Zinc contamination in surface water of the Umeda River, Japan

P Andarani1,2*, H Alimuddin1, R Suzuki1, K Yokota1, T Inoue1

1 Department of Architecture and Civil Engineering, Toyohashi University of Technology, Toyohashi – 441-8580, Japan
2 Department of Environmental Engineering, Faculty of Engineering, Universitas Diponegoro, Semarang – 50275, Indonesia

andarani@ft.undip.ac.id

Abstract. Due to the adverse effects of zinc (Zn) on the aquatic organisms, environmental quality standards (EQS) for zinc of 0.03 mg/L in surface water has been enacted in Japan since 2003. However, "zinc elevated sites" persist, including Aichi Prefecture. This study aims to assess the spatial and temporal variability of zinc contamination for 14 months in surface water of the Umeda River, Aichi Prefecture. The water samples were analyzed using Flame Atomic Absorption Spectrometry. The zinc concentrations tended to be higher in a downstream direction. The concentration means of nine sampling stations in surface water in August 2019 to July 2020 varied from 0.011 to 0.031 mg/L. The annual mean concentration value has already exceeded the EQS. Meanwhile, the yearly concentration means of the industrial wastewater were 0.036 to 0.079 mg/L, lower than the National Effluent Standards of 2 mg/L in Japan. All sampling points had relatively high concentrations ranged from 0.021 to 0.062 mg/L in February during the winter season. The reduced precipitation causing low river discharges might consequently elevate the zinc concentrations. The total zinc load at the most downstream section was approximately 0.012 t/km²/year. According to this study, the Umeda River has been affected by anthropogenic activities.

1. Introduction

Although living organisms use zinc for metabolisms, previous studies found toxicological effects on aquatic organisms [1–3]. This issue raises concerns, particularly in European [4–6] and Asian countries [7–10]. In 2003, Japan enacted an Environmental Quality Standards (EQS) for the annual mean of zinc concentration, i.e., 0.03 mg/L, which is stricter than preceding regulation in order to protect the aquatic life. However, the zinc concentrations in surface water remain high, exceeding 0.03 mg/L in several prefectures, including Aichi Prefecture [9].

Zinc could be discharged to receiving water bodies by anthropogenic activities and natural origins. Based on the monitoring data in Japan from 1991 to 2002, the total zinc concentrations ranged from undetected to 2.9 mg/L, in which approximately 20% of the monitoring sites exceeded the EQS [9]. In 2016-2017, industrial areas contributed approximately 3,400 g/day to Aizumame River, Aichi Prefecture, which was more evident during non-irrigation period [8]. Moreover, several studies revealed that the zinc exhibited various concentrations depend on the season [4,7,11] and even during 24 hours [5,12]. It is necessary to identify the seasonal variation and the zinc concentration fluctuation in a
watershed in Japan. Therefore, this study aimed to assess the temporal and spatial variability of zinc contamination for 14 months in surface water of the Umeda River, Aichi Prefecture, Japan.

2. Methodology

2.1. Study area
This study was undertaken in the Umeda River, which flows into Mikawa bay through Toyohashi City in the Aichi Prefecture, Japan. The field surveys were carried out monthly from June 2019 to July 2020 in fine weather when there was also no precipitation on the previous day. Five sampling stations in the mainstream of Umeda River were indicated by station 1 (st. 1) to st. 5 (st. 5), as shown in figure 1. The water sampling was also taken in one tributary sampling stations located in Ochiai River (st. 31) and three stations in Sakai River (st. 41 to st. 43). The details of the surrounding land-uses of sampling stations were described in table 1.

Table 1. Description of sampling stations.

| Sampling station (st.) | Description                                      | Longitude  | Latitude  |
|-----------------------|--------------------------------------------------|------------|-----------|
| 1                     | Downstream section of Umeda River, dominated by agricultural area | 137°23'46.8" | 34°42'44.0" |
| 2                     | Residential area, near railways, highway, Zoo and Botanical Park | 137°25'32.6" | 34°43'21.3" |
| 3                     | Residential area, near railways and highway      | 137°27'21.9" | 34°43'16.8" |
| 4                     | Residential and agricultural area                | 137°28'57.2" | 34°43'22.9" |
| 5                     | Upstream section of Umeda River                  | 137°28'42.3" | 34°44'02.4" |
| 31                    | Ochiai River; Industrial area                    | 137°27'22.8" | 34°43'15.0" |
| 41                    | Sakai River; Industrial area                     | 137°28'55.2" | 34°43'20.3" |
| 42                    | Sakai River; Industrial area                     | 137°29'19.3" | 34°42'49.5" |
| 43                    | Sakai River; Agriculture and residential area    | 137°29'33.9" | 34°42'07.1" |
| WW-A                  | Point source of wastewater A (metal-based product manufacture) | 137°28'56.2" | 34°43'13.2" |
| WW-B                  | Point source of wastewater B (battery lithium manufacture) | 137°29'20.0" | 34°42'50.5" |
| WW-C                  | Point source of wastewater C (electronic product manufacture) | 137°29'20.1" | 34°42'50.7" |

2.2. Water samples treatment and river discharge measurement
In this study, water samples were taken from five mainstream stations and four samples from two tributaries, as shown in table 1. A 100-ml water sample was collected and acidified using 1.0 ml concentrated HNO₃ to preserve the metal solute. Then the water samples were stored at 4°C until zinc analysis. Meanwhile, the velocity area method was used to calculate the river discharges according to Andarani et al.(2020) [8].
2.3. Zinc analysis
A 25-ml of sub-sample was taken in a fluorine bottle then heated up on top of a hotplate with temperature set at 205°C. After cooled in a room temperature, the samples were filtered by a 0.45 μm cellulose acetate syringe filter (Advantec Co., Ltd., Japan). The total zinc concentrations were measured using a Flame Atomic Absorption Spectrometry AA-7000 (Shimadzu Corporation, Japan). The measurement was conducted three times both for samples and standard solutions. Four standard solutions, started from 0 to 0.5 mg/L, were re-measured every six samples to ensure the Quality Assurance/Quality Control.

3. Results and discussion
3.1. Spatial and temporal variation of total zinc concentrations
The total zinc concentrations in surface water of Umeda River and its tributaries for 14 months can be seen in figure 2. The means of zinc concentrations varied from 0.11 mg/L (st.5) to 0.029 mg/L (st.1) during the study period. According to the Environmental Quality Standards (EQS) in Japan, the means of total zinc concentrations were still within the permissible limit (0.030 mg/L) for 14 months. However, from August 2019 to July 2020, the annual means at st.1 (0.031) has already exceeded the EQS while the average concentrations at st.2, st.3, st.4, and st.5 were 0.029 mg/L, 0.028 mg/L, 0.023 mg/L, 0.011 mg/L, respectively. The annual zinc concentrations of st.2 and st.3 almost reached the EQS. These results indicate the necessity to identify the sources of zinc in the Umeda River watershed.

Generally, the zinc concentrations increased toward the downstream direction. The most upstream stations (st.5) exhibited low concentrations (<0.005 – 0.026 mg/L) that often could not be detected (<0.005 mg/L). The st.4 was located just before the confluence with Sakai River (st.41, st.42, and st.43). The zinc concentrations at st.4 ranged from (<0.005 to 0.062 mg/L) started to increase from October
and exceeded 0.03 mg/L in February and April 2020. An air conditioner dumped in January 2020 at the confluence might affect the zinc concentrations at st.4.

Meanwhile, st.3 located prior to the confluence with Ochiai River (st.31) showed relatively higher concentrations (varied from 0.010 – 0.062 mg/L) than those at st.4, except in November and April. The elevated zinc concentrations of st.3 could be due to the point sources from an industrial area located in the vicinity of the Sakai River. The point source input from the industrial zone located adjacent to the river might increase the zinc fluxes into the mainstream. All zinc concentrations of industrial wastewater (0.036-0.079 mg/L), shown in figure 3, were still below the National Effluent Standards of 2.0 mg/L, enacted in 2006. The industrial wastewaters were discharged after st.42, which affected the concentrations in st.41. Station 42 has zinc concentrations below the detection limit in July-September 2019, November 2019-January 2020, April, and July 2020. The most upstream station of Sakai River (st.43) occasionally exhibited high concentration, even exceeded the EQS in April 2020. The land-use near st.43 was an agricultural and residential area that might contribute to elevated concentrations.

Figure 2. Total zinc concentrations in surface water of the Umeda River and its tributaries. The undetectable concentrations were below 0.005 mg/L.

Figure 3. Total zinc concentrations of industrial wastewater located in the Sakai River, a tributary of the Umeda River
Figure 4. River discharges of the Umeda River and its tributaries.

The zinc concentrations at st.2 were generally higher than st.3 except for August, October, February 2019, and June 2020. The zinc concentrations varied from 0.011 to 0.048 mg/L. The st.2, located in the proximity of railways, highway, and Zoo and Botanical Park, might contribute zinc flux as the non-point source. The st.1 was the most downstream section of the Umeda River. The zinc concentrations at st.1 exhibited relatively higher concentrations (0.010 – 0.090 mg/L) than other sampling stations. It has total zinc concentrations higher than 0.030 mg/L in November, December 2019, February, and March 2020. As aforementioned, the EQS was breached according to the annual average value of total zinc concentration at st.1. Anthropogenic activities might severely impact on the zinc concentrations of the most downstream section. Changes in water quality might influenced by non-point source pollutants in the river basin area [13,14].

The zinc concentrations in the Umeda River were relatively higher from January to April 2020 than other months that might be caused by the activity of the industrial zone, which reflected in the zinc concentration values of wastewaters. During the fall (September-November) and winter season (December-February), the zinc concentrations increased compared to other seasons (spring and summer). The peak concentration (0.090 mg/L) occurred in December, whereas all of the sampling stations in February exhibited relatively higher concentrations (0.021-0.062 mg/L) than other months. Given that the zinc concentrations of wastewater were low in December, it could be caused by other anthropogenic sources. Moreover, the precipitation during the winter season was low, causing decreased river discharges, which might consequently elevate the instream zinc concentrations. Figure 4 showed the river discharges values for each sampling event.

Japan has high precipitation in June, July (during Tsuyu or 'rainy' season), September and October (due to typhoons), which might promote dilution of zinc concentrations. Both in 2019 and 2020, the concentrations during the Tsuyu were relatively lower than in other months. The Pearson correlation between total zinc and river discharges was significant but weak (r = 0.275, p<0.05). If non-point sources dominated the contribution to zinc flux, the higher the river discharge, the higher the total zinc concentration, particularly the particulate fraction, such as the case study from Gozzard, et al. (2011) [4].

3.2. Total zinc loads in the water samples
Figure 5 shows the total zinc load in the water samples of the Umeda River from June 2019 to July 2020. It can be seen clearly that the highest zinc flux occurred in November, December, February to April. The zinc loads varied from 954 to 7,833 g/day at the most downstream sampling point (st.1). Meanwhile, the upper stream section (st. 2 – st.5) exhibited lower loads from 2 to 3,551 g/day. The total zinc fluxes could decrease down the stream, i.e., in July 2019, October 2019, March 2020, which might be due to dilution and precipitation. However, in the Umeda River, the total zinc fluxes generally increased in a downstream direction. From August 2019 to July 2020, the total zinc fluxes of st.1 reached approximately 1.06 t, which then flowed to Mikawa Bay. Naito et al. (2010) [9] estimated that the total zinc load to Japanese surface waters during normal water levels was 1,731 t/year. As a comparison, the
total zinc loads to Aizumame River, Aichi Prefecture, at the most downstream section was 0.050 t/km²/year. The zinc fluxes to Umeda River was lower (0.012 t/km²/year) than those in Aizumame River because of high total zinc concentrations in the Aizumame River.

![Figure 5. Total zines loads in the water samples of Umeda River.](image)

4. Conclusions
The total zinc concentrations along the Umeda River temporally and spatially varied throughout the year. The highest concentrations were found during the fall and winter season with the concentrations generally increased toward a downstream direction. All sampling points had relatively high concentrations ranged from 0.021 mg/L to 0.062 mg/L in February during the winter season. The annual mean concentration value of 0.031 mg/L at the most downstream section of Umeda River has breached the EQS (0.030 mg/L). According to this study, the Umeda River has been affected by anthropogenic activities. Further investigation is necessary to identify the possible sources of zinc fluxes to the Umeda River.

References
[1] Hatakeyama S 1989 Hydrobiologia 174 17–27
[2] Jensen J, Larsen M M and Bak J 2016 Environ. Pollut. 214 334–40
[3] Wada S and Suzuki S 2011 Aquat. Microb. Ecol. 63 47–59
[4] Gozzard E, Mayes W M, Potter H A B and Jarvis A P 2011 Environ. Pollut. 159 3113–22
[5] Rudall S and Jarvis A P 2012 Water Sci. Technol. 65 164–70
[6] Hüffmeyer N, Klasmeier J and Matthies M 2009 Sci. Total Environ. 407 2296–305
[7] Chen M, Wang D, Ding S, Fan X, Jin Z, Wu Y, Wang Y and Zhang C 2019 Sci. Total Environ. 670 361–8
[8] Andarani P, Yokota K, Saga M, Inoue T and Matsumoto Y 2020 River Res. Appl. 1286–95
[9] Naito W, Kamo M, Tsushima K and Iwasaki Y 2010 Sci. Total Environ. 408 4271–84
[10] Wen Y, Yang Z and Xia X 2013 Appl. Geochemistry 31 199–208
[11] Wang X, Zhao L, Xu H and Zhang X 2018 Mar. Pollut. Bull. 137 465–73
[12] Resongles E, Casiot C, Freydier R, Le Gall M and Elbaz-Poulichet F 2015 J. Geochemical Explor. 158 132–42
[13] Rezagama A, Sutrisno E and Handayani D S 2020 E3S Web Conf. 448(1)
[14] Sarminingsih A and Rezagama A 2019 J. Phys. Conf. Ser. 1217(1) 012134