TFe increase was at the same time as the PO$_4$-P increase and there was a strong correlation between these increases, as shown in the correlation matrix tables (Table 1, 2, 3, and 4). Thus, the increase in PO$_4$-P was attributed to its elution, which was produced by iron reduction, from the bottom sediment. Both TFe and PO$_4$-P increased as a linear regression line in the long-term anoxic state until the disappearance of thermal stratification in November in 2014 and mid-December in 2015. In 2016 and 2017, PO$_4$-P and TFe increased quickly from July to September and then maintained constant values after October. The rates of increase in PO$_4$-P in 2015, 2016, and 2017 were almost the same (0.0019 mg/L/d, 0.0020 mg/L/d, and 0.0015 mg/L/d, respectively), while the rate in 2014 was lower (0.00062 mg/L/d). Although the increase rates of PO$_4$-P were not
negative correlation with the linear decrease of SO$_4^{2-}$. These results imply that an increase in sulfide caused by SO$_4^{2-}$ reduction begins after completion of denitrification. In addition, unlike beaker scale water quality laboratory experiments (Thach et al., 2017), iron and SO$_4^{2-}$ reduction occurs concurrently in the actual water area under conditions of DO and NO$_3$-N = 0. In all 4 years, sulfide reached a peak and then gradually decreased or kept steady. The decrease in sulfide was because of soluble metal iron precipitation in the bottom mud by manganese and iron binding after sulfate reduction obtained the equilibrium state. The increase in sulfides to their maximum values could be modeled by a regression line. The rate of sulfide increase in 2014 (12.2 μg/L/d) was much higher than that in 2015 (6.1 μg/L/d), 2016 (7.2 μg/L/d), and 2017 (3.8 μg/L/d). The rate of sulfide increase was also reflected in the relative magnitude of the rates of SO$_4^{2-}$ decline in 2014 (0.069 mg/L/d), 2015 (0.051 mg/L/d), 2016 (0.057 mg/L/d), and 2017 (0.041 mg/L/d). As concentration of SO$_4^{2-}$ at the starting point of SO$_4^{2-}$ reduction in 2014 was larger than that in 2015, 2016, and 2017, generation rate of sulfide in 2014 was also higher. After stable equilibrium of SO$_4^{2-}$ reduction was reached, SO$_4^{2-}$ concentrations kept stable in 2014 and 2015, but increased gradually in 2016 and slightly in 2017, even under anaerobic conditions. This is because SO$_4^{2-}$ can be increased due to the oxidation reaction of sulfur under anaerobic conditions. This reaction could relate to methane fermentation - an anaerobic reductive half-reaction might shift from sulfuric acid reduction to methane fermentation as the next step. In 2016 and 2017, the reductive state periods of the sediment surface were longer than those in 2014 and 2015 so that methane fermentation could occur because of the progression of anaerobic respiration.

In all four years, NH$_4$-N increased concurrently at the time when denitrification completed. It is known that the increase in NH$_4$-N in anaerobic conditions is caused by the separation of ammonia from organic matter connected with anaerobic respiration. Therefore, iron reduction has a stronger impact on the increase in NH$_4$-N than denitrification. For this reason, the redox state of the sediment surface would affect the elution of NH$_4$-N as well as PO$_4$-P. As a result, NH$_4$-N increased as a linear line during the observed time in 2014 and 2015, while NH$_4$-N increased linearly until October in 2016 and mid-September in 2017, then remained constant. However, the rate of increase in NH$_4$-N showed a larger gradient in both 2016 (0.019 mg/L/d) and 2017 (0.022 mg/L/d) than that in 2014 (0.0101 mg/L/d) and 2015 (0.015 mg/L/d). In addition, NH$_4$-N has a strong correlation with E254, which can be an indicator of humic acid in the environment, as shown in Tables 1, 2, 3, and 4. High correlation between NH$_4$-N and E254 suggests that dissolved organic matter from anaerobic organic matter decomposition in the sediment could be eluted concurrently with NH$_4$-N. The anoxic water around the bottom could cause the release of oxidizing ions such as Fe$^{2+}$ and sulfide, as well as in dissolved organic matter, which could easily and instantly utilize dissolved oxygen. As the reductive state of the sediment surface existed for a long time (including the winter season), a quick recovery from the aerobic state near the sediment would make formation of the oxidation layer difficult, even if water temperature has a uniform distribution due to vertical mixing in the reservoir, and DO could be easily transferred downward.

| Table 1: Correlation matrix of NH$_4$-N, PO$_4$-P, and DOC at 8 m in 2014 |
|---------------------|--------|--------|--------|
| NH$_4$-N            | 1.00   |        |        |
| PO$_4$-P            | 0.96   | 1.00   |        |
| DOC                 | 0.94   | 0.91   | 1.00   |

| Table 2: Correlation matrix of NH$_4$-N, PO$_4$-P, TFe, E254, and DOC at 8 m in 2015 |
|---------------------|--------|--------|--------|--------|
| NH$_4$-N            | 1.00   |        |        |
| PO$_4$-P            | 0.91   | 1.00   |        |
| TFe                 | 0.94   | 0.94   | 1.00   |
| E254                | 0.83   | 0.70   | 0.81   | 1.00   |
| DOC                 | 0.86   | 0.73   | 0.81   | 0.76   | 1.00   |

| Table 3: Correlation matrix of NH$_4$-N, PO$_4$-P, TFe, E254, and DOC at 8 m in 2016 |
|---------------------|--------|--------|--------|--------|
| NH$_4$-N            | 1.00   |        |        |
| PO$_4$-P            | 0.98   | 1.00   |        |
| TFe                 | 0.93   | 0.92   | 1.00   |
| E254                | 0.91   | 0.91   | 0.81   | 1.00   |
| DOC                 | 0.93   | 0.90   | 0.87   | 0.89   | 1.00   |

| Table 4: Correlation matrix of NH$_4$-N, PO$_4$-P, TFe, E254, and DOC at 8 m in 2017 |
|---------------------|--------|--------|--------|--------|
| NH$_4$-N            | 1.00   |        |        |
| PO$_4$-P            | 0.87   | 1.00   |        |
| TFe                 | 0.89   | 0.93   | 1.00   |
| E254                | 0.87   | 0.87   | 0.91   | 1.00   |
| DOC                 | 0.76   | 0.81   | 0.80   | 0.88   | 1.00   |
4 Conclusions
In this study, we aimed to evaluate the impacts of thermal stratification in a closed water body on the water quality dynamics. The temporal changes of nitrogen, phosphorus, and sulfide were measured with water quality monitoring for four years in an organically polluted reservoir where an anaerobic state persisted near the bottom sediment for over six months.

The significant findings from this study are summarized here. First, the denitrification reaction, an essential anaerobic reduction reaction which causes decreases in NO₃⁻-N, occurs when DO = 0. Second, both iron and SO₄²⁻ reduction occurred at the same time when NO₃⁻-N = 0 and DO = 0. Third, iron reduction was regarded as the major cause of the elution of PO₄³⁻-P, and it had a stronger impact on the elution of NH₄⁺-N from the bottom mud than denitrification. Fourth, the dissolved organic matter represented by E254 was released from the bottom sediment along with NH₄⁺-N through anaerobic decomposition of organic matter in the sediment. Fifth, sulfide started to increase because of SO₄²⁻ reducing bacteria when NO₃⁻-N was zero. The increase of sulfide to its maximum value was modeled as a regression line, and the amount of sulfide generation was dependent on SO₄²⁻ concentration in the water column.

Furthermore, the redox state of the bottom sediment surface at the onset of anoxification (due to thermal stratification) had a strong influence on water quality dynamics, caused by biochemical reduction reactions in the bottom water, near the bottom bed. The reductive state not only promoted the occurrence of denitrification, iron reduction, and SO₄²⁻ reduction, but also increased the rate of change in concentrations of NO₃⁻-N, NH₄⁺-N, and PO₄³⁻-P compared to the oxidative state. During the oxidative state of the sediment surface, the activities of microorganisms are suppressed and reduction reactions are delayed under anaerobic conditions. In 2016 and 2017, the strong reductive state of sediment lasted for a long period under anoxic water, leading to a shift from SO₄²⁻ reduction to methane fermentation as a progression of the anaerobic reductive reaction. As a future prospect, the findings obtained from the study could provide useful information for improving water quality models predicting the internal loadings of nitrogen, phosphorus, and sulfide.

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