CLEAN - Soil, Air, Water

Decision Letter (clen.202100151.R1)

From: phenheik@wiley-vch.de

To: andarani@ft.undip.ac.id, andarani@gmail.com

CC: phenheik@wiley-vch.de

Subject: Decision on Manuscript # clen.202100151.R1 for "CLEAN - Soil, Air, Water"

Body: *** HTML-Vorlage
<B>FETT</B>
<U>UNTERSTRICHEN</U>
<I>KURSIV</I>
****

Dear Dr. Andarani:

It is my pleasure to inform you that the manuscript clen.202100151.R1, "An assessment of zinc fluxes by analyzing monthly, weekday, and weekend levels in a river" has been reviewed and recommended for publication pending satisfactory revisions in CLEAN - Soil, Air, Water. The reviewer comments are given below.

I invite you to respond to the reviewer comments and make the necessary revisions to your manuscript.

Before you submit your revision, please adjust your manuscript according to the author guidelines (www.clean-journal.com, For Authors) and proof-read the manuscript carefully to minimize typographical, grammatical, and bibliographic errors. In addition, check to make sure that all abbreviations are defined.

In revised manuscripts the areas containing the major required changes should be marked and the color of the text changed; please do not use the tracking mode.

Please include a cover letter which indicates in detail the changes you have made and why, and mark these changed sections in the revision using a different color. Also, indicate which of the suggested changes, if any, you have elected not to make and your reasons. I will contact you as soon as possible with a final editorial decision.

The submission of a Graphical Abstract is mandatory for all provisionally accepted papers. Please provide the following in a word file:
- one summary figure that best represents your article;
- 2-3 sentences of layman's description of your work covering: background, what was done in your study, and implications of the results;
- see also the attached example.

References: This Journal is currently introducing a new reference style. Please make sure to list all author names in all references, not only seven authors et al.

You can upload your revised manuscript and submit it either by clicking on this link:
*** PLEASE NOTE: This is a two-step process. After clicking on the link, you will be directed to a webpage to confirm. ***

https://mc.manuscriptcentral.com/clean?URL_MASK=9cf6ecffb28c4ce4bcfb1e6db1a76803

Alternatively log into https://mc.manuscriptcentral.com/clean and enter your Author Center, where you will find your manuscript title listed under "Manuscripts with Decisions".

PLEASE NOTE that there is a 10 day time limit for uploading the revised paper.

When submitting your revised manuscript, you will be able to respond to the comments made by the reviewer(s) in the space provided. You can use this space to document any changes you make to the original manuscript.

IMPORTANT: We have your original files. When submitting (uploading) your revised manuscript, please delete the file(s) that you wish to replace and then upload the revised file(s).

Wiley Editing Services Available to All Authors
Should you be interested, Wiley Editing Services offers expert help with manuscript, language, and format editing, along with other article preparation services. You can learn more about this service option at www.wileyauthors.com/eeo/preparation. You can also check out Wiley's collection of free article preparation resources for general guidance about writing and preparing your manuscript at www.wileyauthors.com/eeo/prepresources.

Once again, thank you for submitting your manuscript to "CLEAN - Soil, Air, Water" and I look forward to receiving your revision.

Sincerely,

Dr. Prisca Henheik
Editor-in-Chief
CLEAN - Soil, Air, Water

** Referee(s)' and Editors' Comments to Author.

Editor: Henheik, Prisca
Comments to the Author:
Please address the following comment:
Did the monthly Zn tests results presented in Figure 2 include a single sample analysis, or is it the result as the average of several tests per month? If a single survey was selected, how was the day chosen for sample collection, except 2 days of dry weather before sampling?
How often were samples taken per day? Once which means n=1? Or is it more often? Are samples mixed? Please be as detailed as possible.

[DL-RW-2]

Date Sent: 13-Sep-2021

File 1: * Graphical-Abstract-example.doc

Close Window

Dear Dr. Prisca Henheik,

Thank you for allowing us to submit to CLEAN – Soil, Air, and Water journal a revised draft of our article titled "An assessment of zinc fluxes by analyzing monthly, weekday, and weekend levels in a river". We appreciate your time and effort to provide us with important feedback on our work. We were able to include most of the recommendations into the revised version by addressing your questions. The modifications in the manuscript have been highlighted by red color.

<i>** Referee(s)' and Editors' Comments to Author.

Editor: Henheik, Prisca
Comments to the Author:
Please address the following comment:
Did the monthly Zn tests results presented in Figure 2 include a single sample analysis, or is it the result as the average of several tests per month? If a single survey was selected, how was the day chosen for sample collection, except 2 days of dry weather before sampling?
How often were samples taken per day? Once which means n=1? Or is it more often? Are samples mixed? Please be as detailed as possible. </i>

Response: Thank you for pointing this out. We have added a comprehensive explanation to the manuscript by addressing your questions.

<i> Question 1: Did the monthly Zn tests results presented in Figure 2 include a single sample analysis, or is it the result as the average of several tests per month? </i>

The monthly survey was a single survey per month. The samples at each sampling station were collected one time.

<i> Question 2: If a single survey was selected, how was the day chosen for sample collection, except 2 days of dry weather before sampling? </i>

The main criteria were dry weather (including the previous two days) and on weekdays. The samples were collected during the daytime approximately from 09:00 to 14:00 in nine sampling stations and three wastewaters.

<i> Question 3: How often were samples taken per day? Once which means n=1? Or is it more often? Are samples mixed? </i>

The water sample at each sampling stations was collected once per day (n = 1). However, a triplicate analysis was conducted for each water sample, then the average and the standard deviations are presented in Figure 2.

<u>Original text (line 113–119):</u>

The monthly survey was conducted for nine months in August 2019, December 2019 to July 2020. The surveys were undertaken on sunny days (daytime weekday) when no precipitation occurred, including the previous two days. The interval period between monthly sampling events ranged from 22 to 43 days (31 days on average). Approximately two liters of water samples were taken manually using acid-cleaned polypropylene bottles at the riverine sampling stations (st.1–st.5, st.31, and st.21–23) and industrial wastewater sampling points (ww-A, ww-B, and ww-C). The river discharges were measured and calculated using a velocity-area method according to Andarani et al.[20]

<u>Revised and added text (line 114–116): </u>

The monthly survey was conducted for nine months in August 2019, December 2019 to July 2020. The monthly survey was a single survey per month. The main criteria of selecting the monthly survey day were dry weather (including the previous two days) and conducted on a weekday. The samples were collected once per day during the daytime, approximately from 09:00 to 14:00 at all riverine sampling stations (st.1–st.5, st.31, and st.21–23) and industrial wastewater sampling points (ww-A, ww-B, and ww-C). The interval period between monthly sampling events ranged from 22 to 43 days (31 days on average).

Approximately two liters of water samples were collected manually using acid-cleaned polypropylene bottles. The water sample at each sampling stations was collected once per day (n = 1). However, a triplicate analysis of each sample was conducted, then the average and the standard deviations are presented in Figure 2. The river discharges were measured and calculated using a velocity-area method according to Andarani et al.[20]

We look forward to hearing from you in due time regarding our submission and to respond to any further questions and comments you may have.

Sincerely yours,

Pertiwi Andarani

Dear Dr. Prisca Henheik,

Thank you for allowing us to submit to CLEAN – Soil, Air, and Water journal a revised draft of our article titled “An assessment of zinc fluxes by analyzing monthly, weekday, and weekend levels in a river”. We appreciate your time and effort to provide us with important feedback on our work. We were able to include most of the recommendations into the revised version by addressing your questions. The modifications in the manuscript have been highlighted in red.

---

*<i>** Referee(s)' and Editors' Comments to Author.*

Editor: Henheik, Prisca
Comments to the Author:
Please address the following comment:
Did the monthly Zn tests results presented in Figure 2 include a single sample analysis, or is it the result as the average of several tests per month? If a single survey was selected, how was the day chosen for sample collection, except 2 days of dry weather before sampling?
How often were samples taken per day? Once which means n=1? Or is it more often? Are samples mixed? Please be as detailed as possible. </i>

Response: Thank you for pointing this out. We have added a comprehensive explanation to the manuscript by addressing your questions:

<i>Question 1: Did the monthly Zn tests results presented in Figure 2 include a single sample analysis, or is it the result as the average of several tests per month?</i>

The monthly survey was a single survey per month. The samples at each sampling station were collected one time.

<i>Question 2: If a single survey was selected, how was the day chosen for sample collection, except 2 days of dry weather before sampling? </i>

The main criteria were dry weather (including the previous two days) and on weekdays. The samples were collected during the daytime approximately from 09:00 to 14:00 in nine sampling stations and three wastewaters.

<i>Question 3: How often were samples taken per day? Once which means n=1? Or is it more often? Are samples mixed? </i>

The water sample at each sampling stations was collected once per day (n = 1). However, a triplicate analysis was conducted for each water sample, then the average and the standard deviations are presented in Figure 2.

<u>Original text (line 113–119):</u>

The monthly survey was conducted for nine months in August 2019, December 2019 to July 2020. The surveys were undertaken on sunny days (daytime weekday) when no precipitation occurred, including the previous two days. The interval period between monthly sampling events ranged from 22 to 43 days (31 days on average). Approximately two liters of water samples were taken manually using acid-cleaned polypropylene bottles at the riverine sampling stations (st.1–st.5, st.31, and st.21–23) and industrial wastewater sampling points (ww-A, ww-B, and ww-C). The river discharges were measured and calculated using a velocity-area method according to Andarani et al.[20]

<u>Revised and added text (line 114–116): </u>

The monthly survey was conducted for nine months in August 2019 and from December 2019 to July 2020. The monthly survey was a single survey per month. The main criteria for selecting the monthly survey day were dry weather (including the previous two days) and conducted on a weekday. The samples were collected once per day during the daytime, approximately between 09:00 and 14:00 at all riverine sampling stations (st.1–st.5, st.31, and st.21–23) and industrial wastewater sampling points (ww-A, ww-B, and ww-C). The interval period between monthly sampling events ranged from 22 to 43 days (31 days on average).

Approximately two liters of water samples were collected manually using acid-cleaned polypropylene bottles which was also triple rinsed by river water. A triplicate analysis of each sample was conducted, then the average and standard deviation are presented in Figure 2. The river discharges were measured and calculated using a velocity-area method according to Andarani et al.[20]

<u>Original caption (line 447 - 450):</u>

Figure 2. (a) Zn and (b) Fe concentrations in the river water. “P” represents particulate metal in the suspended solids and “D” denotes concentrations in dissolved phase (<0.2 μm). Undetected levels were assumed to have half of the detection limit concentration (0.00025 mg/L for Zn and 0.005 mg/L for Fe)

<u>Revised caption (line 452 – 456):</u>

Figure 2. (a) Zn and (b) Fe concentrations in the river water during the monthly survey. “P” represents particulate metal in the suspended solids and “D” denotes concentrations in dissolved phase (<0.2 μm). Undetected levels were assumed to have half of the detection limit concentration (0.00025 mg/L for Zn and 0.005 mg/L for Fe). Error bars are regarded as standard deviations of the triplicate analysis.

We look forward to hearing from you in due time regarding our submission and to respond to any further questions and comments you may have.

Sincerely yours,

Pertiwi Andarani

Dear Dr. Prisca Henheik,

Thank you for allowing us to submit to CLEAN – Soil, Air, and Water journal a revised draft of our article titled “An assessment of zinc fluxes by analyzing monthly, weekday, and weekend levels in a river”. We appreciate your time and effort to provide us with important feedback on our work. We were able to include most of the recommendations into the revised version by addressing your questions. The modifications in the manuscript have been highlighted in red.

*** Referee(s)' and Editors' Comments to Author.*

Editor: Henheik, Prisca
Comments to the Author:
Please address the following comment:
Did the monthly Zn tests results presented in Figure 2 include a single sample analysis, or is it the result as the average of several tests per month? If a single survey was selected, how was the day chosen for sample collection, except 2 days of dry weather before sampling?
How often were samples taken per day? Once which means n=1? Or is it more often? Are samples mixed? Please be as detailed as possible.

Response: Thank you for pointing this out. We have added a comprehensive explanation to the manuscript by addressing your questions:

Question 1: Did the monthly Zn tests results presented in Figure 2 include a single sample analysis, or is it the result as the average of several tests per month?

The monthly survey was a single survey per month. The samples at each sampling station were collected one time.

Question 2: If a single survey was selected, how was the day chosen for sample collection, except 2 days of dry weather before sampling?

The main criteria were dry weather (including the previous two days) and on weekdays. The samples were collected during the daytime approximately from 09:00 to 14:00 in nine sampling stations and three wastewaters.

Question 3: How often were samples taken per day? Once which means n=1? Or is it more often? Are samples mixed?

The water sample at each sampling stations was collected once per day (n = 1). However, a triplicate analysis was conducted for each water sample, then the average and the standard deviations are presented in Figure 2.

Original text (line 113–119):

The monthly survey was conducted for nine months in August 2019, December 2019 to July 2020. The surveys were undertaken on sunny days (daytime weekday) when no precipitation occurred, including the previous two days. The interval period between monthly sampling events ranged from 22 to 43 days (31 days on average). Approximately two liters of water samples were taken manually using acid-cleaned polypropylene bottles at the riverine sampling stations (st.1–st.5, st.31, and st.21–23) and industrial wastewater sampling points (ww-A, ww-B, and ww-C). The river discharges were measured and calculated using a velocity-area method according to Andarani et al.[20]

Revised and added text (line 114–116):

The monthly survey was conducted for nine months in August 2019 and from December 2019 to July 2020. The monthly survey was a single survey per month. The main criteria for selecting the monthly survey day were dry weather (including the previous two days) and conducted on a weekday. The samples were collected once per day during the daytime, approximately between 09:00 and 14:00 at all riverine sampling stations (st.1–st.5, st.31, and st.21–23) and industrial wastewater sampling points (ww-A, ww-B, and ww-C). The interval period between monthly sampling events ranged from 22 to 43 days (31 days on average).

Approximately two liters of water samples were collected manually using acid-cleaned polypropylene bottles which was also triple rinsed by river water. A triplicate analysis of each sample was conducted, then the average and standard deviation are presented in Figure 2. The river discharges were measured and calculated using a velocity-area method according to Andarani et al.[20]

Original caption (line 447–450):

Figure 2. (a) Zn and (b) Fe concentrations in the river water. “P” represents particulate metal in the suspended solids and “D” denotes concentrations in dissolved phase (<0.2 μm). Undetected levels were assumed to have half of the detection limit concentration (0.00025 mg/L for Zn and 0.005 mg/L for Fe)

Revised caption (line 452 – 456):

Figure 2. (a) Zn and (b) Fe concentrations in the river water during the monthly survey. “P” represents particulate metal in the suspended solids and “D” denotes concentrations in dissolved phase (<0.2 μm). Undetected levels were assumed to have half of the detection limit concentration (0.00025 mg/L for Zn and 0.005 mg/L for Fe). Error bars are regarded as standard deviations of the triplicate analysis.

We look forward to hearing from you in due time regarding our submission and to respond to any further questions and comments you may have.

Sincerely yours,

Pertiwi Andarani

Dear Dr. Prisca Henheik,

Thank you for allowing us to submit to CLEAN – Soil, Air, and Water journal a revised draft of our article titled “An assessment of zinc fluxes by analyzing monthly, weekday, and weekend levels in a river”. We appreciate your time and effort to provide us with important feedback on our work. We were able to include most of the recommendations into the revised version by addressing your questions. The modifications in the manuscript have been highlighted in red.

<i>** Referee(s)' and Editors' Comments to Author.

Editor: Henheik, Prisca

Comments to the Author:

Please address the following comment:

Did the monthly Zn tests results presented in Figure 2 include a single sample analysis, or is it the result as the average of several tests per month? If a single survey was selected, how was the day chosen for sample collection, except 2 days of dry weather before sampling?

How often were samples taken per day? Once which means n=1? Or is it more often? Are samples mixed? Please be as detailed as possible. </i>

Response: Thank you for pointing this out. We have added a comprehensive explanation to the manuscript by addressing your questions:

<i>Question 1: Did the monthly Zn tests results presented in Figure 2 include a single sample analysis, or is it the result as the average of several tests per month?</i>

Response 1: The monthly survey was a single survey per month. The samples at each sampling station were collected one time.

<i>Question 2: If a single survey was selected, how was the day chosen for sample collection, except 2 days of dry weather before sampling? </i>

Response 2: The main criteria were dry weather (including the previous two days) and on weekdays. The samples were collected during the daytime approximately from 09:00 to 14:00 in nine sampling stations and three wastewaters.

<i>Question 3: How often were samples taken per day? Once which means n=1? Or is it more often? Are samples mixed? </i>

Response 3: The water sample at each sampling stations was collected once per day (n = 1). However, a triplicate analysis was conducted for each water sample, then the average and the standard deviations are presented in Figure 2.

<u>Original text (line 113–119):</u>

The monthly survey was conducted for nine months in August 2019, December 2019 to July 2020. The surveys were undertaken on sunny days (daytime weekday) when no precipitation occurred, including the previous two days. The interval period between monthly sampling events ranged from 22 to 43 days (31 days on average). Approximately two liters of water samples were taken manually using acid-cleaned polypropylene bottles at the riverine sampling stations (st.1–st.5, st.31, and st.21–23) and industrial wastewater sampling points (ww-A, ww-B, and ww-C). The river discharges were measured and calculated using a velocity-area method according to Andarani et al.[20]

<u>Revised and added text (line 114–116): </u>

The monthly survey was conducted for nine months in August 2019 and from December 2019 to July 2020. The monthly survey was a single survey per month. The main criteria for selecting the monthly survey day were dry weather (including the previous two days) and conducted on a weekday. The samples were collected once per day during the daytime, approximately between 09:00 and 14:00 at all riverine sampling stations (st.1–st.5, st.31, and st.21–23) and industrial wastewater sampling points (ww-A, ww-B, and ww-C). The interval period between monthly sampling events ranged from 22 to 43 days (31 days on average).

Approximately two liters of water samples were collected manually using acid-cleaned polypropylene bottles which was also triple rinsed by the river water. A triplicate analysis of each sample was conducted, then the average and standard deviation are presented in Figure 2. The river discharges were measured and calculated using a velocity-area method according to Andarani et al.[20]

<u>Original caption (line 447 - 450):</u>

Figure 2. (a) Zn and (b) Fe concentrations in the river water. “P” represents particulate metal in the suspended solids and “D” denotes concentrations in dissolved phase (<0.2 μm). Undetected levels were assumed to have half of the detection limit concentration (0.00025 mg/L for Zn and 0.005 mg/L for Fe)

<u>Revised caption (line 452 – 456):</u>

Figure 2. (a) Zn and (b) Fe concentrations in the river water during the monthly survey. “P” represents particulate metal in the suspended solids and “D” denotes concentrations in dissolved phase (<0.2 μm). Undetected levels were assumed to have half of the detection limit concentration (0.00025 mg/L for Zn and 0.005 mg/L for Fe). Error bars are regarded as standard deviations of the triplicate analysis.

We look forward to hearing from you in due time regarding our submission and to respond to any further questions and comments you might have.

Sincerely yours,

Pertiwi Andarani

An assessment of zinc fluxes by analyzing monthly, weekday, and weekend levels in a river

Pertiwi Andarani[1,2*], Kuriko Yokota[3], Takanobu Inoue[3], Hardianti Alimuddin[2], Nguyen Minh Ngoc[3]

[1]Department of Environmental Engineering, Diponegoro University, Semarang, Central Java, Indonesia
[2]Graduate Program of Architecture and Civil Engineering, Toyohashi University of Technology, Toyohashi, Aichi, Japan
[3]Department of Architecture and Civil Engineering, Toyohashi University of Technology, Toyohashi, Aichi, Japan

*Correspondence: Pertiwi Andarani, M.Eng, Graduate Program of Architecture and Civil Engineering, Toyohashi University of Technology, Toyohashi, Aichi, 441-8580, Japan
e-mail: andarani@ft.undip.ac.id

Abstract

Unlike other heavy metals, zinc (Zn) is indispensable to life but also poses environmental risks to aquatic organisms. Aichi Prefecture has the Japan's fourth-highest discharges of Zn into water bodies. As a major industrial area, it is likely that the Zn fluxes in Aichi's water bodies originate from industrial wastewater. This study evaluated the spatial-temporal and diel variability of Zn concentrations and loads on sunny days during weekdays and weekends in the Umeda River, Aichi. The most downstream point was considered as the most polluted section according to the monthly survey (dissolved Zn: 0.0046–0.0719 mg/L, particulate Zn: 0.42–2.01 mg/g) that varied between seasons (coefficient of variation: 95% for dissolved Zn; 53% for particulate Zn). The total Zn concentrations on weekdays (0.015–0.043 mg/L) at the most downstream point exhibited much higher concentrations than those during the weekends (undetected–0.032 mg/L). Given the dissolved phase of these Zn levels (77 ± 11%), it is apparent that the Zn concentrations were discharged into the Umeda River by industrial facilities on weekdays. The total Zn loading on weekdays (56 g/km^2/day) was approximately three times higher than that on weekends (18 g/km^2/day). At least 67% of the total Zn (37 g/km^2/day) and 70% of the dissolved Zn (35 g/km^2/day) fluxes from industrial point sources were potentially discharged on weekdays.

Abbreviations: CRM, certified reference material; CV, coefficient of variation; D-Zn, Zn in dissolved phase; D-Fe, Fe in dissolved phase; EQS, environmental quality standards; n.d, not detected (Fe ≤ 0.01 mg/L, Zn ≤ 0.0005 mg/L); NES, national effluent standards; POC, particulate organic carbon; PRTR, Pollutant Release and Transfer Register; P-Fe, Fe in particulate phase; P-Zn, Zn in particulate phase; Q, river discharge; SD, standard deviation; SS, suspended solids; st., sampling station; US-EPA, United States - Environmental Protection Agency; WFD, Water Framework Directive; H, water level; Water Framework Directive; ww, industrial wastewater

Keywords: Flux; Heavy metal; Industrial wastewater; Organic matter; Zinc

1 Introduction

Zinc (Zn) is the third most-produced non-ferrous metal in Japan, after copper and aluminum.[1] Based on the Pollutant Release and Transfer Register (PRTR) data from 2018,[1] approximately 641 tons of Zn compounds (water-soluble) are annually discharged into public bodies of water in Japan, and it is the third most-released chemical in these water bodies.[1] The most common use of Zn around the world is galvanizing, to protect steel against corrosion, which accounts for over 50% of the Zn annually produced, followed by ZnO, die casting, a vulcanizing agent of tire rubber, and other application to produce brass, tiles, ceramics, glass[2], dyes[3], battery[4], and electronic products[5]. Unlike other heavy metal pollution, Zn does not pose a health risk to humans indirectly exposed through the environment, whereas direct exposure to ZnO and $ZnCl_2$ may indeed carry potential health risks.[6,7] On the other hand, humans, animals, plants, and even microorganisms, require Zn for development and growth; hence, it is indispensable to life processes.[8] However, its chronic toxicity to aquatic life has been observed when it reaches a specific threshold, which is often as a result of Zn pollution.[7,9–12]

In riverine ecosystems, Zn is typically present in its most ecotoxic form, i.e., Zn^{2+}.[13,14] Consequently, in European countries, stringent environmental quality standards (EQS) on the total fraction of Zn have set the range from 0.008 to 0.125 mg/L, depending on the water hardness.[15] Specifically, in the UK and Wales, the standards for dissolved bioavailable Zn have been set at 10.9 μg/L, plus ambient background concentrations that depend on catchments/groups thereof.[16] Meanwhile, in order to protect freshwater aquatic life, the US Environmental Protection Agency (US-EPA) set the criterion for total recoverable Zn to 0.047 mg/L as a 24-hour average.[17] In order to protect the aquatic ecosystem, in 2003, Japan enacted EQS for Zn of 0.03 mg/L as the annual mean value. Nevertheless, according to the Ministry of Environment of Japan, in 2019, 19 riverine sites breached the EQS, in contrast to lakes and the ocean, which all of them were below the EQS threshold.[18] Naito et al.[19] also noted that Aichi Prefecture did not show a clear Zn reduction trend after 2002. Based on the PRTR Data[1], from 2001 to 2019, Aichi Prefecture had the fourth-largest Zn discharges into public bodies of water (approximately 38 tons/year) after Osaka, Tokyo, and Kanagawa Prefecture.

Due to irregular effluent discharges into the river, a high concentration could be temporarily found, and was possibly missed, during the monitoring period. Anthropogenic activities tend to be more intensive during weekdays, apart from in recreational areas. In this case, a survey conducted measuring weekdays and weekends featured different Zn concentrations. Previous research revealed that surveys undertaken on weekdays exhibited higher concentrations of contaminants.[20,21] Furthermore, Andarani et al.[20] found that throughout 2017, Zn concentrations in the most downstream point in the Aizumame River, located in Aichi Prefecture, exceeded the EQS. The Zn fluxes in the Aizumame River were found to mostly originate from point sources of industrial wastewater, which contributed about 77.3 g/km^2/day.[20] The Zn concentrations in the river may also become elevated due to point or non-point (diffuse) sources.[19,22] Given that industrial facilities do not operate on weekends and holidays, it was possible to estimate the contribution of industrial point sources to the river by comparing the measurement results between weekdays and weekends.

Moreover, hydrological and biogeochemical processes may influence dynamic diel fluctuation in metal concentrations, including Zn.[23] Bourg and Bertin[24] and Brick and Moore[25] were the first to report a diel cycle of Zn concentrations in near-neutral and alkaline rivers, followed by Nimick et al.[26] The diel Zn cycles had already been intensively observed in several near-neutral environments and rivers in the United States[25,27–31], United Kingdom[23], and France[24,32,33]. However, comparisons of diel Zn concentrations during weekdays and weekends remain scarce. The sources of Zn could also be traced by narrowing down activities conducted on weekdays and weekends. The spatial and temporal variations of Zn are also necessary to be assessed in order to verify the input of point sources and seasonal changes. In addition, iron (Fe) was also compared to Zn variation; hence, the impact of anthropogenic activities to the riverine Zn levels could be identified. Fe is a naturally occurring element in river[34] and the adsorption of Zn on the Fe hydroxides might occur in the surface water[26,28]. Therefore, the main objective of this study was to assess the spatial-temporal and diel variation of Zn in a near-neutral stream located in Aichi Prefecture, Japan, particularly on weekdays and weekends.

2 Materials and Methods

2.1 Sampling Site

For this study, monthly surveys (nine months) and a 24-hour survey were conducted in the Umeda River, Aichi Prefecture, Japan. Both surveys were undertaken during low flow on a sunny day (no precipitation on two previous days and the sampling event). The Umeda River is a second grade river with a catchment area of 86.6 km^2, crossing Toyohashi City and flowing into Mikawa Bay.

Figure 1 shows the sampling stations in the study area. Station 5 (st.5) was below Hatakeda Bridge, located at the most downstream point without tidal influence. With st.5 as the outlet, the watershed area accounted for 43.7 km^2. This station was the sampling point for both the monthly survey the hourly survey (the weekdays and weekend sampling). St.1, 2, 3, 4, and 5 were in the Umeda River, with its corresponding tributaries, such as st.31 (Ochiai River) and st.21–23 (Sakai River). The sampling stations (st.2 and st.3) in the Umeda River were located approximately 10 meters before the confluence of its respective tributary.

Land use significantly comprises urban areas (29.8%), including residential, commercial, and industrial areas, mostly located in the catchment's upper-middle reach, particularly in the vicinity of st.2, st.3, and st.4. The industrial areas discharge the wastewater to the Sakai River, which were identified as point sources ww-A, ww-B, and ww-C contributed Zn to the st.23. An industrial area adjacent to the Ochiai River was identified and the water samples were taken at st.31. However, the largest area of land use is agricultural (48.8%), consisting of paddy (5.8%) and other crops (43.0%),[35] including cabbage and tea.

2.2 Samples Collection

2.2.1 Monthly Survey

The monthly survey was conducted for nine months in August 2019, December 2019 to July 2020. The surveys were undertaken on sunny days (daytime weekday) when no precipitation occurred, including the previous two days. The interval period between monthly sampling events ranged from 22 to 43 days (31 days on average). Approximately two liters of water samples were taken manually using acid-cleaned polypropylene bottles at the riverine sampling stations (st.1–st.5, st.31, and st.21–23) and industrial wastewater sampling points (ww-A, ww-B, and ww-C). The river discharges were measured and calculated using a velocity-area method according to Andarani et al.[20]

2.2.2 Hourly Survey (during Weekdays and the Weekend)

Clear sunny weather events on weekdays (Wednesday-Thursday) and weekends (Saturday-Sunday) were monitored in the first week of February 2020 (winter) at st.5. The winter season has the lowest precipitation levels throughout the year, indicating that the point sources may substantially affect Zn fluxes into the stream. An autosampler (Teledyne ISCO-6712, US) was deployed and programmed to take one-liter samples hourly between 17:00 and 16:00. Twenty-four bottles (holding up to a liter of water) made of polypropylene were collected for each sampling event. The water samples were taken by polypropylene pipe and pumped by a peristaltic pump with a purge phase in order to avoid cross-contamination. A one-liter water sample was taken manually using acid-cleaned polypropylene bottles at 17:00 on the second day in order to obtain data over 25 hours. All of the autosampler and polypropylene sample bottles were triple rinsed with deionized water and oven-dried prior to each sampling procedure. The water samples were taken after all samples were collected in autosampler bottles and then immediately filtered and pre-treated in the laboratory within 48 hours.

2.3 River Discharge Measurement Methods

The water level-discharge (H-Q) equation model[36] was used to estimate river discharge (Q) of the Umeda River at Hatakeda Bridge. The water level (H) over every hour at Hamamichi Station, located about one kilometer from Hatakeda Bridge, was obtained from the River Division of Aichi Prefectural Construction Bureau. According to the model, the water level at Hamamichi Station needed to be converted to that at Hatakeda Bridge.[36]

2.4 Analytical Methods

2.4.1 Suspended Solids (SS)

Two types of membranes were used to obtain the SS, namely GF/F membranes and cellulose acetate membranes. The GF/F (0.7 µm, glass microfiber filters, Whatman™, UK) membrane was further used to measure particulate organic carbon (POC), whereas cellulose acetate membrane (Advantec®, Japan) was utilized to obtain filtrate as a dissolved fraction of Zn (D-Zn) and Fe (D-Fe). The SS on the cellulose acetate membrane was further digested to obtain the particulate Zn and Fe fraction.

For the measurement of suspended solids (SS) concentrations, 100 ml water samples were filtered using wash-dried and pre-weigh GF/F membranes. The GF/F membranes were oven-dried at 400 °C before filtering the samples. The concentrations were determined by subtracting the weight of the membrane with SS (oven-dried at 105 °C) and the pre-weight divided by filtered volume. This filtration was performed three times, and the mean values were calculated for further assessment in this study.

2.4.2 Zn and Fe Concentrations

Five-hundred milliliters of water was filtered using a cellulose acetate membrane (0.2 µm, Advantec®, Japan). The filter bottle was triple rinsed with deionized water prior to the filtration of each sample. The first 100 ml of filtrate was then discarded to avoid cross-contamination. With respect to the D-Zn and D-Fe, 1.0 ml of concentrated HNO_3 (ultrapure analytical reagent, Tamachemicals Co., Ltd., Japan) was added to 100 ml of filtrate and then digested. The digestion required heating up the samples on a hotplate to a temperature of 205 °C for 20 minutes. In order to prevent contamination, the first five milliliters of the filtrate were discarded. The metals in suspended solids were analyzed based on the US-EPA Method 3050B with addition of concentrated HCl (suprapure guaranteed reagent, Wako Pure Chemical Corporation, Japan). The concentrations of Zn and Fe were then measured three times using the flame and graphite furnace atomic absorption spectrometry instrument (AA-7000 Shimadzu, Shimadzu Corporation, Japan) with four calibration standards (the detection limits of Zn and Fe were 0.0005 mg/L and 0.01 mg/L, respectively).

Re-validation of the standard solutions every six sample measurements for the calibration curves was necessary for quality assurance and quality control (QA/QC) purposes. The method blanks were analyzed together with a set of the six samples. The Zn and Fe contained in the procedures and reagents were not detected according to the method blank. The triplicate analysis of all samples showed that the coefficient of variation (CV) was less than 7% both for Zn and Fe concentrations of the water samples. The CVs of particulate sample measurements were up to 12%. The analytical procedure was checked using a certified reference material (CRM) for trace elements (National Metrology Institute of Japan, CRM 7202-c No. 0356). The recovery rates for the analytical procedure were 84–92% (Zn) and 93–99% (Fe).

All of the reagents used were of ultrapure and standard solutions were prepared using ultrapure water. All glass and plasticware for the elemental analysis were soaked in 1% HNO_3 (Kanto Chemical, Co., Inc., Japan) solution overnight. They were then triple rinsed using ultrapure water, with the glass and plasticware used dried prior to use.

2.3.3 Particulate Organic Carbon (POC)

POC concentrations of the SS on GF/F membranes were measured using an NC analyzer instrument (Sumigraph NC-22A, Sumika Chemical Analysis Service, Ltd., Japan), with suspended solids on the GF/F membrane combusted at a temperature of 600 °C. The acetalinide standard (Wako Pure Chemical Industries, Japan) was measured to create the calibration curves. Less than 30 μm of drift and zero noise of the instrument baselines were required to conduct the sample measurement. The triplicate measurement and method blank were then carried out for quality assurance and quality control purposes.

2.4 Data Analysis

The statistical description was used to discuss the study results, mainly the mean, standard deviation (SD), the range of the values, and CV. A Pearson correlation (*r*) analysis was used to clarify the relationship among the parameters, calculated using a Minitab® 19. A probability (*p*) value of less than 0.05 was considered a statistically significant correlation.

3 Results and Discussion

3.1 Spatial and Temporal Variation of Zn and Fe Concentrations

The results of Zn and Fe concentrations in the monthly survey from August, December 2019, to July 2020 are illustrated in Figure 2a and b, respectively. The summary of all parameters (SS, Zn, Fe, POC, and river discharge) can be seen in Table 1. Generally, the Zn levels varied among seasons as indicated by high CVs (50–155% for P-Zn; 33–202% for D-Zn). The Zn concentrations, mainly in dissolved form, tended to increase toward the downstream direction. The Zn clearly exhibited high concentrations, namely st.3, 4, 5, and 23. In the vicinity of st.23, three manufacturing industries discharge their wastewater to the Sakai River. The detailed wastewater measurement results (Zn and Fe) are illustrated in Figure 3. Based on the Figure 3a, the total fraction of Zn concentrations in the wastewater did not exceed the national effluent standards (NES) of 2.0 mg/L. However, the Zn remained high downstream part of the Umeda River. Other point sources of Zn were not identified during the preliminary survey. The Zn concentrations in st.3, 4, and 5 exceeded the environmental quality standards (EQS) in December 2019 and February 2020. In March 2020, the EQS exceedances were also observed in st.4 (February, March), 3 (February, March), and 23 (February). From December 2019 to April 2020, relatively high Zn concentrations were obtained in almost all sampling stations. Figure 2a clearly shows that the Zn levels were considerably higher in winter and spring than those in summer. According to Andarani et al.[37], the annual value of total fraction of Zn at st.5 in the 12-month survey exceeded the EQS.

Fe measurement is necessary as the possible natural element in river water. Fe could be considered as the inorganic fraction of SS, whereas the POC indicates the organic part of SS. The Fe levels during the monthly survey did not exhibit clear tendencies to the downstream (Figure 2b). Seasonal variation of Fe levels was not observed. Nevertheless, relatively high Fe concentrations were observed in June 2020 (summer). The dynamic of Zn and Fe concentrations in river water could be influenced by wastewater input or leaching from soil or sediment. Metal redistribution between particulate and dissolved fractions might occur due to the changes in physiochemical properties. The pH was near neutral (7.17 ± 0.17) and relatively stable (CV < 6%), which might not be considered as the main possible cause of Zn variability.

The diel concentrations of Zn during weekdays and weekends over the 24 hours from 17:00 to 17:00 on the next day are shown in Figure 4a and b, respectively. The total Zn concentrations during weekdays exhibited much higher concentrations than those on weekends. Table 2 summarizes the descriptive statistics of the hourly surveys both during weekdays and the weekend. On weekdays, the total Zn concentrations ranged from 0.015 to 0.043 mg/L (0.029 ± 0.008 mg/L), while during weekends, the total Zn varied from undetected to 0.032 mg/L (0.010 ± 0.007 mg/L). Figure 4a illustrates that the total Zn reached its highest value (0.043 mg/L) at 3:00. The discharge peaked in the afternoon at 1.01 m^3/s, whereas the total Zn decreased gradually and then slightly increased to 0.026 mg/L. The lowest concentration was reached at 13:00 (0.015 mg/L) in a relatively higher river discharge of 0.96 m^3/s. Figure 4a also clearly shows that the diel Zn fluctuations of both the total Zn and D-Zn were synchronous to the river discharge variations. The higher the river discharges, the lower the Zn concentrations owing to dilution, as was also seen in Nimick et al.[26], Gozzard et al.[22], and Resongles et al.[32] The increases in the detected minimum to maximum concentrations of D-Zn (the amplitude) during weekdays and weekends were 293% and 1778%, respectively. Meanwhile, different amplitudes were observed in other studies, namely 140–326% for total Zn[23], 800% for dissolved and colloidal Zn[29], and almost 1000% for D-Zn in the least buffered stream.[38] Various possible processes that promote diel variation of Zn in a non-acidic stream were summarized in Gammons et al.[28]

Meanwhile, the diel Zn fluctuations exhibited a similar pattern during the weekend, but with lower concentration values, as is shown in Figure 4b. During the weekend, the total Zn concentrations ranged from undetected (14:00, 16:00, and 17:00 on Sunday) to 0.032 mg/L (at 20:00 on Saturday). The D-Zn always presented over 24 hours on weekdays, whereas it exhibited lower concentrations from 12:00 to 17:00 on Sunday. The weekend's D-Zn concentration fluctuations were relatively similar to those during weekdays at a smaller magnitude, except at 23:00. The D-Zn fractions over the weekend (56 ± 23%, 9–98%) were lower than those during weekdays (77 ± 11%, 57–98%). It is apparent that Zn was introduced to the mainstream of the Umeda River on weekdays as a result of anthropogenic activities. Le Pape et al.[39] also found that natural trace elements, including Zn, were carried by suspended solids, whereas the dissolved phase contribution increased along the river toward the lower reach, where the urbanization was located.

The total Zn concentrations were still present in the daytime during the weekend, but below the detection limit (0.0005 mg/L) at 14:00, 16:00, and 17:00. It is possible that a few industrial facilities still operated on Saturday, but the diel cycles might also have occurred when, during the daytime, the concentrations became lower than at night. The total Zn concentrations varied in a similar trend of discharges, from 19:00 to 23:00 and 04:00 to 08:00.

Because these high temporally resolved samplings (weekdays and the weekend) were conducted in clear weather, the differences in concentrations could be due to the influence of the Zn point sources. The EQS of the total Zn in Japan were set to an annual average value of 0.03 mg/L. All of the Zn concentrations during the weekend remained low and did not exceed 0.03 mg/L. However, the Zn concentrations exceeded the EQS from 19:00 on Wednesday to 09:00 on Thursday, with the exception at 23:00. Although the value of 0.03 mg/L is a standard of the annual average value, a possible breach could be assumed during the 24-hour period. This diel variation of the Zn should be considered in order to determine the time of water quality monitoring for river water quality assessments.

Figure 4c and d show the Fe concentrations in both the total and dissolved fractions. There was no difference between the total Fe concentrations on weekdays (0.147 ± 0.028 mg/L, 0.104–0.215 mg/L) and during the weekend (0.180 ± 0.101 mg/L, 0.125–0.648 mg/L). In contrast to the Zn concentrations, the Fe did not exhibit a distinct variation on either weekdays or during the weekend. The Fe concentrations showed no discernible variability in either the daytime or at night, even though the Zn concentrations clearly demonstrated a diel fluctuation. However, during the daytime, the D-Fe concentrations were relatively lower than during the night, which could only be seen on weekdays. Because the Umeda River has near-neutral pH, the diurnal variation in the D-Fe concentrations due to photoreduction was not observed, in contrast to previous studies.[40,41]

3.2 Adsorption of Zn in the Umeda River

Anthropogenic activities conducted during weekdays could include industrial operations, mining, traffic, municipal solid waste treatment, and agriculture. Domestic activities performed every day could also have contributed to the elevated Zn[19] during both weekdays and the weekend. However, in this study, only the Zn concentrations on weekdays significantly increased. The elevated Zn concentrations could be originated from agricultural runoff[42–44], road runoff[45], traffic emissions, and atmospheric deposition[1,46,47], as well as natural occurrences[48], industrial[20,43,49], and mining activities.[22,23,50] The increased Zn may come from point sources because the survey was undertaken in clear weather (no runoff discharges). Hence, there was no wet deposition or surface runoff introduced into the Umeda River. Sakata et al.[46] found that the Zn fluxes into Tokyo Bay substantially originated from atmospheric depositions. However, most of the Zn fraction in the Umeda River was in dissolved form, especially during the night; hence, it is unlikely that the source was from the dry atmospheric deposition of particulate matter. According to the monthly survey in the Umeda River, the most downstream station had the highest mean of total Zn concentrations over 14 months from August 2019 to July 2020. By considering the land use of the Umeda River catchment, the Zn contamination could be contributed from the wastewater point sources of manufacturing industries located in the upper-middle stream area. Three manufacturing industries discharging their treated wastewater to Sakai River, a tributary of Umeda River, were identified, but the Zn concentrations (0.036–0.079 mg/L) did not exceed the NES of 2.0 mg/L during the 14-month sampling period.[37] However, the instream Zn levels of the Umeda River after the confluence of the Sakai River were relatively higher than those in the upstream section.[37]

Adsorption is considered an important chemical process that influences the mobility of trace elements in natural waters due to its kinetically rapid reactions.[28] In light of previous studies[28,31], a suitable mineral or organic surface is necessary to cause trace elements to be adsorbed on the surface, such as organic matter and hydrous metal oxides (Fe or Mn). The case in Osaka Bay also showed that Zn was mostly concentrated in the Fe-Mn oxide fraction.[51] The present study also observed a strong correlation between P-Zn and P-Fe at st.5 on weekdays, weekends, and during the monthly survey ($r = 0.703$; $p < 0.001$). A correlation between P-Zn and P-Fe ($r = 0.430$; $p < 0.05$) was also observed in the sediment of the lower Seyhan River.[52]

Aquatic organisms and anthropogenic sources may contribute the organic-rich SS to the riverine system.[53] A strong positive correlation between P-Zn and POC has been found in a previous study.[54] In this study, the P-Zn concentrations also strongly correlated to the corresponding POC concentrations ($r = 0.456$; $p < 0.001$) at st.5 during the monthly and hourly survey. At st.5, Zn generally presented in a dissolved phase (67 ± 20%) during the monthly and hourly survey. Compared to the industrial wastewaters, the D-Zn (61 ± 25%) also exhibited a higher proportion than P-Zn. Nevertheless, the particulate fraction of Zn might be adsorbed by both the organic matter and Fe oxides.

3.3 Zn Fluxes Comparisons

According to Figure 6, the cumulative Zn loadings from the most upstream (st.1, 0.0002–0.0657 kg/day) to the downstream (st.5, 1.56–9.91 kg/day) significantly increased, except those in March 2020. The Zn fluxes attenuation was only observed in March where the Zn input declined after approximately 7.59 km. The cumulative D-Zn fluxes also exhibited a similar trend from upstream to downstream of the Umeda River. The input of tributary st.23 led to a further increase in st.3 (particularly in the dissolved phase), substantially observed in December 2019 and January–April 2020. However, it should be noted that in December, the D-Zn significantly contributed to cumulative Zn loading at st.5 because of the Zn input that could not be identified. The Ochiai River (st.31) did not have a substantial Zn loading to the Umeda River.

The total and D-Zn fluxes varied greatly over 24 hours during both time events (Figure 7). The mean of the total Zn (97.15 ± 25.43 g/h) and D-Zn load (87.45 ± 23.72 g/h) on weekdays was much higher than that during the weekend (32.20 ± 23.30 g/h and 26.26 ± 16.31, respectively). On weekdays, the maximum load of the total Zn (142.72 g/h) was present at 3:00, whereas the minimum (50.94 g/h) occurred at 13:00 during daytime and in the presence of a higher river discharge. As for the weekend, a similar pattern whereby the loads decreased during the daytime was also observed. However, the fluctuation exhibited a lower magnitude than that during the weekend. The total Zn load reached its highest value of 106.93 g/h and declined until it was below the detection limit at 14:00, whereas the D-Zn load had remained low since 12:00. Two peaks of total Zn appeared during the weekend due to the increased P-Zn concentrations. At 20:00, the suspended solids may have contributed to the elevated Zn, which also included Fe. Meanwhile, at 23:00, the D-Zn significantly influenced the total Zn load.

The total daily Zn loading on weekdays (28.0 g/km^2/day) was approximately three times higher than during the weekend (9.3 g/km^2/day). These differences could originate from the industrial point sources. The industrial point sources may have contributed at least 67% of the total Zn fluxes (37 g/km^2/day) and 70% of the D-Zn fluxes (35 g/km^2/day) on weekdays. Meanwhile, the industrial area along the Aizumame River in the Aichi Prefecture, discharged approximately 68 g/km^2/day (57%) in 2017[20]; much higher than in the case of the Umeda River. Wen et al.[50] estimated that non-mining industrial activities contributed 3.8 g/km^2/day (Chongqing region) and 0.3 g/km^2/day (Wuhan region) of D-Zn to the Yangtze River according to a survey from July 2007 (flood season) and January 2008 (dry season). In 2000, the Zn input from industrial discharges in the Rhine catchment area in

Germany were 1.0 g/km^2/day.[55] It implies that the Japanese river catchments (Aizumame and Umeda) relatively have substantially higher Zn yield from industrial area than other rivers (Yangtze and Rhine) that has much larger catchment area.

4 Concluding Remarks

This study assessed the spatial and temporal variations of Zn and Fe for nine months as well as its diel weekday and weekend levels comparison on sunny days in the Umeda River in Japan's Aichi Prefecture. The increasing Zn levels were observed from upstream to downstream section of the Umeda River. The industrial wastewater point sources were identified in the Ochiai River and Sakai River, the tributaries of the Umeda River. However, only the Sakai River contributed a significant Zn input to the Umeda River.

The hourly survey was undertaken to verify the impact of anthropogenic activities conducted during weekdays. The distinct differences in the Zn concentrations and loads between weekdays and the weekend indicated that the industrial wastewater impacted the elevated Zn concentrations on weekdays. Meanwhile, the variations in the Fe concentrations on weekdays were relatively similar to those during the weekend. Organic matter and hydrous Fe oxides might have adsorbed the Zn in the riverine system, as was indicated by a strong correlation between P-Zn, P-Fe, and POC concentrations at the most downstream sampling station (st.5). The elevated Zn concentrations in the Umeda River were mostly contributed (more than 67%) by point sources of industrial wastewater based on the hourly survey.

Conflict of Interest

The authors have declared no conflict of interest.

Acknowledgment

This study was funded by the Research Institute for Technological Science and Innovation (RITI) of Toyohashi University of Technology, Japan. The authors would like to sincerely thank Ms. Widyastuti Kusuma and Mr. Ryosuke Suzuki for their assistance in performing the field survey.

References

[1] Ministry of Environment of Japan, *Pollutant Release and Transfer Register (PRTR) Data Page*, **2021**.
[2] F. Jones, D. Bankiewicz, M. Hupa, *Fuel* **2014**, *117*, 763.
[3] O. A. Oguntade, M. T. Adetunji, J. O. Azeez, *J. Environ. Chem. Eng.* **2015**, *3*, 2875.
[4] H. J. Mansoorian, A. H. Mahvi, A. J. Jafari, *Sep. Purif. Technol.* **2014**, *135*, 165.
[5] R. A. Wahaab, F. A. Alseroury, *Int. J. Environ. Sci. Technol.* **2019**, *16*, 47.
[6] H. Autrup, P. Calow, W. Dekant, H. Greim, H. Wojciech, C. Janssen, B. Jansson, H. Komulainen, O. Ladefoged, J. Linders, I. Mangelsdorf, M. Nuti, A. Steenhout, J. Tarazona, E. Testai, M. Vighi, M. Viluksela, *Scientific Committee on Health and Environmental Risks Opinion on: Risk Assessment*

Report on Zinc Environmental Part, European Commission, Brussels **2007**.

[7] C. W. M. Bodar, M. E. J. Pronk, D. T. H. M. Sijm, *Integr. Environ. Assess. Manag.* **2005**, *1*, 301.

[8] C. T. Chasapis, C. A. Spiliopoulou, A. C. Loutsidou, M. E. Stefanidou, *Arch. Toxicol.* **2012**, *86*, 521.

[9] P. Amoatey, M. S. Baawain, *Water Environ. Res.* **2019**, *91*, 1272.

[10] S. Hatakeyama, *Hydrobiologia* **1989**, *174*, 17.

[11] J. Jensen, M. M. Larsen, J. Bak, *Environ. Pollut.* **2016**, *214*, 334.

[12] M. Seto, S. Wada, S. Suzuki, *Chemosphere* **2013**, *90*, 1091.

[13] A. Gogoi, G. G. Tushara Chaminda, A. K. J. An, D. D. Snow, Y. Li, M. Kumar, *Chemosphere* **2016**, *163*, 322.

[14] International Zinc Association, "Zinc in the Environment: an Introduction," can be found under https://www.zinc.org/wp-content/uploads/sites/4/2015/01/Zinc-in-the-Environment-Understanding-the-Science_web.pdf, **2014**.

[15] Water Framework Directive, *The River Basin Districts Typology, Standards and Groundwater Threshold Values (Water Framework Directive) (England and Wales) Directions*, **2010**.

[16] Water Framework Directive, *The Water Framework Directive (Standards and Classification) Directions (England and Wales)*, **2015**.

[17] US-EPA, *Ambient Water Quality Criteria for Zinc*, United States, **1980**.

[18] Ministry of the Environment of Japan: Water and Air Environment Bureau, *2019 Public Water Quality Measurement Results*, **2020**.

[19] W. Naito, M. Kamo, K. Tsushima, Y. Iwasaki, *Sci. Total Environ.* **2010**, *408*, 4271.

[20] P. Andarani, K. Yokota, M. Saga, T. Inoue, Y. Matsumoto, *River Res. Appl.* **2020**, *36*, 1286.

[21] B. Petrie, L. Lopardo, K. Proctor, J. Youdan, R. Barden, B. Kasprzyk-Hordern, *Sci. Total Environ.* **2019**, *650*, 900.

[22] E. Gozzard, W. M. Mayes, H. A. B. Potter, A. P. Jarvis, *Environ. Pollut.* **2011**, *159*, 3113.

[23] S. Rudall, A. P. Jarvis, *Water Sci. Technol.* **2012**, *65*, 164.

[24] A. C. M. Bourg, C. Bertin, *Water. Air. Soil Pollut.* **1996**, *86*, 101.

[25] C. M. Brick, J. N. Moore, *Environ. Sci. Technol.* **1996**, *30*, 1953.

[26] D. A. Nimick, C. H. Gammons, T. E. Cleasby, J. P. Madison, D. Skaar, C. M. Brick, *Water Resour. Res.* DOI: 10.1029/2002WR001571.

[27] J. L. Barringer, T. P. Wilson, Z. Szabo, J. L. Bonin, J. M. Fischer, N. P. Smith, *Environ. Geol.* **2008**, *53*, 1183.

[28] C. H. Gammons, D. A. Nimick, S. R. Parker, *Appl. Geochemistry* **2015**, *57*, 35.

[29] B. A. Kimball, R. L. Runkel, *Mine Water Environ.* **2009**, *28*, 274.

[30] M. J. Kurz, V. de Montety, J. B. Martin, M. J. Cohen, C. R. Foster, *Chem. Geol.* **2013**, *358*, 61.

[31] D. A. Nimick, C. H. Gammons, S. R. Parker, *Chem. Geol.* **2011**, *283*, 3.

[32] E. Resongles, C. Casiot, R. Freydier, M. Le Gall, F. Elbaz-Poulichet, *J. Geochemical Explor.* **2015**, *158*, 132.

[33] P. J. Superville, E. Prygiel, O. Mikkelsen, G. Billon, *Sci. Total Environ.* **2015**, *506–507*, 585.

[34] H. Guo, A. S. Barnard, *J. Mater. Chem. A* **2013**, *1*, 27.

[35] JAXA (Japan Aerspace Exploration Agency), "ALOS2-2/ALOS Science Project," can be found under

https://www.eorc.jaxa.jp/ALOS/en/lulc/lulc_jpn.htm, **2021**.

[36] K. Yokota, T. Inoue, M. Yokokawa, R. Shimoyama, Y. Okubo, *Environ. Sci.* **2013**, *26*, 140 (in Japanese).

[37] P. Andarani, H. Alimuddin, R. Suzuki, K. Yokota, T. Inoue, *IOP Conf. Ser. Earth Environ. Sci.* **2021**, *623*, 012064.

[38] L. S. Balistrieri, D. A. Nimick, C. A. Mebane, *Sci. Total Environ.* **2012**, *425*, 155.

[39] P. Le Pape, S. Ayrault, C. Quantin, *J. Hydrol.* **2012**, *472–473*, 99.

[40] R. T. Kay, G. E. Groschen, G. Cygan, D. H. Dupré David H., *Chem. Geol.* **2011**, *283*, 99.

[41] A. B. Sullivan, J. I. Drever, *J. Hydrol.* **2001**, *252*, 237.

[42] X. Ke, S. Gui, H. Huang, H. Zhang, C. Wang, W. Guo, *Chemosphere* **2017**, *175*, 473.

[43] F. F. Xu, Z. Liu, Y. Cao, L. Qiu, J. Feng, F. F. Xu, X. Tian, *Catena* **2017**, *150*, 9.

[44] Y. Yang, Z. He, Y. Lin, E. J. Phlips, P. J. Stoffella, C. A. Powell, *Water Environ. Res.* **2009**, *81*, 40.

[45] N. Hüffmeyer, J. Klasmeier, M. Matthies, *Sci. Total Environ.* **2009**, *407*, 2296.

[46] M. Sakata, M. Narukawa, K. Marumoto, *Atmospheric and Riverine Inputs of Trace Substances to Tokyo Bay*, **2005**.

[47] L. Sörme, R. Lagerkvist, *Sci. Total Environ.* **2002**, *298*, 131.

[48] D. A. dos Reis, A. da Fonseca Santiago, L. P. Nascimento, H. M. P. Roeser, *Environ. Sci. Pollut. Res.* **2017**, *24*, 7456.

[49] G. Zhen, Y. Li, Y. Tong, L. Yang, Y. Zhu, W. Zhang, *Environ. Sci. Pollut. Res.* **2016**, *23*, 8410.

[50] Y. Wen, Z. Yang, X. Xia, *Appl. Geochemistry* **2013**, *31*, 199.

[51] M. M. Billah, E. Kokushi, S. Uno, *Water. Air. Soil Pollut.* **2019**, *230*, DOI 10.1007/s11270-019-4196-8.

[52] O. I. Davutluoglu, G. Seckin, C. B. Ersu, T. Yilmaz, B. Sari, *Clean - Soil, Air, Water* **2011**, *39*, 185.

[53] G. Huang, M. Zhang, C. Liu, L. Li, Z. Chen, *Sci. Total Environ.* **2018**, *635*, 913.

[54] J. Zeng, G. Han, *Ecol. Indic.* **2020**, *118*, 106723.

[55] S. Fuchs, U. Scherer, T. Hillenbrand, F. Marscheider-Weidemann, H. Behrendt, D. Opitz, *Emissions of Heavy Metals and Lindane into River Basins of Germany*, Federal Environmental Agency (Umweltbundesamt), Berlin, **2002**.

Figure Legends

Figure 1. Sampling stations in the Umeda River and its tributaries

Legend 1

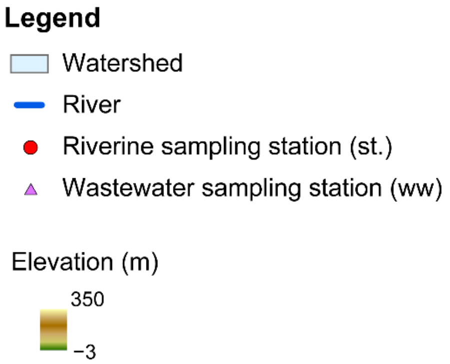
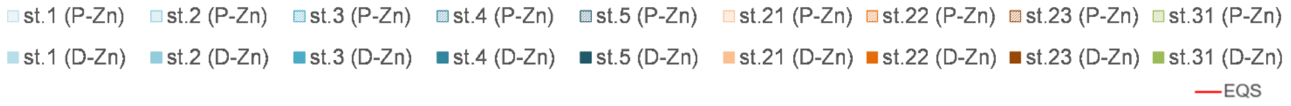


Figure 2. (a) Zn and (b) Fe concentrations in the river water. “P” represents particulate metal in the suspended solids and “D” denotes concentrations in dissolved phase (<0.2 µm). Undetected levels were assumed to have half of the detection limit concentration (0.00025 mg/L for Zn and 0.005 mg/L for Fe)

Legend 2a



Legend 2b

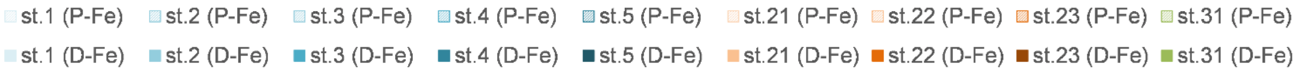
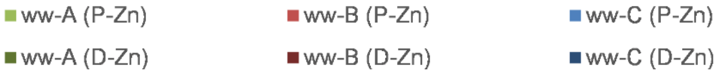


Figure 3. (a) Zn and (b) Fe concentrations in the wastewater

Legend 3a



Legend 3b

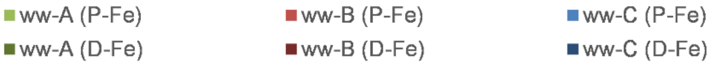


Figure 4. (a) The total and dissolved Zn concentrations during weekdays; (b) The total and dissolved Zn concentrations during the weekend; (c) The total and dissolved Fe concentrations during weekdays; (d) The total and dissolved Fe concentrations during the weekend in February 2020. The error bars represent the standard deviations. The gray shaded area indicates the night-time hours (from 18:00 to 06:00).

Legend 4a

▬ Total Zn concentration ▭ Dissolved Zn concentration — River discharge (Q) during weekdays

Legend 4b

▬ Total Zn concentration ▭ Dissolved Zn concentration — River discharge (Q) during weekend

Legend 4c

▬ Total Fe concentration ▭ Dissolved Fe concentration — River discharge (Q) during weekdays

Legend 4d

▬ Total Fe concentration ▭ Dissolved Fe concentration — River discharge (Q) during weekend

Figure 5. Correlations between (a) Fe and Zn concentrations in particulate phase (P-Fe and P-Zn); (b) particulate organic carbon (POC) and P-Zn concentrations at st.5 during the monthly and hourly surveys (all correlations were significantly strong positive relationship)

Figure 6. Cumulative Zn load in the Umeda River and instream load of the tributary: (a) total Zn; (b) dissolved Zn

Legend 6

-□- Aug -●- Dec -✕- Jan -■- Feb -▲- Mar
-◆- Apr -○- May -+- Jun -✱- Jul

Figure 7. (a) Total and dissolved Zn load (a) on weekdays; (b) during the weekend. The gray shaded area indicates night-time hours (from 18:00 to 06:00).

Legend 7a

-●- Total Zn load during weekdays -▲- Dissolved Zn load during weekdays

Legend 7b

-●- Total Zn load during weekend -▲- Dissolved Zn load during weekend

Table 1. Summary of water analysis results in the monthly survey

		Sampling station								
		st.1	**st.2**	**st.3**	**st.4**	**st.5**	**st.31**	**st.21**	**st.22**	**st.23**
D-Zn (mg/L)	Minimum	n.d.	0.0036	0.0056	0.0055	0.0046	0.0019	n.d.	n.d.	0.0052
	Maximum	0.0236	0.0278	0.0207	0.0396	0.0719	0.0139	0.0224	0.0273	0.0154
	Mean	0.0038	0.0117	0.0119	0.0198	0.0214	0.0057	0.0067	0.0047	0.0111
	SD	0.0076	0.0082	0.0056	0.0122	0.0204	0.0041	0.0077	0.0085	0.0036
	CV	202%	70%	47%	62%	95%	71%	114%	180%	33%
P-Zn (mg/L)	Minimum	n.d.	0.0010	0.0011	0.0029	0.0028	0.0023	n.d.	0.0007	0.0020
	Maximum	0.0039	0.0083	0.0261	0.0097	0.0142	0.0074	0.0122	0.0051	0.0334
	Mean	0.0010	0.0036	0.0100	0.0053	0.0062	0.0044	0.0027	0.0027	0.0093
	SD	0.0016	0.0028	0.0094	0.0027	0.0039	0.0019	0.0041	0.0017	0.0094
	CV	163%	75%	93%	50%	63%	44%	155%	64%	101%
D-Fe (mg/L)	Minimum	0.052	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Maximum	0.118	0.179	0.180	0.085	0.096	0.081	n.d.	0.103	0.171
	Mean	0.081	0.075	0.102	0.058	0.040	0.028	n.d.	0.050	0.098
	SD	0.026	0.063	0.053	0.024	0.037	0.033	n.d.	0.033	0.044
	CV	32%	83%	52%	41%	92%	117%	-	67%	45%
P-Fe (mg/L)	Minimum	0.055	0.035	0.079	0.095	0.102	0.105	0.035	0.059	0.043
	Maximum	0.259	0.183	0.580	0.349	0.169	0.434	1.259	0.615	0.197
	Mean	0.111	0.108	0.207	0.159	0.133	0.194	0.213	0.220	0.147
	SD	0.065	0.051	0.153	0.078	0.026	0.102	0.394	0.201	0.049
	CV	58%	47%	74%	49%	19%	52%	185%	92%	33%
POC (mg/g)	Minimum	27	25	67	153	141	73	85	95	132
	Maximum	281	528	283	297	283	312	330	207	422
	Mean	124	275	176	215	228	194	175	159	234
	SD	83	148	70	48	52	74	81	47	99
	CV	67%	54%	40%	22%	23%	38%	46%	30%	43%
SS (mg/L)	Minimum	2.3	3.1	5.6	5.2	3.6	1.4	1.3	2.7	4.5
	Maximum	38.5	9.6	11.3	9.0	8.6	20.2	23.3	19.1	18.1
	Mean	9.3	6.5	7.9	6.8	6.1	8.2	6.1	7.4	9.1
	SD	11.6	1.9	2.0	1.2	1.7	5.2	6.8	6.4	4.3
	CV	126%	29%	26%	18%	28%	63%	111%	86%	48%
River discharge (m^3/s)	Minimum	0.01	0.04	0.33	0.57	0.76	0.11	0.01	0.07	0.17
	Maximum	0.06	0.11	0.86	1.18	1.36	0.30	0.05	0.21	0.42
	Mean	0.03	0.08	0.51	0.79	1.06	0.18	0.03	0.14	0.28
	SD	0.02	0.02	0.18	0.19	0.18	0.06	0.02	0.06	0.07
	CV	68%	30%	36%	24%	17%	33%	64%	40%	27%

n.d. : not detected (detection limit: 0.0005 mg/L for Zn and 0.01 mg/L for Fe)

CV, coefficient of variation; D-Zn, Zn in dissolved phase; D-Fe, Fe in dissolved phase; POC, particulate organic carbon; P-Fe, Fe in particulate phase; P-Zn, Zn in particulate phase; SD, standard deviation; SS, suspended solids; st., sampling station

Table 2. Summary of water analysis results in the hourly survey

	T-Zn (mg/L)	D-Zn (mg/L)	T-Fe (mg/L)	D-Fe (mg/L)	POC (mg/L)	SS (mg/L)	River discharge (m^3/s)
Weekdays							
Minimum	0.015	0.014	0.104	0.034	112	5.5	0.89
Maximum	0.043	0.040	0.215	0.086	315	21.5	1.01
Mean	0.029	0.026	0.147	0.055	172	9.9	0.93
SD	0.008	0.007	0.028	0.014	50	3.5	0.03
CV	27%	29%	19%	26%	29%	35%	3%
Weekends							
Minimum	n.d.	n.d.	0.125	0.036	102	7.3	0.89
Maximum	0.032	0.0178	0.648	0.063	163	59.7	0.96
Mean	0.010	0.0079	0.180	0.051	131	14.1	0.93
SD	0.007	0.0049	0.101	0.007	17	10.0	0.02
CV	73%	62%	56%	14%	13%	71%	2%

n.d. : not detected (detection limit: 0.0005 mg/L for Zn and 0.01 mg/L for Fe)

CV, coefficient of variation; D-Zn, Zn in dissolved phase; D-Fe, Fe in dissolved phase; POC, particulate organic carbon; SD, standard deviation; SS, suspended solids; st., sampling station; T-Fe, Fe in total fraction; T-Zn, Zn in total fraction;

CLEAN - Soil, Air, Water

Decision Letter (clen.202100151.R2)

From: phenheik@wiley-vch.de

To: andarani@ft.undip.ac.id, andarani@gmail.com, yokota@ace.tut.ac.jp, inoue.takanobu.zy@tut.jp, hardianti.alimuddin94@gmail.com, nguyen.minh.ngoc.hw@tut.jp

CC: phenheik@wiley-vch.de

Subject: Decision on Manuscript # clen.202100151.R2 for "CLEAN"

Body: *** HTML-Vorlage
<B>FETT</B>
<U>UNTERSTRICHEN</U>
<I>KURSIV</I>
****

Dear Dr. Andarani:

I am pleased to inform you that your manuscript, "An assessment of zinc fluxes by analyzing monthly, weekday, and weekend levels in a river", is now acceptable for publication in CLEAN.

With the acceptance of your manuscript the final version of your manuscript and all uploaded files (Figures, Tables, Graphical Abstract, Supporting Information - if provided) in ScholarOne will be used for the subsequent publication process.

Should you have any images related to your article that you believe it might be appropriate for use on the cover of CLEAN - Soil, Air, Water, please email us your layout suggestions with a short description.
For details on cover image preparation please visit http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1863-0669. Each PDF of a published article in an issue will show the cover and will increase visibility of your article. Please be aware that the additional service costs to produce a cover will need to be partially covered by you.

Copyright Information
Collection of Copyright Transfer Agreement (CTA) form: Your article cannot be published until the publisher has received the appropriate signed license agreement. The corresponding author will receive an email from Wiley´s Author Services system which will ask them to log in and will present them with the appropriate license for completion after the paper is processed for production.

As the next step, your paper will go to production and you will receive a galley proof by e-mail in due course. Once you have corrected the proof, the paper will then be published online via Wiley Online Library.

Thank you supporting CLEAN. I look forward to seeing more of your work in the future.

Sincerely,

Dr. Prisca Henheik
Editor-in-Chief
CLEAN

P.S. – You can help your research get the attention it deserves! Wiley Editing Services offers professional video abstract and infographic creation to help you promote your research at www.wileyauthors.com/eeo/promotion. And, check out Wiley’s free Promotion Guide for best-practice recommendations for promoting your work at www.wileyauthors.com/eeo/guide.

** Referee(s)' and Editors' Comments to Author **

Editor: Henheik, Prisca
Comments to the Author:
Many thanks for the transfer to our journal. I enjoyed reading the manuscript.

[DL-SW-1]

Date Sent: 24-Feb-2022

☒ Close Window

An assessment of zinc fluxes by analyzing monthly, weekday, and weekend levels in a river

Pertiwi Andarani[1,2*], Kuriko Yokota[3], Takanobu Inoue[3], Hardianti Alimuddin[2], Nguyen Minh Ngoc[3]

[1]Department of Environmental Engineering, Diponegoro University, Semarang, Central Java, Indonesia
[2]Graduate Program of Architecture and Civil Engineering, Toyohashi University of Technology, Toyohashi, Aichi, Japan
[3]Department of Architecture and Civil Engineering, Toyohashi University of Technology, Toyohashi, Aichi, Japan

*Correspondence: Pertiwi Andarani, M.Eng, Graduate Program of Architecture and Civil Engineering, Toyohashi University of Technology, Toyohashi, Aichi, 441-8580, Japan
e-mail: andarani@ft.undip.ac.id

Abstract

Unlike other heavy metals, zinc (Zn) is indispensable to life but also poses environmental risks to aquatic organisms. Aichi Prefecture has the Japan's fourth-highest discharges of Zn into water bodies. As a major industrial area, it is likely that the Zn fluxes in Aichi's water bodies originate from industrial wastewater. This study evaluated the spatial-temporal and diel variability of Zn concentrations and loads on sunny days during weekdays and weekends in the Umeda River, Aichi. The most downstream point was considered as the most polluted section according to the monthly survey (dissolved Zn: 0.0046–0.0719 mg/L, particulate Zn: 0.42–2.01 mg/g) that varied between seasons (coefficient of variation: 95% for dissolved Zn; 53% for particulate Zn). The total Zn concentrations on weekdays (0.015–0.043 mg/L) at the most downstream point exhibited much higher concentrations than those during the weekends (undetected–0.032 mg/L). Given the dissolved phase of these Zn levels (77 ± 11%), it is apparent that the Zn concentrations were discharged into the Umeda River by industrial facilities on weekdays. The total Zn loading on weekdays (56 g/km^2/day) was approximately three times higher than that on weekends (18 g/km^2/day). At least 67% of the total Zn (37 g/km^2/day) and 70% of the dissolved Zn (35 g/km^2/day) fluxes from industrial point sources were potentially discharged on weekdays.

Abbreviations: CRM, certified reference material; CV, coefficient of variation; D-Zn, Zn in dissolved phase; D-Fe, Fe in dissolved phase; EQS, environmental quality standards; n.d, not detected (Fe ≤ 0.01 mg/L, Zn ≤ 0.0005 mg/L); NES, national effluent standards; POC, particulate organic carbon; PRTR, Pollutant Release and Transfer Register; P-Fe, Fe in particulate phase; P-Zn, Zn in particulate phase; Q, river discharge; SD, standard deviation; SS, suspended solids; st., sampling station; US-EPA, United States - Environmental Protection Agency; WFD, Water Framework Directive; H, water level; Water Framework Directive; ww, industrial wastewater

Keywords: Flux; Heavy metal; Industrial wastewater; Organic matter; Zinc

1 Introduction

Zinc (Zn) is the third most-produced non-ferrous metal in Japan, after copper and aluminum.[1] Based on the Pollutant Release and Transfer Register (PRTR) data from 2018,[1] approximately 641 tons of Zn compounds (water-soluble) are annually discharged into public bodies of water in Japan, and it is the third most-released chemical in these water bodies.[1] The most common use of Zn around the world is galvanizing, to protect steel against corrosion, which accounts for over 50% of the Zn annually produced, followed by ZnO, die casting, a vulcanizing agent of tire rubber, and other application to produce brass, tiles, ceramics, glass[2], dyes[3], battery[4], and electronic products[5]. Unlike other heavy metal pollution, Zn does not pose a health risk to humans indirectly exposed through the environment, whereas direct exposure to ZnO and $ZnCl_2$ may indeed carry potential health risks.[6,7] On the other hand, humans, animals, plants, and even microorganisms, require Zn for development and growth; hence, it is indispensable to life processes.[8] However, its chronic toxicity to aquatic life has been observed when it reaches a specific threshold, which is often as a result of Zn pollution.[7,9–12]

In riverine ecosystems, Zn is typically present in its most ecotoxic form, i.e., Zn^{2+}.[13,14] Consequently, in European countries, stringent environmental quality standards (EQS) on the total fraction of Zn have set the range from 0.008 to 0.125 mg/L, depending on the water hardness.[15] Specifically, in the UK and Wales, the standards for dissolved bioavailable Zn have been set at 10.9 µg/L, plus ambient background concentrations that depend on catchments/groups thereof.[16] Meanwhile, in order to protect freshwater aquatic life, the US Environmental Protection Agency (US-EPA) set the criterion for total recoverable Zn to 0.047 mg/L as a 24-hour average.[17] In order to protect the aquatic ecosystem, in 2003, Japan enacted EQS for Zn of 0.03 mg/L as the annual mean value. Nevertheless, according to the Ministry of Environment of Japan, in 2019, 19 riverine sites breached the EQS, in contrast to lakes and the ocean, which all of them were below the EQS threshold.[18] Naito et al.[19] also noted that Aichi Prefecture did not show a clear Zn reduction trend after 2002. Based on the PRTR Data[1], from 2001 to 2019, Aichi Prefecture had the fourth-largest Zn discharges into public bodies of water (approximately 38 tons/year) after Osaka, Tokyo, and Kanagawa Prefecture.

Due to irregular effluent discharges into the river, a high concentration could be temporarily found, and was possibly missed, during the monitoring period. Anthropogenic activities tend to be more intensive during weekdays, apart from in recreational areas. In this case, a survey conducted measuring weekdays and weekends featured different Zn concentrations. Previous research revealed that surveys undertaken on weekdays exhibited higher concentrations of contaminants.[20,21] Furthermore, Andarani et al.[20] found that throughout 2017, Zn concentrations in the most downstream point in the Aizumame River, located in Aichi Prefecture, exceeded the EQS. The Zn fluxes in the Aizumame River were found to mostly originate from point sources of industrial wastewater, which contributed about 77.3 g/km^2/day.[20] The Zn concentrations in the river may also become elevated due to point or non-point (diffuse) sources.[19,22] Given that industrial facilities do not operate on weekends and holidays, it was possible to estimate the contribution of industrial point sources to the river by comparing the measurement results between weekdays and weekends.

Moreover, hydrological and biogeochemical processes may influence dynamic diel fluctuation in metal concentrations, including Zn.[23] Bourg and Bertin[24] and Brick and Moore[25] were the first to report a diel cycle of Zn concentrations in near-neutral and alkaline rivers, followed by Nimick et al.[26] The diel Zn cycles had already been intensively observed in several near-neutral environments and rivers in the United States[25,27–31], United Kingdom[23], and France[24,32,33]. However, comparisons of diel Zn concentrations during weekdays and weekends remain scarce. The sources of Zn could also be traced by narrowing down activities conducted on weekdays and weekends. The spatial and temporal variations of Zn are also necessary to be assessed in order to verify the input of point sources and seasonal changes. In addition, iron (Fe) was also compared to Zn variation; hence, the impact of anthropogenic activities to the riverine Zn levels could be identified. Fe is a naturally occurring element in river[34] and the adsorption of Zn on the Fe hydroxides might occur in the surface water[26,28]. Therefore, the main objective of this study was to assess the spatial-temporal and diel variation of Zn in a near-neutral stream located in Aichi Prefecture, Japan, particularly on weekdays and weekends.

2 Materials and Methods

2.1 Sampling Site

For this study, monthly surveys (nine months) and a 24-hour survey were conducted in the Umeda River, Aichi Prefecture, Japan. Both surveys were undertaken during low flow on a sunny day (no precipitation on two previous days and the sampling event). The Umeda River is a second grade river with a catchment area of 86.6 km^2, crossing Toyohashi City and flowing into Mikawa Bay.

Figure 1 shows the sampling stations in the study area. Station 5 (st.5) was below Hatakeda Bridge, located at the most downstream point without tidal influence. With st.5 as the outlet, the watershed area accounted for 43.7 km^2. This station was the sampling point for both the monthly survey the hourly survey (the weekdays and weekend sampling). St.1, 2, 3, 4, and 5 were in the Umeda River, with its corresponding tributaries, such as st.31 (Ochiai River) and st.21–23 (Sakai River). The sampling stations (st.2 and st.3) in the Umeda River were located approximately 10 meters before the confluence of its respective tributary.

Land use significantly comprises urban areas (29.8%), including residential, commercial, and industrial areas, mostly located in the catchment's upper-middle reach, particularly in the vicinity of st.2, st.3, and st.4. The industrial areas discharge the wastewater to the Sakai River, which were identified as point sources ww-A, ww-B, and ww-C contributed Zn to the st.23. An industrial area adjacent to the Ochiai River was identified and the water samples were taken at st.31. However, the largest area of land use is agricultural (48.8%), consisting of paddy (5.8%) and other crops (43.0%),[35] including cabbage and tea.

2.2 Samples Collection

2.2.1 Monthly Survey

The monthly survey was conducted for nine months in August 2019 and from December 2019 to July 2020. The monthly survey was a single survey per month. The main criteria for selecting the monthly survey day were dry weather (including the previous two days) and undertaken on a weekday. The samples were collected once per day during the daytime, approximately between 09:00 and 14:00 at all riverine sampling stations (st.1–st.5, st.31, and st.21–23) and industrial wastewater sampling points (ww-A, ww-B, and ww-C). The interval period between monthly sampling events ranged from 22 to 43 days (31 days on average).

Approximately two liters of water samples were collected manually using acid-cleaned polypropylene bottles which were also triple rinsed by river water. A triplicate analysis of each sample was conducted, then the average and standard deviation are presented in Figure 2. The river discharges were measured and calculated using a velocity-area method according to Andarani et al.[20]

2.2.2 Hourly Survey (during Weekdays and the Weekend)

Clear sunny weather events on weekdays (Wednesday-Thursday) and weekends (Saturday-Sunday) were monitored in the first week of February 2020 (winter) at st.5. The winter season has the lowest precipitation levels throughout the year, indicating that the point sources may substantially affect Zn fluxes into the stream. An autosampler (Teledyne ISCO-6712, US) was deployed and programmed to take one-liter samples hourly between 17:00 and 16:00. Twenty-four bottles (holding up to a liter of water) made of polypropylene were collected for each sampling event. The water samples were taken by polypropylene pipe and pumped by a peristaltic pump with a purge phase in order to avoid cross-contamination. A one-liter water sample was taken manually using acid-cleaned polypropylene bottles at 17:00 on the second day in order to obtain data over 25 hours. All of the autosampler and polypropylene sample bottles were triple rinsed with deionized water and oven-dried prior to each sampling procedure. The water samples were taken after all samples were collected in autosampler bottles and then immediately filtered and pre-treated in the laboratory within 48 hours.

2.3 River Discharge Measurement Methods

The water level-discharge (H-Q) equation model[36] was used to estimate river discharge (Q) of the Umeda River at Hatakeda Bridge. The water level (H) over every hour at Hamamichi Station, located about one kilometer from Hatakeda Bridge, was obtained from the River Division of Aichi Prefectural Construction Bureau. According to the model, the water level at Hamamichi Station needed to be converted to that at Hatakeda Bridge.[36]

2.4 Analytical Methods

2.4.1 Suspended Solids (SS)

Two types of membranes were used to obtain the SS, namely GF/F membranes and cellulose acetate membranes. The GF/F (0.7 µm, glass microfiber filters, Whatman™, UK) membrane was further used to measure particulate organic carbon (POC), whereas cellulose acetate membrane (Advantec®, Japan) was utilized to obtain filtrate as a dissolved fraction of Zn (D-Zn) and Fe (D-Fe). The SS on the cellulose acetate membrane was further digested to obtain the particulate Zn and Fe fraction.

For the measurement of suspended solids (SS) concentrations, 100 ml water samples were filtered using wash-dried and pre-weigh GF/F membranes. The GF/F membranes were oven-dried at 400 °C before filtering the samples. The concentrations were determined by subtracting the weight of the membrane with SS (oven-dried at 105 °C) and the pre-weight divided by filtered volume. This filtration was performed three times, and the mean values were calculated for further assessment in this study.

2.4.2 Zn and Fe Concentrations

Five-hundred milliliters of water was filtered using a cellulose acetate membrane (0.2 µm, Advantec®, Japan). The filter bottle was triple rinsed with deionized water prior to the filtration of each sample. The first 100 ml of filtrate was then discarded to avoid cross-contamination. With respect to the D-Zn and D-Fe, 1.0 ml of concentrated HNO_3 (ultrapure analytical reagent, Tamachemicals Co., Ltd., Japan) was added to 100 ml of filtrate and then digested. The digestion required heating up the samples on a hotplate to a temperature of 205 °C for 20 minutes. In order to prevent contamination, the first five milliliters of the filtrate were discarded. The metals in suspended solids were analyzed based on the US-EPA Method 3050B with addition of concentrated HCl (suprapure guaranteed reagent, Wako Pure Chemical Corporation, Japan). The concentrations of Zn and Fe were then measured three times using the flame and graphite furnace atomic absorption spectrometry instrument (AA-7000 Shimadzu, Shimadzu Corporation, Japan) with four calibration standards (the detection limits of Zn and Fe were 0.0005 mg/L and 0.01 mg/L, respectively).

Re-validation of the standard solutions every six sample measurements for the calibration curves was necessary for quality assurance and quality control (QA/QC) purposes. The method blanks were analyzed together with a set of the six samples. The Zn and Fe contained in the procedures and reagents were not detected according to the method blank. The triplicate analysis of all samples showed that the coefficient of variation (CV) was less than 7% both for Zn and Fe concentrations of the water samples. The CVs of particulate sample measurements were up to 12%. The analytical procedure was checked using a certified reference material (CRM) for trace elements (National Metrology Institute of Japan, CRM 7202-c No. 0356). The recovery rates for the analytical procedure were 84–92% (Zn) and 93–99% (Fe).

All of the reagents used were of ultrapure and standard solutions were prepared using ultrapure water. All glass and plasticware for the elemental analysis were soaked in 1% HNO_3 (Kanto Chemical, Co., Inc., Japan) solution overnight. They were then triple rinsed using ultrapure water, with the glass and plasticware used dried prior to use.

2.3.3 Particulate Organic Carbon (POC)

POC concentrations of the SS on GF/F membranes were measured using an NC analyzer instrument (Sumigraph NC-22A, Sumika Chemical Analysis Service, Ltd., Japan), with suspended solids on the GF/F membrane combusted at a temperature of 600 °C. The acetalinide standard (Wako Pure Chemical Industries, Japan) was measured to create the calibration curves. Less than 30 µm of drift and zero noise of the instrument baselines were required to conduct the sample measurement. The triplicate measurement and method blank were then carried out for quality assurance and quality control purposes.

2.4 Data Analysis

The statistical description was used to discuss the study results, mainly the mean, standard deviation (SD), the range of the values, and CV. A Pearson correlation (*r*) analysis was used to clarify the relationship among the parameters, calculated using a Minitab® 19. A probability (*p*) value of less than 0.05 was considered a statistically significant correlation.

3 Results and Discussion

3.1 Spatial and Temporal Variation of Zn and Fe Concentrations

The results of Zn and Fe concentrations in the monthly survey from August, December 2019, to July 2020 are illustrated in Figure 2a and b, respectively. The summary of all parameters (SS, Zn, Fe, POC, and river discharge) can be seen in Table 1. Generally, the Zn levels varied among seasons as indicated by high CVs (50–155% for P-Zn; 33–202% for D-Zn). The Zn concentrations, mainly in dissolved form, tended to increase toward the downstream direction. The Zn clearly exhibited high concentrations, namely st.3, 4, 5, and 23. In the vicinity of st.23, three manufacturing industries discharge their wastewater to the Sakai River. The detailed wastewater measurement results (Zn and Fe) are illustrated in Figure 3. Based on the Figure 3a, the total fraction of Zn concentrations in the wastewater did not exceed the national effluent standards (NES) of 2.0 mg/L. However, the Zn remained high downstream part of the Umeda River. Other point sources of Zn were not identified during the preliminary survey. The Zn concentrations in st.3, 4, and 5 exceeded the environmental quality standards (EQS) in December 2019 and February 2020. In March 2020, the EQS exceedances were also observed in st.4 (February, March), 3 (February, March), and 23 (February). From December 2019 to April 2020, relatively high Zn concentrations were obtained in almost all sampling stations. Figure 2a clearly shows that the Zn levels were considerably higher in winter and spring than those in summer. According to Andarani et al.[37], the annual value of total fraction of Zn at st.5 in the 12-month survey exceeded the EQS.

Fe measurement is necessary as the possible natural element in river water. Fe could be considered as the inorganic fraction of SS, whereas the POC indicates the organic part of SS. The Fe levels during the monthly survey did not exhibit clear tendencies to the downstream (Figure 2b). Seasonal variation of Fe levels was not observed. Nevertheless, relatively high Fe concentrations were observed in June 2020 (summer). The dynamic of Zn and Fe concentrations in river water could be influenced by wastewater input or leaching from soil or sediment. Metal redistribution between particulate and dissolved fractions might occur due to the changes in physiochemical properties. The pH was near neutral (7.17 ± 0.17) and relatively stable (CV < 6%), which might not be considered as the main possible cause of Zn variability.

The diel concentrations of Zn during weekdays and weekends over the 24 hours from 17:00 to 17:00 on the next day are shown in Figure 4a and b, respectively. The total Zn concentrations during weekdays exhibited much higher concentrations than those on weekends. Table 2 summarizes the descriptive statistics of the hourly surveys both during weekdays and the weekend. On weekdays, the total Zn concentrations ranged from 0.015 to 0.043 mg/L (0.029 ± 0.008 mg/L), while during weekends, the total Zn varied from undetected to 0.032 mg/L (0.010 ± 0.007 mg/L). Figure 4a illustrates that the total Zn reached its highest value (0.043 mg/L) at 3:00. The discharge peaked in the afternoon at 1.01 m^3/s, whereas the total Zn decreased gradually and then slightly increased to 0.026 mg/L. The lowest concentration was reached at 13:00 (0.015 mg/L) in a relatively higher river discharge of 0.96 m^3/s. Figure 4a also clearly shows that the diel Zn fluctuations of both the total Zn and D-Zn were synchronous to the river discharge variations. The higher the river discharges, the lower the Zn concentrations owing to dilution, as was also seen in Nimick et al.[26], Gozzard et al.[22], and Resongles et al.[32] The increases in the detected minimum to maximum concentrations of D-Zn (the amplitude) during weekdays and weekends were 293% and 1778%, respectively. Meanwhile, different amplitudes were observed in other studies, namely 140–326% for total Zn[23], 800% for dissolved and colloidal Zn[29], and almost 1000% for D-Zn in the least buffered stream.[38] Various possible processes that promote diel variation of Zn in a non-acidic stream were summarized in Gammons et al.[28]

Meanwhile, the diel Zn fluctuations exhibited a similar pattern during the weekend, but with lower concentration values, as is shown in Figure 4b. During the weekend, the total Zn concentrations ranged from undetected (14:00, 16:00, and 17:00 on Sunday) to 0.032 mg/L (at 20:00 on Saturday). The D-Zn always presented over 24 hours on weekdays, whereas it exhibited lower concentrations from 12:00 to 17:00 on Sunday. The weekend's D-Zn concentration fluctuations were relatively similar to those during weekdays at a smaller magnitude, except at 23:00. The D-Zn fractions over the weekend (56 ± 23%, 9–98%) were lower than those during weekdays (77 ± 11%, 57–98%). It is apparent that Zn was introduced to the mainstream of the Umeda River on weekdays as a result of anthropogenic activities. Le Pape et al.[39] also found that natural trace elements, including Zn, were carried by suspended solids, whereas the dissolved phase contribution increased along the river toward the lower reach, where the urbanization was located.

The total Zn concentrations were still present in the daytime during the weekend, but below the detection limit (0.0005 mg/L) at 14:00, 16:00, and 17:00. It is possible that a few industrial facilities still operated on Saturday, but the diel cycles might also have occurred when, during the daytime, the concentrations became lower than at night. The total Zn concentrations varied in a similar trend of discharges, from 19:00 to 23:00 and 04:00 to 08:00.

Because these high temporally resolved samplings (weekdays and the weekend) were conducted in clear weather, the differences in concentrations could be due to the influence of the Zn point sources. The EQS of the total Zn in Japan were set to an annual average value of 0.03 mg/L. All of the Zn concentrations during the weekend remained low and did not exceed 0.03 mg/L. However, the Zn concentrations exceeded the EQS from 19:00 on Wednesday to 09:00 on Thursday, with the exception at 23:00. Although the value of 0.03 mg/L is a standard of the annual average value, a possible breach could be assumed during the 24-hour period. This diel variation of the Zn should be considered in order to determine the time of water quality monitoring for river water quality assessments.

Figure 4c and d show the Fe concentrations in both the total and dissolved fractions. There was no difference between the total Fe concentrations on weekdays (0.147 ± 0.028 mg/L, 0.104–0.215 mg/L) and during the weekend (0.180 ± 0.101 mg/L, 0.125–0.648 mg/L). In contrast to the Zn concentrations, the Fe did not exhibit a distinct variation on either weekdays or during the weekend. The Fe concentrations showed no discernible variability in either the daytime or at night, even though the Zn concentrations clearly demonstrated a diel fluctuation. However, during the daytime, the D-Fe concentrations were relatively lower than during the night, which could only be seen on weekdays. Because the Umeda River has near-neutral pH, the diurnal variation in the D-Fe concentrations due to photoreduction was not observed, in contrast to previous studies.[40,41]

3.2 Adsorption of Zn in the Umeda River

Anthropogenic activities conducted during weekdays could include industrial operations, mining, traffic, municipal solid waste treatment, and agriculture. Domestic activities performed every day could also have contributed to the elevated Zn[19] during both weekdays and the weekend. However, in this study, only the Zn concentrations on weekdays significantly increased. The elevated Zn concentrations could be originated from agricultural runoff[42–44], road runoff[45], traffic emissions, and atmospheric deposition[1,46,47], as well as natural occurrences[48], industrial[20,43,49], and mining activities.[22,23,50] The increased Zn may come from point sources because the survey was undertaken in clear weather (no runoff discharges). Hence, there was no wet deposition or surface runoff introduced into the Umeda River. Sakata et al.[46] found that the Zn fluxes into Tokyo Bay substantially originated from atmospheric depositions. However, most of the Zn fraction in the Umeda River was in dissolved form, especially during the night; hence, it is unlikely that the source was from the dry atmospheric deposition of particulate matter. According to the monthly survey in the Umeda River, the most downstream station had the highest mean of total Zn concentrations over 14 months from August 2019 to July 2020. By considering the land use of the Umeda River catchment, the Zn contamination could be contributed from the wastewater point sources of manufacturing industries located in the upper-middle stream area. Three manufacturing industries discharging their treated wastewater to Sakai River, a tributary of Umeda River, were identified, but the Zn concentrations (0.036–0.079 mg/L) did not exceed the NES of 2.0 mg/L during the 14-month sampling period.[37] However, the instream Zn levels of the Umeda River after the confluence of the Sakai River were relatively higher than those in the upstream section.[37]

Adsorption is considered an important chemical process that influences the mobility of trace elements in natural waters due to its kinetically rapid reactions.[28] In light of previous studies[28,31], a suitable mineral or organic surface is necessary to cause trace elements to be adsorbed on the surface, such as organic matter and hydrous metal oxides (Fe or Mn). The case in Osaka Bay also showed that Zn was mostly concentrated in the Fe-Mn oxide fraction.[51] The present study also observed a strong correlation between P-Zn and P-Fe at st.5 on weekdays, weekends, and during the monthly survey ($r = 0.703$; $p < 0.001$). A correlation between P-Zn and P-Fe ($r = 0.430$; $p < 0.05$) was also observed in the sediment of the lower Seyhan River.[52]

Aquatic organisms and anthropogenic sources may contribute the organic-rich SS to the riverine system.[53] A strong positive correlation between P-Zn and POC has been found in a previous study.[54] In this study, the P-Zn concentrations also strongly correlated to the corresponding POC concentrations ($r = 0.456$; $p < 0.001$) at st.5 during the monthly and hourly survey. At st.5, Zn generally presented in a dissolved phase (67 ± 20%) during the monthly and hourly survey. Compared to the industrial wastewaters, the D-Zn (61 ± 25%) also exhibited a higher proportion than P-Zn. Nevertheless, the particulate fraction of Zn might be adsorbed by both the organic matter and Fe oxides.

3.3 Zn Fluxes Comparisons

According to Figure 6, the cumulative Zn loadings from the most upstream (st.1, 0.0002–0.0657 kg/day) to the downstream (st.5, 1.56–9.91 kg/day) significantly increased, except those in March 2020. The Zn fluxes attenuation was only observed in March where the Zn input declined after approximately 7.59 km. The cumulative D-Zn fluxes also exhibited a similar trend from upstream to downstream of the Umeda River. The input of tributary st.23 led to a further increase in st.3 (particularly in the dissolved phase), substantially observed in December 2019 and January–April 2020. However, it should be noted that in December, the D-Zn significantly contributed to cumulative Zn loading at st.5 because of the Zn input that could not be identified. The Ochiai River (st.31) did not have a substantial Zn loading to the Umeda River.

The total and D-Zn fluxes varied greatly over 24 hours during both time events (Figure 7). The mean of the total Zn (97.15 ± 25.43 g/h) and D-Zn load (87.45 ± 23.72 g/h) on weekdays was much higher than that during the weekend (32.20 ± 23.30 g/h and 26.26 ± 16.31, respectively). On weekdays, the maximum load of the total Zn (142.72 g/h) was present at 3:00, whereas the minimum (50.94 g/h) occurred at 13:00 during daytime and in the presence of a higher river discharge. As for the weekend, a similar pattern whereby the loads decreased during the daytime was also observed. However, the fluctuation exhibited a lower magnitude than that during the weekend. The total Zn load reached its highest value of 106.93 g/h and declined until it was below the detection limit at 14:00, whereas the D-Zn load had remained low since 12:00. Two peaks of total Zn appeared during the weekend due to the increased P-Zn concentrations. At 20:00, the suspended solids may have contributed to the elevated Zn, which also included Fe. Meanwhile, at 23:00, the D-Zn significantly influenced the total Zn load.

The total daily Zn loading on weekdays (28.0 g/km^2/day) was approximately three times higher than during the weekend (9.3 g/km^2/day). These differences could originate from the industrial point sources. The industrial point sources may have contributed at least 67% of the total Zn fluxes (37 g/km^2/day) and 70% of the D-Zn fluxes (35 g/km^2/day) on weekdays. Meanwhile, the industrial area along the Aizumame River in the Aichi Prefecture, discharged approximately 68 g/km^2/day (57%) in 2017[20]; much higher than in the case of the Umeda River. Wen et al.[50] estimated that non-mining industrial activities contributed 3.8 g/km^2/day (Chongqing region) and 0.3 g/km^2/day (Wuhan region) of D-Zn to the Yangtze River according to a survey from July 2007 (flood season) and January 2008 (dry season). In 2000, the Zn input from industrial discharges in the Rhine catchment area in Germany were 1.0 g/km^2/day.[55] It implies that the Japanese river catchments (Aizumame and Umeda) relatively have substantially higher Zn yield from industrial area than other rivers (Yangtze and Rhine) that has much larger catchment area.

4 Concluding Remarks

This study assessed the spatial and temporal variations of Zn and Fe for nine months as well as its diel weekday and weekend levels comparison on sunny days in the Umeda River in Japan’s Aichi Prefecture. The increasing Zn levels were observed from upstream to downstream section of the Umeda River. The industrial wastewater point sources were identified in the Ochiai River and Sakai River, the tributaries of the Umeda River. However, only the Sakai River contributed a significant Zn input to the Umeda River.

The hourly survey was undertaken to verify the impact of anthropogenic activities conducted during weekdays. The distinct differences in the Zn concentrations and loads between weekdays and the weekend indicated that the industrial wastewater impacted the elevated Zn concentrations on weekdays. Meanwhile, the variations in the Fe concentrations on weekdays were relatively similar to those during the weekend. Organic matter and hydrous Fe oxides might have adsorbed the Zn in the riverine system, as was indicated by a strong correlation between P-Zn, P-Fe, and POC concentrations at the most downstream sampling station (st.5). The elevated Zn concentrations in the Umeda River were mostly contributed (more than 67%) by point sources of industrial wastewater based on the hourly survey.

Conflict of Interest

The authors have declared no conflict of interest.

Acknowledgment

This study was funded by the Research Institute for Technological Science and Innovation (RITI) of Toyohashi University of Technology, Japan. The authors would like to sincerely thank Ms. Widyastuti Kusuma and Mr. Ryosuke Suzuki for their assistance in performing the field survey.

References

[1] Ministry of Environment of Japan, *Pollutant Release and Transfer Register (PRTR) Data Page*, **2021**.

[2] F. Jones, D. Bankiewicz, M. Hupa, *Fuel* **2014**, *117*, 763.

[3] O. A. Oguntade, M. T. Adetunji, J. O. Azeez, *J. Environ. Chem. Eng.* **2015**, *3*, 2875.

[4] H. J. Mansoorian, A. H. Mahvi, A. J. Jafari, *Sep. Purif. Technol.* **2014**, *135*, 165.

[5] R. A. Wahaab, F. A. Alseroury, *Int. J. Environ. Sci. Technol.* **2019**, *16*, 47.

[6] H. Autrup, P. Calow, W. Dekant, H. Greim, H. Wojciech, C. Janssen, B. Jansson, H. Komulainen, O. Ladefoged, J. Linders, I. Mangelsdorf, M. Nuti, A. Steenhout, J. Tarazona, E. Testai, M. Vighi, M. Viluksela, *Scientific Committee on Health and Environmental Risks Opinion on: Risk Assessment Report on Zinc Environmental Part*, European Commission, Brussels **2007**.

[7] C. W. M. Bodar, M. E. J. Pronk, D. T. H. M. Sijm, *Integr. Environ. Assess. Manag.* **2005**, *1*, 301.

[8] C. T. Chasapis, C. A. Spiliopoulou, A. C. Loutsidou, M. E. Stefanidou, *Arch. Toxicol.* **2012**, *86*, 521.

[9] P. Amoatey, M. S. Baawain, *Water Environ. Res.* **2019**, *91*, 1272.

[10] S. Hatakeyama, *Hydrobiologia* **1989**, *174*, 17.

[11] J. Jensen, M. M. Larsen, J. Bak, *Environ. Pollut.* **2016**, *214*, 334.

[12] M. Seto, S. Wada, S. Suzuki, *Chemosphere* **2013**, *90*, 1091.

[13] A. Gogoi, G. G. Tushara Chaminda, A. K. J. An, D. D. Snow, Y. Li, M. Kumar, *Chemosphere* **2016**, *163*, 322.

[14] International Zinc Association, "Zinc in the Environment: an Introduction," can be found under https://www.zinc.org/wp-content/uploads/sites/4/2015/01/Zinc-in-the-Environment-Understanding-the-Science_web.pdf, **2014**.

[15] Water Framework Directive, *The River Basin Districts Typology, Standards and Groundwater Threshold Values (Water Framework Directive) (England and Wales) Directions*, **2010**.

[16] Water Framework Directive, *The Water Framework Directive (Standards and Classification) Directions (England and Wales)*, **2015**.

[17] US-EPA, *Ambient Water Quality Criteria for Zinc*, United States, **1980**.

[18] Ministry of the Environment of Japan: Water and Air Environment Bureau, *2019 Public Water Quality Measurement Results*, **2020**.

[19] W. Naito, M. Kamo, K. Tsushima, Y. Iwasaki, *Sci. Total Environ.* **2010**, *408*, 4271.

[20] P. Andarani, K. Yokota, M. Saga, T. Inoue, Y. Matsumoto, *River Res. Appl.* **2020**, *36*, 1286.

[21] B. Petrie, L. Lopardo, K. Proctor, J. Youdan, R. Barden, B. Kasprzyk-Hordern, *Sci. Total Environ.* **2019**, *650*, 900.

[22] E. Gozzard, W. M. Mayes, H. A. B. Potter, A. P. Jarvis, *Environ. Pollut.* **2011**, *159*, 3113.

[23] S. Rudall, A. P. Jarvis, *Water Sci. Technol.* **2012**, *65*, 164.

[24] A. C. M. Bourg, C. Bertin, *Water. Air. Soil Pollut.* **1996**, *86*, 101.

[25] C. M. Brick, J. N. Moore, *Environ. Sci. Technol.* **1996**, *30*, 1953.

[26] D. A. Nimick, C. H. Gammons, T. E. Cleasby, J. P. Madison, D. Skaar, C. M. Brick, *Water Resour. Res.* DOI: 10.1029/2002WR001571.

[27] J. L. Barringer, T. P. Wilson, Z. Szabo, J. L. Bonin, J. M. Fischer, N. P. Smith, *Environ. Geol.* **2008**, *53*, 1183.

[28] C. H. Gammons, D. A. Nimick, S. R. Parker, *Appl. Geochemistry* **2015**, *57*, 35.

[29] B. A. Kimball, R. L. Runkel, *Mine Water Environ.* **2009**, *28*, 274.

[30] M. J. Kurz, V. de Montety, J. B. Martin, M. J. Cohen, C. R. Foster, *Chem. Geol.* **2013**, *358*, 61.

[31] D. A. Nimick, C. H. Gammons, S. R. Parker, *Chem. Geol.* **2011**, *283*, 3.

[32] E. Resongles, C. Casiot, R. Freydier, M. Le Gall, F. Elbaz-Poulichet, *J. Geochemical Explor.* **2015**, *158*, 132.

[33] P. J. Superville, E. Prygiel, O. Mikkelsen, G. Billon, *Sci. Total Environ.* **2015**, *506–507*, 585.

[34] H. Guo, A. S. Barnard, *J. Mater. Chem. A* **2013**, *1*, 27.

[35] JAXA (Japan Aerspace Exploration Agency), “ALOS2-2/ALOS Science Project,” can be found under https://www.eorc.jaxa.jp/ALOS/en/lulc/lulc_jpn.htm, **2021**.

[36] K. Yokota, T. Inoue, M. Yokokawa, R. Shimoyama, Y. Okubo, *Environ. Sci.* **2013**, *26*, 140 (in Japanese).

[37] P. Andarani, H. Alimuddin, R. Suzuki, K. Yokota, T. Inoue, *IOP Conf. Ser. Earth Environ. Sci.* **2021**, *623*, 012064.

[38] L. S. Balistrieri, D. A. Nimick, C. A. Mebane, *Sci. Total Environ.* **2012**, *425*, 155.

[39] P. Le Pape, S. Ayrault, C. Quantin, *J. Hydrol.* **2012**, *472–473*, 99.

[40] R. T. Kay, G. E. Groschen, G. Cygan, D. H. Dupré David H., *Chem. Geol.* **2011**, *283*, 99.

[41] A. B. Sullivan, J. I. Drever, *J. Hydrol.* **2001**, *252*, 237.

[42] X. Ke, S. Gui, H. Huang, H. Zhang, C. Wang, W. Guo, *Chemosphere* **2017**, *175*, 473.

[43] F. F. Xu, Z. Liu, Y. Cao, L. Qiu, J. Feng, F. F. Xu, X. Tian, *Catena* **2017**, *150*, 9.

[44] Y. Yang, Z. He, Y. Lin, E. J. Phlips, P. J. Stoffella, C. A. Powell, *Water Environ. Res.* **2009**, *81*, 40.

[45] N. Hüffmeyer, J. Klasmeier, M. Matthies, *Sci. Total Environ.* **2009**, *407*, 2296.

[46] M. Sakata, M. Narukawa, K. Marumoto, *Atmospheric and Riverine Inputs of Trace Substances to Tokyo Bay*, **2005**.

[47] L. Sörme, R. Lagerkvist, *Sci. Total Environ.* **2002**, *298*, 131.

[48] D. A. dos Reis, A. da Fonseca Santiago, L. P. Nascimento, H. M. P. Roeser, *Environ. Sci. Pollut. Res.* **2017**, *24*, 7456.

[49] G. Zhen, Y. Li, Y. Tong, L. Yang, Y. Zhu, W. Zhang, *Environ. Sci. Pollut. Res.* **2016**, *23*, 8410.

[50] Y. Wen, Z. Yang, X. Xia, *Appl. Geochemistry* **2013**, *31*, 199.

[51] M. M. Billah, E. Kokushi, S. Uno, *Water. Air. Soil Pollut.* **2019**, *230*, DOI 10.1007/s11270-019-4196-8.

[52] O. I. Davutluoglu, G. Seckin, C. B. Ersu, T. Yilmaz, B. Sari, *Clean - Soil, Air, Water* **2011**, *39*, 185.

[53] G. Huang, M. Zhang, C. Liu, L. Li, Z. Chen, *Sci. Total Environ.* **2018**, *635*, 913.

[54] J. Zeng, G. Han, *Ecol. Indic.* **2020**, *118*, 106723.

[55] S. Fuchs, U. Scherer, T. Hillenbrand, F. Marscheider-Weidemann, H. Behrendt, D. Opitz, *Emissions of*

Heavy Metals and Lindane into River Basins of Germany, Federal Environmental Agency (Umweltbundesamt), Berlin, **2002**.

Figure Legends

Figure 1. Sampling stations in the Umeda River and its tributaries

Legend 1

Legend

□ Watershed
━ River
● Riverine sampling station (st.)
▲ Wastewater sampling station (ww)

Elevation (m)
350
−3

Figure 2. (a) Zn and (b) Fe concentrations in the river water during the monthly survey. “P” represents particulate metal in the suspended solids and “D” denotes concentrations in dissolved phase (<0.2 µm). Undetected levels were assumed to have half of the detection limit concentration (0.00025 mg/L for Zn and 0.005 mg/L for Fe). Error bars are regarded as standard deviations of the triplicate analysis.

Legend 2a

▨ st.1 (P-Zn) ▨ st.2 (P-Zn) ▨ st.3 (P-Zn) ▨ st.4 (P-Zn) ▨ st.5 (P-Zn) ▨ st.21 (P-Zn) ▨ st.22 (P-Zn) ▨ st.23 (P-Zn) ▨ st.31 (P-Zn)
■ st.1 (D-Zn) ■ st.2 (D-Zn) ■ st.3 (D-Zn) ■ st.4 (D-Zn) ■ st.5 (D-Zn) ■ st.21 (D-Zn) ■ st.22 (D-Zn) ■ st.23 (D-Zn) ■ st.31 (D-Zn)
— EQS

Legend 2b

▨ st.1 (P-Fe) ▨ st.2 (P-Fe) ▨ st.3 (P-Fe) ▨ st.4 (P-Fe) ▨ st.5 (P-Fe) ▨ st.21 (P-Fe) ▨ st.22 (P-Fe) ▨ st.23 (P-Fe) ▨ st.31 (P-Fe)
■ st.1 (D-Fe) ■ st.2 (D-Fe) ■ st.3 (D-Fe) ■ st.4 (D-Fe) ■ st.5 (D-Fe) ■ st.21 (D-Fe) ■ st.22 (D-Fe) ■ st.23 (D-Fe) ■ st.31 (D-Fe)

Figure 3. (a) Zn and (b) Fe concentrations in the wastewater

Legend 3a

■ ww-A (P-Zn) ■ ww-B (P-Zn) ■ ww-C (P-Zn)
■ ww-A (D-Zn) ■ ww-B (D-Zn) ■ ww-C (D-Zn)

Legend 3b

■ ww-A (P-Fe) ■ ww-B (P-Fe) ■ ww-C (P-Fe)
■ ww-A (D-Fe) ■ ww-B (D-Fe) ■ ww-C (D-Fe)

Figure 4. (a) The total and dissolved Zn concentrations during weekdays; (b) The total and dissolved Zn concentrations during the weekend; (c) The total and dissolved Fe concentrations during weekdays; (d) The total and dissolved Fe concentrations during the weekend in February 2020. The error bars represent the standard deviations. The gray shaded area indicates the night-time hours (from 18:00 to 06:00).

Legend 4a

■ Total Zn concentration □ Dissolved Zn concentration — River discharge (Q) during weekdays

Legend 4b

■ Total Zn concentration □ Dissolved Zn concentration — River discharge (Q) during weekend

Legend 4c

■ Total Fe concentration □ Dissolved Fe concentration — River discharge (Q) during weekdays

Legend 4d

■ Total Fe concentration □ Dissolved Fe concentration — River discharge (Q) during weekend

Figure 5. Correlations between (a) Fe and Zn concentrations in particulate phase (P-Fe and P-Zn); (b) particulate organic carbon (POC) and P-Zn concentrations at st.5 during the monthly and hourly surveys (all correlations were significantly strong positive relationship)

Figure 6. Cumulative Zn load in the Umeda River and instream load of the tributary: (a) total Zn; (b) dissolved Zn

Legend 6

□ Aug ● Dec ✕ Jan ■ Feb ▲ Mar
◆ Apr ○ May + Jun ✳ Jul

Figure 7. (a) Total and dissolved Zn load (a) on weekdays; (b) during the weekend. The gray shaded area indicates night-time hours (from 18:00 to 06:00).

Legend 7a

● Total Zn load during weekdays ▲ Dissolved Zn load during weekdays

Legend 7b

● Total Zn load during weekend ▲ Dissolved Zn load during weekend

Table 1. Summary of water analysis results in the monthly survey

		Sampling station								
		st.1	**st.2**	**st.3**	**st.4**	**st.5**	**st.31**	**st.21**	**st.22**	**st.23**
D-Zn (mg/L)	Minimum	n.d.	0.0036	0.0056	0.0055	0.0046	0.0019	n.d.	n.d.	0.0052
	Maximum	0.0236	0.0278	0.0207	0.0396	0.0719	0.0139	0.0224	0.0273	0.0154
	Mean	0.0038	0.0117	0.0119	0.0198	0.0214	0.0057	0.0067	0.0047	0.0111
	SD	0.0076	0.0082	0.0056	0.0122	0.0204	0.0041	0.0077	0.0085	0.0036
	CV	202%	70%	47%	62%	95%	71%	114%	180%	33%
P-Zn (mg/L)	Minimum	n.d.	0.0010	0.0011	0.0029	0.0028	0.0023	n.d.	0.0007	0.0020
	Maximum	0.0039	0.0083	0.0261	0.0097	0.0142	0.0074	0.0122	0.0051	0.0334
	Mean	0.0010	0.0036	0.0100	0.0053	0.0062	0.0044	0.0027	0.0027	0.0093
	SD	0.0016	0.0028	0.0094	0.0027	0.0039	0.0019	0.0041	0.0017	0.0094
	CV	163%	75%	93%	50%	63%	44%	155%	64%	101%
D-Fe (mg/L)	Minimum	0.052	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Maximum	0.118	0.179	0.180	0.085	0.096	0.081	n.d.	0.103	0.171
	Mean	0.081	0.075	0.102	0.058	0.040	0.028	n.d.	0.050	0.098
	SD	0.026	0.063	0.053	0.024	0.037	0.033	n.d.	0.033	0.044
	CV	32%	83%	52%	41%	92%	117%	-	67%	45%
P-Fe (mg/L)	Minimum	0.055	0.035	0.079	0.095	0.102	0.105	0.035	0.059	0.043
	Maximum	0.259	0.183	0.580	0.349	0.169	0.434	1.259	0.615	0.197
	Mean	0.111	0.108	0.207	0.159	0.133	0.194	0.213	0.220	0.147
	SD	0.065	0.051	0.153	0.078	0.026	0.102	0.394	0.201	0.049
	CV	58%	47%	74%	49%	19%	52%	185%	92%	33%
POC (mg/g)	Minimum	27	25	67	153	141	73	85	95	132
	Maximum	281	528	283	297	283	312	330	207	422
	Mean	124	275	176	215	228	194	175	159	234
	SD	83	148	70	48	52	74	81	47	99
	CV	67%	54%	40%	22%	23%	38%	46%	30%	43%
SS (mg/L)	Minimum	2.3	3.1	5.6	5.2	3.6	1.4	1.3	2.7	4.5
	Maximum	38.5	9.6	11.3	9.0	8.6	20.2	23.3	19.1	18.1
	Mean	9.3	6.5	7.9	6.8	6.1	8.2	6.1	7.4	9.1
	SD	11.6	1.9	2.0	1.2	1.7	5.2	6.8	6.4	4.3
	CV	126%	29%	26%	18%	28%	63%	111%	86%	48%
River discharge (m^3/s)	Minimum	0.01	0.04	0.33	0.57	0.76	0.11	0.01	0.07	0.17
	Maximum	0.06	0.11	0.86	1.18	1.36	0.30	0.05	0.21	0.42
	Mean	0.03	0.08	0.51	0.79	1.06	0.18	0.03	0.14	0.28
	SD	0.02	0.02	0.18	0.19	0.18	0.06	0.02	0.06	0.07
	CV	68%	30%	36%	24%	17%	33%	64%	40%	27%

n.d. : not detected (detection limit: 0.0005 mg/L for Zn and 0.01 mg/L for Fe)

CV, coefficient of variation; D-Zn, Zn in dissolved phase; D-Fe, Fe in dissolved phase; POC, particulate organic carbon; P-Fe, Fe in particulate phase; P-Zn, Zn in particulate phase; SD, standard deviation; SS, suspended solids; st., sampling station

Table 2. Summary of water analysis results in the hourly survey

	T-Zn (mg/L)	D-Zn (mg/L)	T-Fe (mg/L)	D-Fe (mg/L)	POC (mg/L)	SS (mg/L)	River discharge (m^3/s)
Weekdays							
Minimum	0.015	0.014	0.104	0.034	112	5.5	0.89
Maximum	0.043	0.040	0.215	0.086	315	21.5	1.01
Mean	0.029	0.026	0.147	0.055	172	9.9	0.93
SD	0.008	0.007	0.028	0.014	50	3.5	0.03
CV	27%	29%	19%	26%	29%	35%	3%
Weekends							
Minimum	n.d.	n.d.	0.125	0.036	102	7.3	0.89
Maximum	0.032	0.0178	0.648	0.063	163	59.7	0.96
Mean	0.010	0.0079	0.180	0.051	131	14.1	0.93
SD	0.007	0.0049	0.101	0.007	17	10.0	0.02
CV	73%	62%	56%	14%	13%	71%	2%

n.d. : not detected (detection limit: 0.0005 mg/L for Zn and 0.01 mg/L for Fe)

CV, coefficient of variation; D-Zn, Zn in dissolved phase; D-Fe, Fe in dissolved phase; POC, particulate organic carbon; SD, standard deviation; SS, suspended solids; st., sampling station; T-Fe, Fe in total fraction; T-Zn, Zn in total fraction;

Dear Dr. Prisca Henheik,

We really appreciate the opportunity to re-submit our manuscript entitled “An assessment of zinc fluxes by analyzing monthly, weekday, and weekend levels in a river”, for your consideration. We are grateful for the insightful the comments on our manuscript. We added several sentences to address the question raised by the reviewer. In addition, we do our best to improve our manuscript for clarity as indicated below. All changes in the manuscript are marked in red. We also updated the graphical abstract and added the layman’s description.

=====================

<i>Reviewer: 1

Comments to the Author

In its current, revised form, the article is definitely more readable than its previous form. However, it is still missing here to extend to zinc concentrations analysis on weekdays and weekends over a longer period of time. Please answer my question below:

Did the monthly Zn tests results presented in Figure 2 include a single sample analysis, or is it the result as the average of several tests per month? If a single survey was selected, how was the day chosen for sample collection, except 2 days of dry weather before sampling?

Editor-in-Chief: Henheik, Prisca

Comments to the Author:

Please address the comment before submitting the revised version.

</i>

Author response:

Thank you for your comment and question. We undertook the monthly survey once per month (single survey). The sampling day was selected according to the weather (sunny/dry) and on a weekday. The minimum interval period was 22 days between each sampling event. Due to weather restriction, it is difficult to conduct the survey in exactly every 30-day. In this study, the interval period ranged from 22 to 43 days. We added this explanation in the manuscript (line 114–116).

Original text (line 114–115):

The surveys were undertaken on sunny days (daytime) when no precipitation occurred, including the previous two days.

Added text (line 114–116):

The surveys were undertaken on sunny days (daytime weekday) when no precipitation occurred, including the previous two days. The interval period between monthly sampling events ranged from 22 to 43 days (31 days on average).

As previously mentioned, we made several changes in the manuscript as follows:

1. Sampling station ID modification

We modified the sampling station ID in sequence from upstream (st.1) to downstream (st.5). We believe it will make the reader easily understand where the upstream and downstream located.

The modification:

st.1 → st.5 (most downstream in the Umeda River)

st. 2 → st.4

st.4 → st.2

st.5 → st.1 (most upstream in the Umeda River)

st. 41 → st.23 (most downstream in the Sakai River)

st.42 → st.22

st. 43 → st.21 (most upstream in the Sakai River)

ww-A → ww-C

ww-C → ww-A

All changes are marked in red.

Accordingly, we also updated the Graphical Abstract, Figure 1, Figure 2, Figure 3, Figure 6, and Table 1.

----

2. We updated the watershed area with st.5 (most downstream) as the outlet, instead of the outlet at Mikawa Bay for the load per km² calculation. We believe that the watershed area at st.5 is more accurate for the calculation of Zn loading per km² watershed. Consequently, the land use area proportion is also changed. In addition, we updated the land use area using ALOS2-2/ALOS Science Project (Japan Aerospace Exploration Agency, 2021) data which recently updated in 2021.

Added text (line 98–99):

With st.5 as the outlet, the watershed area accounted for 43.7 km².

Original text (line 103–105):

Land use is dominated by urban areas (21.8%), including residential, commercial, and industrial areas, mostly located in the catchment's upper-middle reach, particularly in the vicinity of st.2, st.3, and st.4.

Revised text (line 104–106):

Land use significantly comprises urban areas (29.8%), including residential, commercial, and industrial areas, mostly located in the catchment's upper-middle reach, particularly in the vicinity of st.2, st.3, and st.4.

Original text (line 107–109):

However, the largest area of land use is agricultural (66.6%), extensively consisting of paddy (17.5%) and other crops (49.1%), including cabbage and tea.^[35]

Revised text (line 108–110):

However, the largest area of land use is agricultural (48.8%), consisting of paddy (5.8%) and other crops (43.0%),^[35] including cabbage and tea.

Original reference (line 414):

[35] J. Mbabazi, T. Inoue, K. Yokota, M. Saga, <i>J. Environ. Chem. Eng.</i> 2019, <i>7</i>, 102960.

Revised reference (line 413–414):

[35] JAXA (Japan Aerspace Exploration Agency), “ALOS2-2/ALOS Science Project,” can be found under https://www.eorc.jaxa.jp/ALOS/en/lulc/lulc_jpn.htm, 2021.

----

3. We slightly change the sequence of Table 2 to highlight the T-Zn and D-Zn data.

Original Table 2:

SS (mg/L) | D-Fe (mg/L) | T-Fe (mg/L) | D-Zn (mg/L) | T-Zn (mg/L) | POC (mg/L) | River discharge (m³/s) |

Revised Table 2:

T-Zn (mg/L) | D-Zn (mg/L) | T-Fe (mg/L) | D-Fe (mg/L) | POC (mg/L) | SS (mg/L) | River discharge (m³/s) |

----

4. We revised the D-Zn load standard deviation on weekday, D-Zn load average on weekend. We also revised total Zn flux per km², proportion and dissolved Zn flux per km² because we used the watershed area at st.5. We apologized for this confusion. We also added the proportion of industrial wastewater input in the Aizumame River to easily compare between the Umeda River and the Aizumame River.

Original text (line 24–27):

The total Zn loading on weekdays (28.0 g/km²/day) was approximately three times higher than that on weekends (9.3 g/km²/day). At least 67% of the total Zn (18.7 g/km²/day) and 72% of the dissolved Zn (18.1 g/km²/day) fluxes from industrial point sources were potentially discharged on weekdays.

Revised text (line 24–27):

The total Zn loading on weekdays (56 g/km²/day) was approximately three times higher than that on weekends (18 g/km²/day). At least 67% of the total Zn (37 g/km²/day) and 70% of the dissolved Zn (35 g/km²/day) fluxes from industrial point sources were potentially discharged on weekdays.

Original text (line 318–320):

The mean of the total Zn (97.15 ± 25.43 g/h) and D-Zn load (87.45 ± 23.61 g/h) on weekdays was much higher than that during the weekend (32.20 ± 23.30 g/h and 36.17 ± 7.78, respectively).

Revised text (line 320–321):

The mean of the total Zn (97.15 ± 25.43 g/h) and D-Zn load (87.45 ± 23.72 g/h) on weekdays was much higher than that during the weekend (32.20 ± 23.30 g/h and 26.26 ± 16.31, respectively).

Original text (line 332–335):

The industrial point sources may have contributed at least 67% of the total Zn fluxes (18.7 g/km²/day) and 72% of the D-Zn fluxes (18.1 g/km²/day) on weekdays. Meanwhile, the industrial area along the Aizumame River in the Aichi Prefecture, discharged approximately 77.3 g/km²/day in 2017^[20]; much higher than in the case of the Umeda River.

Revised text (line 334–337):

The industrial point sources may have contributed at least 67% of the total Zn fluxes (37 g/km²/day) and 70% of the D-Zn fluxes (35 g/km²/day) on weekdays. Meanwhile, the industrial area along the Aizumame River in the Aichi Prefecture, discharged approximately 68 g/km²/day (57%) in 2017^[20]; much higher than in the case of the Umeda River.

----

5. We list all author names in all references, including Reference [6]. We also revised the title because the previous one was incorrect.

Original reference [6] (line 371–373):

H. Autrup, P. Calow, W. Dekant, H. Greim, H. Wojciech, C. Janssen, B. Jansson, H. Komulainen, O. Ladefoged, J. Linders, et al., <i>Scientific Committee on Health and Environmental Risks Opinion on: Risk Assessment Report on Calcium Fluoride Environmental Part</i>, Brussels, 2011.

Revised reference [6] (line 372–375):

H. Autrup, P. Calow, W. Dekant, H. Greim, H. Wojciech, C. Janssen, B. Jansson, H. Komulainen, O. Ladefoged, J. Linders, I. Mangelsdorf, M. Nuti, A. Steenhout, J. Tarazona, E. Testai, M. Vighi, M. Viluksela, <i>Scientific Committee on Health and Environmental Risks Opinion on: Risk Assessment Report on Zinc Environmental Part,</i> European Commission, Brussels 2007.

----

6. We deleted the year and volume of journal in Reference [26].

Original reference [26] (line 402–403):

[26] D. A. Nimick, C. H. Gammons, T. E. Cleasby, J. P. Madison, D. Skaar, C. M. Brick, <i>Water Resour. Res.</i> 2003, <i>39</i>, DOI 10.1029/2002WR001571.

Revised reference [26] (line 402–403):

[26] D. A. Nimick, C. H. Gammons, T. E. Cleasby, J. P. Madison, D. Skaar, C. M. Brick, <i>Water Resour. Res. </i>DOI: 10.1029/2002WR001571.

----

7. We updated the reference [1] and [18] so that the manuscript has the most recent data.

Original text (line 59–61):

Nevertheless, according to the Ministry of Environment of Japan, in 2008, 118 riverine sites breached the EQS, in contrast to lakes and the ocean, which only had one and seven sites, respectively, that exceeded the EQS threshold.[18]

Revised text (line 59–60):

Nevertheless, according to the Ministry of Environment of Japan, in 2019, 19 riverine sites breached the EQS, in contrast to lakes and the ocean, which all of them were below the EQS threshold.[18]

Original reference [18] (line 392–393):

[18] Ministry of the Environment: Water and Air Environment Bureau, <i>2008 Public Water Quality Measurement Results</i>, 2009.

Revised reference [18] (line 392–393):

[18] Ministry of the Environment of Japan: Water and Air Environment Bureau, <i>2019 Public Water Quality Measurement Results</i>, 2020.

Original text (line 62–64):

Based on the PRTR Data^[1], from 2001 to 2018, Aichi Prefecture had the fourth-largest Zn discharges into public bodies of water (approximately 38 tons/year) after Osaka, Tokyo, and Kanagawa Prefecture.

Revised text (line 62–64):

Based on the PRTR Data^[1], from 2001 to 2019, Aichi Prefecture had the fourth-largest Zn discharges into public bodies of water (approximately 38 tons/year) after Osaka, Tokyo, and Kanagawa Prefecture.

Original reference [1] (line 365–366):

[1] Ministry of Environment of Japan, <i>Pollutant Release and Transfer Register (PRTR) Data Page</i>, 2018.

Revised reference [1] (line 367):

[1] Ministry of Environment of Japan, <i>Pollutant Release and Transfer Register (PRTR) Data Page</i>, 2021 .

----

8. We deleted ‘regression’ because we think the Pearson correlation is adequate to show the relationship.

Original text (line 188–189):

A Pearson correlation (r) analysis and regression were used to clarify the relationship among the parameters, calculated using a Minitab® 19.

Revised text (line 190–191):

A Pearson correlation (r) analysis was used to clarify the relationship among the parameters, calculated using a Minitab® 19.

----

9. We removed ‘in Japan’ to make the sentence more concise.

Original text (line 256–258):

However, the Zn concentrations in Japan exceeded the EQS from 19:00 on Wednesday to 09:00 on Thursday, with the exception at 23:00.

Revised text (line 258–260);

However, the Zn concentrations exceeded the EQS from 19:00 on Wednesday to 09:00 on Thursday, with the exception at 23:00.

----

10. We revised the sentence for clarity.

Original text (line 266–267):

The Fe concentrations showed no discernible variability on either the weekdays or weekends, even though the Zn concentrations clearly demonstrated a diel fluctuation.

Revised text (line 268–269);

The Fe concentrations showed no discernible variability in either the daytime or at night, even though the Zn concentrations clearly demonstrated a diel fluctuation.

--

Original text (line 272–273):

Anthropogenic activities conducted during weekdays could include industrial operations, mining, urban runoff, traffic emissions, atmospheric deposition, and agricultural runoff.

Revised text (line 274–275);

Anthropogenic activities conducted during weekdays could include industrial operations, mining, traffic, municipal solid waste treatment, and agriculture.

--

Original text (line 280–281):

Sakata et al.^[46] found that the Zn fluxes substantially contributed to atmospheric depositions into Tokyo Bay.

Revised text (line 282 – 283):

Sakata et al.^[46] found that the Zn fluxes into Tokyo Bay substantially originated from atmospheric depositions.

----

11. We changed the name of autosampler bottle for clarity.

Original text (line 128–131):

All of the ISCO and polypropylene sample bottles were triple rinsed with deionized water and oven-dried prior to each sampling procedure. The water samples were taken after all samples were collected in ISCO bottles and then immediately filtered and pre-treated in the laboratory within 48 hours.

Revised text (line 130–133):

All of the autosampler and polypropylene sample bottles were triple rinsed with deionized water and oven-dried prior to each sampling procedure. The water samples were taken after all samples were collected in autosampler bottles and then immediately filtered and pre-treated in the laboratory within 48 hours.

======================

Once again, we made every effort to cautiously revise the manuscript. We look forward to hearing from you regarding our submission and to respond to any further questions and comments you may have.

Sincerely yours,

Pertiwi Andarani

CLEAN - Soil, Air, Water

Decision Letter (clen.202100151.R2)

From: phenheik@wiley-vch.de

To: andarani@ft.undip.ac.id, andarani@gmail.com, yokota@ace.tut.ac.jp, inoue.takanobu.zy@tut.jp, hardianti.alimuddin94@gmail.com, nguyen.minh.ngoc.hw@tut.jp

CC: phenheik@wiley-vch.de

Subject: Decision on Manuscript # clen.202100151.R2 for "CLEAN"

Body: *** HTML-Vorlage
<B>FETT</B>
<U>UNTERSTRICHEN</U>
<I>KURSIV</I>
****

Dear Dr. Andarani:

I am pleased to inform you that your manuscript, "An assessment of zinc fluxes by analyzing monthly, weekday, and weekend levels in a river", is now acceptable for publication in CLEAN.

With the acceptance of your manuscript the final version of your manuscript and all uploaded files (Figures, Tables, Graphical Abstract, Supporting Information - if provided) in ScholarOne will be used for the subsequent publication process.

Should you have any images related to your article that you believe it might be appropriate for use on the cover of CLEAN - Soil, Air, Water, please email us your layout suggestions with a short description.
For details on cover image preparation please visit http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1863-0669. Each PDF of a published article in an issue will show the cover and will increase visibility of your article. Please be aware that the additional service costs to produce a cover will need to be partially covered by you.

Copyright Information
Collection of Copyright Transfer Agreement (CTA) form: Your article cannot be published until the publisher has received the appropriate signed license agreement. The corresponding author will receive an email from Wiley´s Author Services system which will ask them to log in and will present them with the appropriate license for completion after the paper is processed for production.

As the next step, your paper will go to production and you will receive a galley proof by e-mail in due course. Once you have corrected the proof, the paper will then be published online via Wiley Online Library.

Thank you supporting CLEAN. I look forward to seeing more of your work in the future.

Sincerely,

Dr. Prisca Henheik
Editor-in-Chief
CLEAN

P.S. – You can help your research get the attention it deserves! Wiley Editing Services offers professional video abstract and infographic creation to help you promote your research at www.wileyauthors.com/eeo/promotion. And, check out Wiley’s free Promotion Guide for best-practice recommendations for promoting your work at www.wileyauthors.com/eeo/guide.

** Referee(s)' and Editors' Comments to Author **

Editor: Henheik, Prisca
Comments to the Author:
Many thanks for the transfer to our journal. I enjoyed reading the manuscript.

[DL-SW-1]

Date Sent: 24-Feb-2022

Close Window