Study of Sumida River, Part 2: Analysis of Identification of COD and EC Characteristics in Fall 2021

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Abstract

The Sumida River streamside makes up a part of the Kitasenjyu campus at Teikyo University of Science (TUS). It is essential for university students and faculty members to learn its environmental and chemical characteristics from the viewpoint of environmental education. A water analysis of the Sumida River was conducted in the fall season (Fall 2021) at 10 locations around the Kitasenjyu campus, along with a 24-hour continuous survey in front of the No. 7 building. The fall analysis was performed using the same procedure as the previous analysis in spring (Spring 2021). The conclusions we reached are as follows: 1) Discharge water from the Mikawagima wastewater purification facility (WPF) was found to be the primary source of chemical contamination in the study area, causing an increase in COD (chemical oxygen demand). Upstream, Miyagi WPF was presumed to be the primary source of the chemical contamination. 2) The discharged high COD water from these WPFs was diffused by the tidal movement of Tokyo Bay and then was homogenized in the study area. 3) From our survey on the streaming motion of the Sumida River and public COD data from the Tokyo metropolitan government, we redefined the boundary between high and low COD zones set under the Agastuma Bridge. 4) Urethane foam with photocatalysis material of TiO_2 was synthesized as a novel wastewater treatment material. As it displayed good decomposition characteristics of organic material in tested water, porous and robust materials with TiO_2 for continuous outdoor use should be investigated to achieve practical applications shortly.

Keywords: COD; EC; Sumida River; environmental education, TiO_2

I. Introduction

The Sumida River consists of part of Teikyo University of Science (TUS) (Fig.1a). However, an unpleasant odor and floating garbage have created an unpleasant environment for residents in the vicinity. Urban rivers serve as symbolic places of leisure and relaxation and have become tools for teaching people the importance of environmental conservation. In particular, for teacher candidate students in our department, knowledge of the surrounding environment is critical for educating their future students.

We previously investigated the chemical conditions of the water in Sumida River as part of our "Spring analysis, 2021," [1] wherein we analyzed water from 10 locations (#1–#10 in Fig.1b) around the TUS campus, performing a 24-hour continuous sampling in front of building No.7 of TUS (#3). The main results were summarized as follows: 1) The Sumida River around TUS was affected by tidal movement, and the river water in our research area (from Otakebashi Bridge to Senju-Ohashi Bridge) was slightly affected by seawater from Tokyo Bay. 2) Significant chemical contaminant sources in the investigated area were thought to be the Miyagi wastewater purification facility (WPF) and the Mikawajima WPF at the upstream and downstream sides of TUS, respectively. 3) We presume a two-fraction zone in the Sumida River from our analytical results and public data [2], including a "high COD zone," with an upstream stagnant zone above the Shirahige Bridge, and a "low COD zone" with a downstream flush zone under the Shirahige Bridge.

In this study, the fall season water analysis of the Sumida River (Fall 2021) was performed at the exact 10 locations (#1–#10) around TUS to confirm conclusion 1 of the previous study of the 24-hour continuous analysis in front of the No.7 building at TUS (#3) was performed to confirm conclusion 2. As for conclusion 3, the boundaries of high and low COD zones were redefined from our surveyed data of flow direction and speed after 24 h continuous sampling. Furthermore, a new type of water-purifying material with photosynthetic features made from TiO_2 was identified for further study.

II. Method

1. Methods of Collecting River Water

The river water was collected using a self-made water sampler made of rope and a 5 L bucket attached to a river wall. The water sampler and a 1 L plastic bottle for transportation were washed using the river water, and then the bottle was filled with the river water collected using the bucket. The parameters of the water surface and surrounding environment (air temperature, river water temperature, flow direction, and flow velocity) were measured simultaneously.

a Sampling at 10 Locations

Ten samples were collected from 10 different locations along the river, from the Otakebashi Bridge to the Senju-Ohashi Bridge (Fig.1 b). The distances between the uppermost and the lowest sampling points were over 2.5 km. A sampling at the lowest tide was conducted at 10:43 on September 6, 2021 (during a cloudy day) to prevent the chemicals from affecting the seawater of Tokyo Bay. The average air and river water temperatures were 22°C and 21°C, respectively (See the collected data in Appendix 1).

b Continuous Sampling for 24 hours at Location #3

Continuous sampling was performed for 24 hours at Location #3 in front of the No.7 building at TUS (Fig.1b). Each sample was collected at two-hour intervals from 15:30, September 8 until 13:30, September 9, 2021. Air and river water temperatures are presented in Appendix 2. During the nighttime, the flow direction and velocity were measured at Location #3 using headlights. The Sumida River flowed back twice during the sampling period when the low tide changed to high tide.

2. Analytical Procedures

The sampled river water was filtered using a 5A filter attached to a Buchner funnel with a vacuum system. After adjusting the temperature to 25 ±2°C using a water bath, portable analytical meters were used to measure pH (Lutron Multi Water Quality Checker PH-230SD with Lutron PH electrode PE-11) and EC (Lutron Multi Water Quality Checker WA-

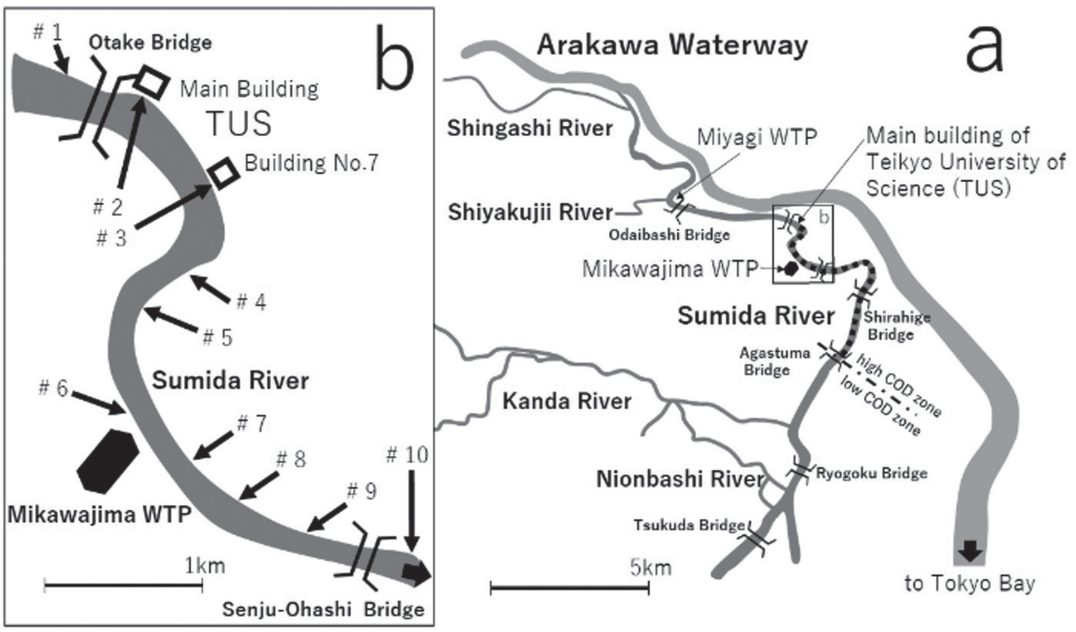

Fig.1 Schematic map shows the study area with the rivers, wastewater purification facilities (WPF), and bridges. Locations of 10 sampling points are shown (#1-#10). Continuous sampling for 24 h was performed at Location #3 in front of the No.7 building at TUS.

2017SD with Lutron Conductivity Probe CDPB-03).

COD analysis was carried out using the official method based on JIS K 0102[3)] (Fig.2) with the formation below.

$$COD = (A-B) \times F \times 1000/V \times 0.2.$$

A: titer amount of 5 mmol/L of $KMnO_4$aq
B: blank determination amount of 5 mmol/L of $KMnO_4$aq
F: factor value of 5 mmol/L of $KMnO_4$aq
V: sample amount (mL)
0.2: oxygen amount equivalent to 1 mL of $KMnO_4$aq

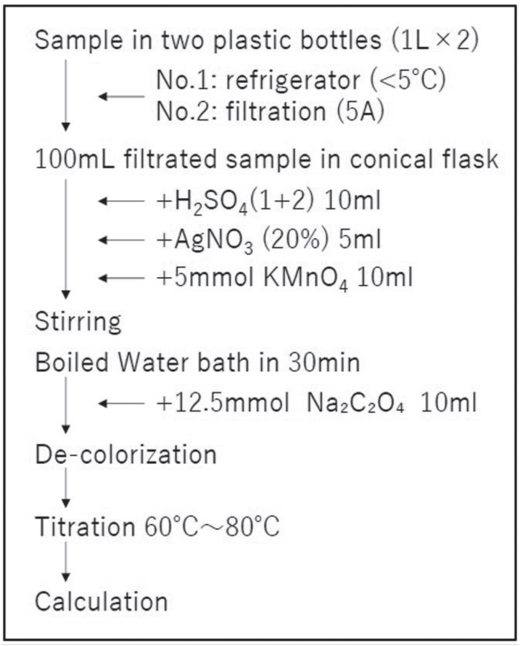

Fig.2 Analytical procedures of COD based on JIS K 0102. H_2SO_4(1+2): one liter of concentrated sulfuric acid with two liters of water was diluted to 6 mol/L.

3. Referenced public data

The Tokyo Metropolitan Government releases water quality survey data from major rivers, lakes, and marine areas to the public annually[2)]. The monthly chemical composition of the river water in the Sumida River was examined under five bridges: Odaibashi, Shirahigebashi, Agastumabashi, Riyogokubashi, and Tukudaohashi. The results were listed on the homepage of the Tokyo Metropolitan Government. The observed COD trend from August to October 2020 is shown in Fig.3 (the horizontal axis is set as the distance from the Odaibashi Bridge).

The Tokyo Metropolitan Government Bureau of Sewerage shows the total amount of influent and effluent water from river water purification facilities (WPF) to the public in the Tokyo Metropolitan Government's Homepage[4)]. The WPF facilities around our survey area were Ukima, Miyagi, and Mikawajima. The total amounts of influent and effluent water from these facilities are shown in Table 1.

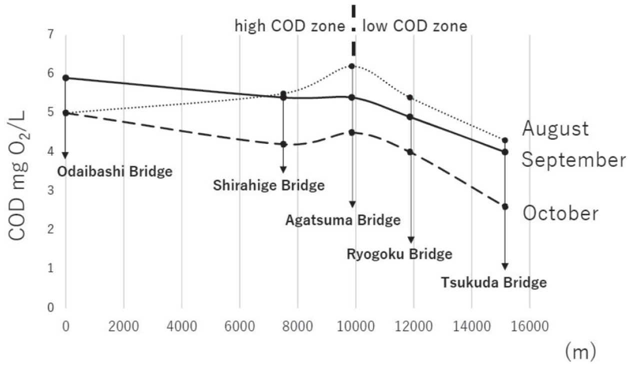

Fig.3 COD trend based of regular surveillance by Tokyo Metropolitan Government from August to October 2020. Horizontal axis showed the sampling point's distance under each bridge from Odaibashi Bridge.

Table 1 Input, output waste water's COD concentration (mgO_2/L), and final amount of effluent water from each wastewater purification facility (WPF) around TUS referenced from Tokyo Metropolitan Government Bureau of Sewerage in September 2020.

	Influent (mgO_2/L)	Effluent (mgO_2/L)	Total effluent volume advanced treatment primary treatment ($1000m^3$/day)
Ukima WPF	78	7	113 8
Miyagi WPF (Shiyakujii series)	70	9 (west)	164 35
Mikawajima WPF (Oku series)	80	11 (general)	366 79

III. Results and Discussion

1. EC and COD data comparison to the "Spring analysis, 2021"

a Analysis Results from 10 locations

EC and COD were analyzed at 10 locations (Fig.1b) and yielded the following results:

1) EC data (Fig.4a) exhibited an increasing trend from upstream to downstream due to the distance from Tokyo Bay. This trend indicated that river water in this area was affected by the salinity of seawater from Tokyo Bay by tidal movement, which is in agreement with previous studies
2) Only Sample #6, collected close to the Mikawagima WPF, displayed a significantly higher value than expected from the increasing trend. This can be explained by the effect of chlorine ions from the hypochlorite treatment of the Mikawagima WPF. Although people may believe that river flows towards Tokyo Bay during the low tidal period, we concluded that the river flow led to mixing, diffusion, and homogenization in this area.
3) The COD trend (Fig.4b) exhibited a homogenous trend with EC during the observation period. The highest COD value was obtained at Location #6, which was the nearest to Mikawajima WPF. This factor suggests that a significant COD source was the facility, which is also supported by the EC data.

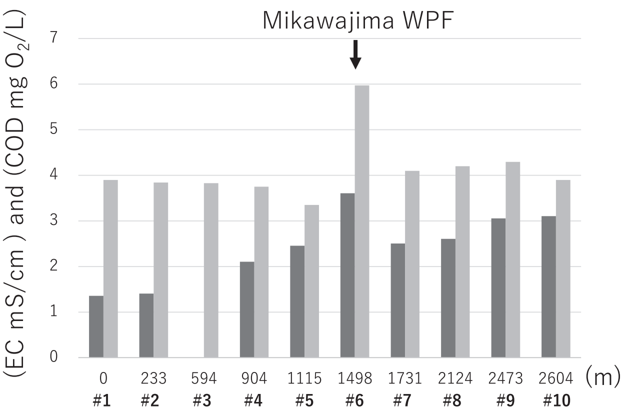

Fig.4 Ten samples analysis results of EC (grey bar) and COD (black bar). Horizontal axis showed the sampling point's distance between No.1 (base point) and No.10 shown in Fig.1b.

b Analysis Results from Continuous Sampling over 24 hours at Location #3

The EC(b) and COD(c) analytical results with the tidal movement(a) of Tokyo Bay during continuous sampling are shown in Fig.5.

We observed similar trends between tidal movement and EC data during a 24-hour period. This indicates that the Sumida River is affected by tidal movement. Two tidal peaks were observed during the survey period. The second tidal peak occurred at 5:50, September 9, and the highest EC value excessed 16 mS/cm, which is approximately 1 wt% of NaCl concentration based on our calibration curve method. When ocean water went upstream of the river, the EC data had peaks of less than one-third of fresh seawater. These results show that although the river water in this area was affected by tidal movement, and that water was only circulated within this area.

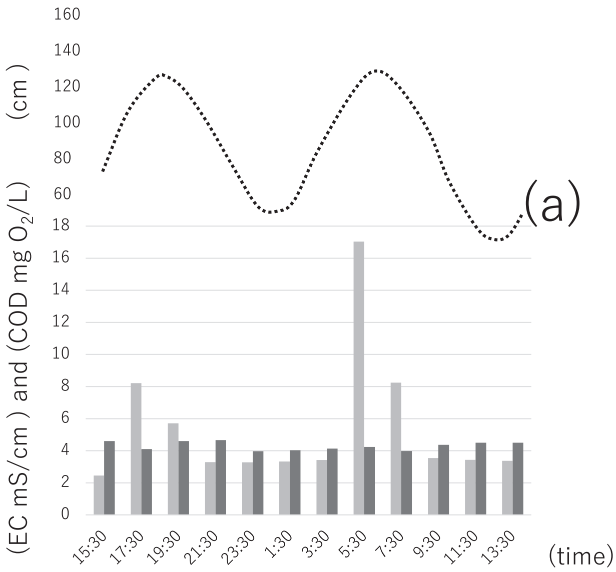

Fig.5 Tidal movement of Tokyo bay (a) and 24 hours continuous sampling analysis results of EC (grey bar) and COD (black bar).

In contrast, the COD trend exhibited a homogenous trend during the observation period. This area's river water might have stagnated, undergone mixing and diffusion due to tidal movement, and homogenized in this area. This homogenized trend was consistent with the analysis results from all 10 locations.

2. Boundary redefinition between high COD and low COD zone

Based on our "Spring analysis, 2021" and public water quality data[3] from the Tokyo Metropolitan Government, we proposed a two-fraction model of the Sumida River: "the high COD zone" where upstream and stagnant zones were observed above the Shirahige Bridge, and "the low COD zone" downstream of

Shirahige Bridge.

For our "Fall analysis, 2021," we redefined this boundary based on our surveyed data of flow direction and speed at the 24-hour continuous survey's point at Location #3 (See Appendix 2) as well as the public data from the Tokyo Metropolitan Government. The travel distance of a part of the river water in front of Location #3 was calculated using the flow direction and speed data. For example, the flow direction and speed at 3:30 A.M. on September 9, shown in Appendix 2, moved upstream at 19.3 m/min.

The travel distance of river water at Location #3 was calculated to be 2316 m from downstream. At 5:30 on September 9, the surveyed data shows that the water moved 9.0 m/min upstream. Under this condition, river water at Location #3 was calculated to be 1080 m from downstream. The total travel distance of river water was calculated as 3396 m from downstream over 4 h. We guessed that the high COD water's travel area from downstream to the Location #3 was the area displayed by dotted line in Fig.1 from our observation of river water's direction and speed, and public data of Tokyo metropolitan Government survey. In this area, river water could only circulate backward and forward, strongly affecting a large volume of high COD discharged water originating from water treatment facilities and being slightly affected by seawater from Tokyo Bay. Therefore, we redefined the boundary between the high and low COD zones under Agastuma Bridge.

3. Trial for waste water treatment with purifying material with TiO_2 photocatalyst

Since the Sumida River high COD zone might be created by water that circulated backward and forward movement within the area, river water quality is mainly dependent on WPS's water purification technique. It is necessary to continue to ask the Tokyo metropolitan government to adopt more efficient wastewater purification techniques to create a comfortable environment around the river. It is also crucial for raising the environmental awareness of neighbors, university students, and staff.

To contribute to environmental improvement as a researcher and students concerned with the Sumida River, we tried to create a new wastewater purification material for its environmental improvement. There was some research on the purification of urban river water by purifying material [5), 6)].

Our method was used flexible urethane foam with a TiO_2 photocatalyst. This material was selected because it quickly (within a few minutes) synthesizes and is readily deformable. The trial material was synthesized using urethane liquid at a specific rate of anatase-type powdered TiO_2 reagent (3:1). As shown in the sample photographs in Fig.6, TiO_2 urethane foam (a: TUF) had a white color with a disordered form size; in contrast, regular urethane foam (b: NUF) was transparent with an ordered form size. A simple adsorption experiment with methylene blue liquid (1g/L) was performed to confirm its organic material decomposition ability. Three 200 ml methylene blue liquid samples in a 300 ml size beaker were prepared for the outdoor decomposition experiment using direct sunlight. Beaker A was prepared for the blank test, Beaker B was added to 1g of powdered anatase-type TiO_2, and Beaker C was added to TUF, which was adjusted to the same TiO_2 content rate as that of Beaker B. As TUF had floatable and porous characteristics, it was readily adsorbed onto organic material and exposed to direct sunlight near the liquid surface. The outdoor experiment was continued from 12:00 (26.4°C) to 16:00 (26.0°C) with 1 ml sampling for absorption spectrochemical analysis (PD-303 by APEL Ltd.) taken each hour on August 30, 2021.

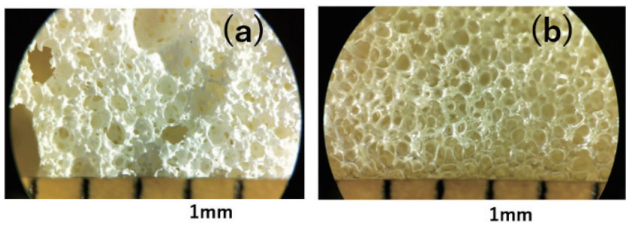

Fig.6 Photos of flexible urethane foam with TiO_2 photocatalyst (a: TUF) and pure urethane foam (b: NUF). Scale: width = 1 mm.

The experimental results for adsorption are shown in Fig.7. The vertical axis shows the adsorption rate, which was divided by the absorbance value of Beaker A. Two similar decreasing tendencies were observed during the experiment. This result showed that TUF showed the same decomposition characteristics for organic chemicals as powdered TiO_2. Next, our study

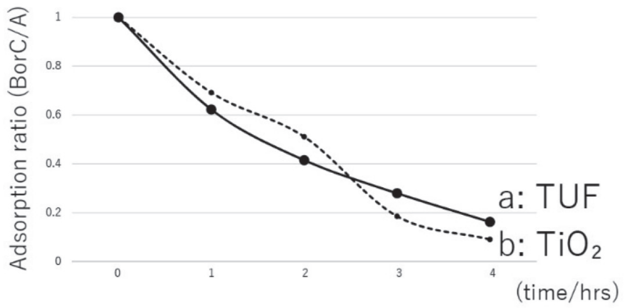

Fig.6 Adsorption experimental results. The vertical axis is adsorption rate divided by absorbance of Beaker A, shown as the rate of B/A and C/A.

will be conducted to improve material characteristics for practical use, such as durable materials with TiO_2 for continuous outdoor usage. Furthermore, suitable materials are going to be synthesized by recycling materials, such as recycled glass.

IV. Conclusion

The fall season's water in Sumida River was analyzed at 10 locations (#1~#10) and through 24h of continuous sampling at Location #3 using the same analytical conditions from "Spring analysis, 2021" to obtain the following results.

1) The discharge water of Mikawagima WPF was predicted to be the major COD source of chemical contamination in the area around TUS in the Sumida River. Upstream of the Miyagi WPF was presumed to be the significant source of chemical contamination in the area as well.
2) The discharged high COD water from these WPFs was mixed and diffused by the tidal movement of Tokyo Bay, and it was subsequently homogenized in the area.
3) From our survey of the speed and direction of the Sumida River and public COD data released by the Tokyo Metropolitan Government, we redefined the boundary between high and low COD zones under the Agastuma Bridge.
4) TiO_2 urethane foam (TUF) was synthesized as a pilot wastewater treatment material using the photocatalysis effect. As it showed good decomposition characteristics of organic materials, durable materials with TiO_2 should be examined for practical use soon.

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Appendix 1
COD and EC data of 10 locations analysis at 10:43 at September 6, 2021. Average air and river water temperature were 22°C and 21°C.

location	COD (mgO_2/L)	EC ($\mu S/cm$)
No.1	3.8	1.36
No.2	3.7	1.41
No.3	3.8	
No.4	3.7	2.11
No.5	5.9	2.46
No.6	3.3	3.61
No.7	4.2	2.51
No.8	4.1	2.61
No.9	4.3	3.06
No.10	3.9	3.11

Appendix 2
COD and EC data of 24 hours continuous sampling at September 8-9, 2021.

Sampling time	Temperature (°C)		COD (mgO_2/L)	EC ($\mu S/cm$)	Current speed (m/min)	direction
	Air	River water				
15:30	23.0	22.0	4.6	2.45	18.9	backflow
17:30	20.0	21.0	4.1	8.21	19.0	backflow
19:30	20.0	22.3	4.6	7.51	19.0	forward
21:30	20.0	21.0	4.7	3.29	19.1	forward
23:30	20.0	22.0	4.0	3.28	19.1	forward
1:30	19.5	22.0	4.0	3.33	19.2	forward
3:30	19.0	22.0	4.1	3.42	19.3	backflow
5:30	18.5	21.5	4.2	17.04	9.0	backflow
7:30	18.7	22.0	4.0	8.24	19.4	forward
9:30	19.0	21.8	4.4	3.54	19.4	forward
11:30	20.0	22.1	4.5	3.43	19.5	forward
13:30	21.8	22.4	4.5	3.37	19.6	forward