## 不忍池の環境分析

---- 2022 年 6 月~ 12 月の化学組成及び酸化還元条件の変化----

Environmental analysis of Shinobazu Pond water in Tokyo
—Changing of chemical characteristics and redox condition From
June to December 2022—

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#### Abstract

Fixed-point observation and chemical analysis of "Boat Pond" in Shinobazu Pond, on the southern edge of Ueno Park in the Taito Ward of Metropolitan Tokyo, was performed to clarify the changing mechanisms of chemical composition and redox status. Owing to the reproduction and extinction of phytoplankton (blue-green algae), the color of Shinobazu Pond turns green during summer, then brown in other seasons. Increasing and decreasing phosphorus (P) and nitrate-nitrogen (NO<sub>3</sub>) concentrations had a strong relationship with the growth and death of phytoplankton, which contribute to changes in redox conditions. This is especially true for the fall season when reducing conditions get induced after excessive phytoplankton growth, and P concentration increases at a fast rate. In order to prevent phytoplankton growth in the urban park pond which is thought to cause landscape deterioration and offensive odor, among others, keeping oxidative conditions by aeration during fall to winter seasons may be effective.

Key words: phosphorus, nitrate-nitrogen, park pond, shinobazu pond.

## 1. Introduction

Shinobazu Pond, an urban park pond in central Tokyo, is noted as a popular sightseeing spot that was often quoted in some famous novels and featured in drawings in Japan. Shinobazu Pond is composed of three ponds: "Hasuike," which is famous for many lotus flowers, "Boat Pond," which has many boats for tourists, and "Unoike," which exclusively belongs to Ueno Zoological Gardens. This area is always visited by many tourists all year round. However, the water quality of the pond has recently been worsening owing to eutrophication, and the pond water has been dominated by phytoplankton (blue-green algae), causing water quality problems, such as landscape deterioration and offensive odor.

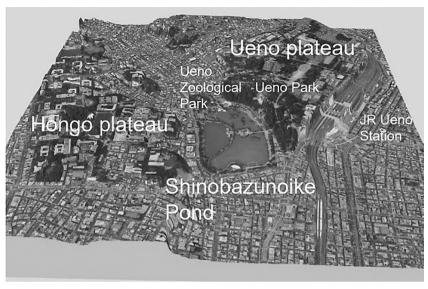
There were some investigative reports about the urban park pond. Yamagishi (2015) showed effective measures for water quality improvement in a eutrophic pond of the urban park. Yohioka et al., (2012) discussed about the evaluation of reclaimed water introduction for water quality improvement of the Edo Castle Outer Moat. Yamagishi et al., (2015) showed environmental factors influencing the occurrence of cyanobacterial blooms in a eutrophic pond in the urban park. Shinohara and Furusato (2017) showed reviews of phosphorus biogeochemistry in lakes.

In this study, chemical analysis data of Shinobazu Pond from June 1 to December 1, 2022 were shown and checked to clarify the changing mechanisms of chemical composition, especially for nitrate-nitrogen and phosphorus, and redox status. Moreover, future tasks for preserving the good condition of the pond were discussed.

## 2. Brief summary of Shinobazu Pond

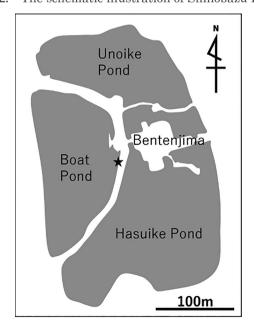
Shinobazu Pond is located on the southern edge of Ueno Park in the Taito Ward of Metropolitan Tokyo (Fig.1). In the past, it was located in an opening between the Ueno Plateau and Hongo Plateau, along the old Shakujii River. The altitude of the pond was over 10 m lower than those of these plateaus and Kanda Mountain in the south. In the Jomon era, the area around the pond was an estuary area of Tokyo Bay. Then, the pond was created by the backward movement of the coastline with marine regression. There is no river flowing into or out of the pond.

Fig. 1 Three-dimensional map around Shinobazu Pond.



The girth distance of Shinobazu Pond is about 2 km, and the whole area is roughly 110,000 m<sup>2</sup>. Nakajima Island is at the center of the pond, and there are three ponds (Hasuike, Boat Ike, Unoike) that were divided by paths to the island (Fig. 2).

Fig. 2. The schematic illustration of Shinobazu Pond.



The main water sources of Shinobazu Pond are the artificial drawing water from the underground of the JR Ueno and Keisei Ueno stations nearby, as well as a small amount of natural underground water. The water purification system, such as the aeration fountain pump system and biological acidic membrane system were introduced by the Tokyo metropolitan government's construction bureau in 1990.

## 3. Methods

#### 3. 1 Methods of sampling pond water and collection date

The sampling point is represented by the star mark ( \*\ ) in Fig. 2. Air and pond water temperatures were measured using a digital thermometer. The surface water at a distance of 50 cm from the edge of the pond at the star mark was collected using original water-collecting equipment which was washed with pond water at least thrice. Collected water was sealed in a 500 mL plastic bottle which was washed with pond water over three times, then quickly returned to the laboratory and stored in the refrigerator until the middle of December 2022.

Pond water samples were collected at around 10 AM on June 1, 8, 14, 22, and 29, July 6, 13, 20, and 27, August 12, 19, 24, and 31, September 7, 14, 22, and 28, October 5, 12, 9, and 2, November 2, 9, 17, and 24, and December 1.

## 3. 2 Analysis items and methods

Fixed-point pond observation was performed by taking photographs, and measurements of air and pond water temperatures were done at the sampling point in Fig. 2. The direction of taking photographs was toward the southwest, and sampling time was at around 10 AM each time.

Chemical analyses of pH, electric conductivity (EC), dissolved oxygen (DO), chemical oxide demand (COD), nitrate-nitrogen (NO<sub>3</sub>·), and phosphorus (P) were done after all samples were collected in the middle of December 2022. Cold storage samples were adjusted at 25°C in the water bath and filtrated by a 5A filter paper. The average value of three analyses of each method was used in this study.

The pH value of each sample was measured by the mulch water quality checker WA-

2017SD with the pH electrode PE-03K7 made by Satoshoji Co., Ltd.

The EC values were measured by WA-2017SD with the electric conductivity meter CD-4307SDM made by Satoshoji Co., Ltd.

The DO values (mg/L) were measured by WA-2017SD with the dissolved oxygen WA-2017SD-DO made by Satoshoji Co., Ltd.

COD analysis was done using the back titration technique with a 5 mmol/L KMnO<sub>4</sub> solution with a 6M H<sub>2</sub>SO<sub>4</sub> solution in the previously treated river water by a 12.5 mmol/L KMnO<sub>4</sub> solution (Ando *et al.*, 2021, 2022).

The NO<sub>3</sub> concentration of each sample was measured by the potable ion meter HM-40P with nitrogen ion combined with the electrode N-2031 made by DKK-TOA Co., Ltd. The analysis data were obtained by a three-sample standard addition method with the highest quality sodium nitrate reagents.

The P concentration of each sample was measured by the molybdenum blue method with sodium molybdate and ascorbic acid. The ultraviolet and visible radiation spectrophotometer UV-1280 by Shimadzu Co., Ltd. was used in absorbance determination. The wavelength was set at 880 nm, and analysis data were obtained by the threesample standard addition method.

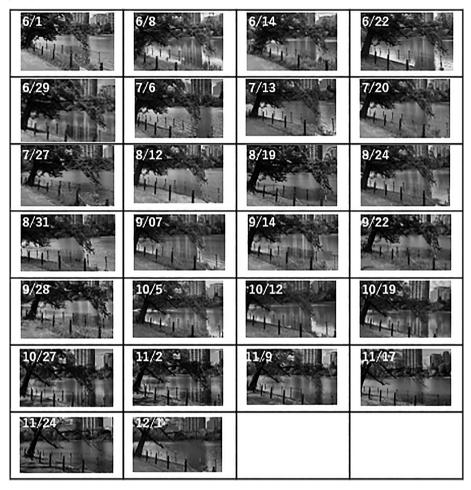
## 4. Results

## Fixed-point observation results

Fixed-point observation results are shown in Fig. 3. The sampling dates are shown on the upper-left side of each photo. The surface color of the pond was green during June, then changed to dark green until the end of August. Then, the surface color of the pond gradually changed to brown from September, then it became deep brown in color starting in October.\*

\* It is impossible for readers who are only to see black and white version of Fig.3 to understand of the description. Please contact the following address, if you need colored version's Fig.3. [author's e-mail: ando@atomi.ac.jp]

Fig. 3. Fixed-point pond observation by taking photographs was performed at the sampling point (★) in Fig. 2. The direction of taking photographs was toward the southwest, and sampling time was at around 10 AM each time.



## 4. 2 Temperatures, EC, and pH measurements

Air and pond water temperatures are shown in Fig. 4, in which the horizontal line shows the sampling date and the vertical line shows the temperatures. The trend of air and pond water temperatures was roughly the same during the investigation period except from the end of June to early September when air temperature was a little higher than that in pond water. Since there was no water inflow in Shinobazu Pond, EC values were limited narrowly  $(0.24\sim0.32~\text{mS/cm})$  and the pH value limited the narrow pH  $(7\sim8)$ . EC showed a gradually decreasing trend and pH showed a gradually increasing trend toward August.

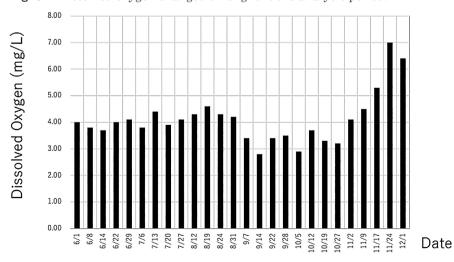
Fig. 4. Air and water temperatures changed throughout the analysis period. The solid line represents air temperature, and the dotted line represents water temperature.



## 4. 3 DO assay result

The DO trend is shown in Fig. 5, in which the horizontal line shows the sampling date and the vertical line shows the DO value. Although the DO values from the middle of August to the end of October showed a decreasing trend, other analyzed periods exhibited nearly constant values.

Fig. 5. Dissolved oxygen changed throughout the analysis period.



## 4. 4 COD assay result

The COD trend is shown in Fig. 6, in which the horizontal line shows the sampling date and the vertical line shows the COD value. The whole trend of COD showed a gradually increasing trend toward August, where it showed the maximum value, then gradually decreased toward December, harmonizing with the temperature trend. A temporally decreasing trend was observed during the rainy season from June to July, the beginning of September, and the end of November.

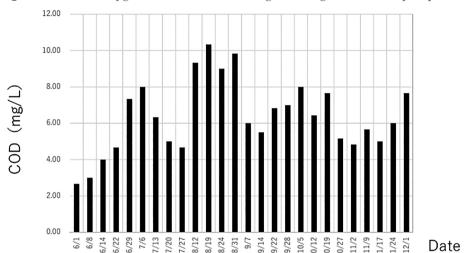


Fig. 6. Chemical oxygen demand (COD) changed throughout the analysis period.

## 4.5 NO<sub>3</sub> assay result

The NO<sub>3</sub> trend is shown in Fig. 7, of which the horizontal line shows the sampling date and the vertical line shows the NO<sub>3</sub> concentration (mg/L). Though the NO<sub>3</sub> concentration varied widely, it showed a gradually increasing trend toward July, then gradually decreasing toward the end of August, and remaining constant (0.5 mg/L) starting October. In particular, high concentrations were observed on June 27 and September 22, with a lot of precipitation with high nitrogen oxide concentrations.

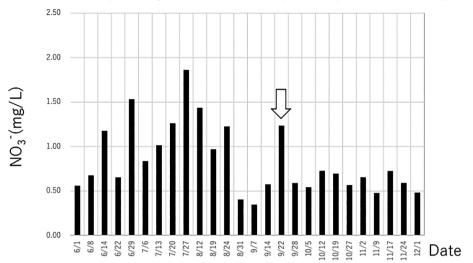


Fig. 7. Nitrate-nitrogen (NO<sub>3</sub>) concentration changed throughout the analysis period.

#### 4.6 Passay result

The P trend is shown in Fig. 8, in which the horizontal line shows the sampling date and the vertical line shows the P concentration (mg/L) . The whole trend of the P concentration exhibited values under 1.0 mg/L. A temporary increase was observed on August 24, August 14, and September 22, then the trend exhibited a constant value (1.0 mg/L) at the end of September and beyond. At the same time, the surface color of the pond turned brown homogeneously.

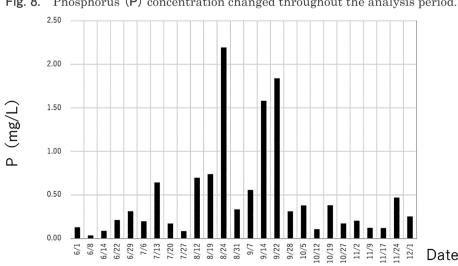


Fig. 8. Phosphorus (P) concentration changed throughout the analysis period.

## 5. Discussion

## 5. 1 Fixed-point observation results and the origin of P and NO<sub>3</sub>

The surface color of the pond was brown throughout winter and early spring. During summer, the color turned green. The main reason for this change was thought to be the reproduction of phytoplankton (blue-green algae) that harmonized with the increase in pond water temperatures. Changing the color from green to brown meant the phytoplankton extinction, leading to their deposition at the bottom of the pond. The DO value decreasing from the end of August (Fig. 5) meant that the dysoxic environment may be generated by the excessive growth of phytoplankton in the pond water. This is the main reason for the extinction of phytoplankton and the change in the surface color of the pond afterward.

Phytoplankton growth essentially requires P and N in the pond water. These elements are essential for maintaining the food chain in the pond. Meanwhile, the enrichment of these elements caused pond eutrophication. The mass propagation of phytoplankton caused the dysoxic environment, then the mass extinction happened shortly after. The concentrations of P and  $NO_3$  are crucial for the pond ecosystem. Furthermore, phytoplankton growth and death due to the changing concentration of these two elements and the increasing pond temperature causes regional environmental issues, such as odor problems and the formation of chlorine byproducts due to sterilization.

Generally, P in the pond was thought to be from the discharged wastewater from factories, homes, and farmlands through the river connected with the pond. As there is no influent river in the Shinobazu Pond, and it is located in the city area, P was thought to have originated from the distributed land, then was enriched by various photosynthetic bacterium in the pond water.

N in Shinobazu Pond was thought to be from the intake of N in the air by living microbes, such as the phytoplankton in the pond, and the addition from precipitation of which high concentrations of nitrogen oxide from city air. As for precipitation data from the Meteorological Office, three days before September 22, the total precipitation reached 68.5 mm. The reason for the high  $NO_3$  concentration (1.24 mg/L) of pond water on September 22 was thought to be the heavy precipitation in the area (arrow in Fig. 7).

## 5. 2 The relationship between chemical composition and redox conditions

The NO<sub>3</sub> concentration increased from June and late August due to the growth of phytoplankton and heavy precipitation. The P concentration increased from mid-August to mid-September, about one month later than the change in the NO<sub>3</sub> concentration. Phytoplankton proliferated from June to August, in harmony with the rising temperature. This trend implies a strong relationship with the redox conditions due to phytoplankton growth and extinction in the pond water. The more phytoplankton grew, the more the oxygen shortage of the pond water happened. Afterward, phytoplankton went extinct, leading to the accumulation of P and N at the bottom of the pond. In particular, P was taken in as organic P (Org-P) and inorganic P combined with iron in the mud (Fe-P). This means that phytoplankton removed P and N from the pond water.

When there was enough NO<sub>3</sub> in the pond, NO<sub>3</sub> was easier to reduce than Org-P and Fe-P (Grüneberg *et al.*, 2015), Meanwhile, when NO<sub>3</sub> shortage occurred, P was released easily from Org-P and Fe-P. The analytical results of NO<sub>3</sub> concentration decreased until the end of August, and P concentration increased after the end of August (Fig. 8). In particular, for P concentration, when pond water became reduced with low NO<sub>3</sub> concentrations, P dissolved into the pond water from Org-P and Fe-P. When P was released into the pond water, phytoplankton would have grown again. However, the pond water was already saturated with phytoplankton and became reduced, making it difficult to grow phytoplankton. When the environment of the pond weakened the reduced conditions after the end of September (fall season), P was fixed as Org-P and Fe-P again and kept at constantly low concentrations from then on.

These trends show the strong relationship between P and NO<sub>3</sub> concentrations and the redox state of pond water.

# 5. 3 Preventing the growth of phytoplankton, and future tasks for preserving the good condition

When the chemical conditions of the pond water became reducing, NO<sub>3</sub> tended to be reduced and released easily into the pond, and then P would release from Org-P and Fe-P subsequently. Therefore, preventing poor oxygen status (reduction condition) is essential to preserve the good condition of the pond. For this purpose, aeration is essential for stopping

the reducing conditions and the dissolution of P from the bottom material. Naturally, blowing wind on the surface of the pond is effective for preventing the reducing conditions of the pond water. As Boat Pond was shallow (about 50 cm deep), aeration and agitation for feeding oxygen to the bottom of the pond would be effective for preventing the pond water redox status.

It is essential to clarify the chemical characteristics of P and N to prevent environmental problems in the pond. For that purpose, it will be necessary to determine in detail the chemical species of nitrogen using the other chemical analysis methods of this study with high accuracy, such as the Kjeldahl method and Dumas' method. Furthermore, the redox status of the pond should be checked with shorter periods not only on the surface but also at the bottom of the pond.

#### 6. Conclusion

Fixed-point observation and chemical analysis of the "Boat Pond" in Shinobazu Pond, on the southern edge of Ueno Park in the Taito Ward of Metropolitan Tokyo, was performed to clarify the changing mechanisms of chemical composition and redox status.

Fixed-point observation results showed that the color of Shinobazu Pond turned green in summer, then brown in other seasons. The main reason for this was the reproduction of phytoplankton (blue-green algae) harmonized with the rising temperature of pond water in summer. Then, the phytoplankton became extinct and accumulated at the bottom of the pond, which became reducing, and the temperature decreased in fall and beyond.

Increasing and decreasing P and NO<sub>3</sub> concentrations were strongly related to the growth and death of phytoplankton, which contributed to the change in redox conditions. The increase and decreasing trend of NO<sub>3</sub> and P concentrations showed slight deference. P concentration increased from mid-August to mid-September (fall season) about one month later than the change in the NO<sub>3</sub> concentration.

When there was enough P and NO<sub>3</sub> in the pond, the growing phytoplankton ingested these elements and harmonized with the temperature rising. Excess phytoplankton growth caused oxygen-poor conditions, leading to phytoplankton decline. This means that P and NO<sub>3</sub> were removed from the pond, and the water conditions became reducing. Under this condition, P could be released from organic and inorganic P to the pond. Therefore, the change to reducing

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conditions by phytoplankton growth would cause increasing P concentrations during the fall season.

In order to prevent phytoplankton growth in the urban park pond which is thought to cause the deterioration of the landscape and the offensive odor, among others, keeping oxidative conditions by aeration during fall to winter may be effective.

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