別紙４－１（課程博士（英文））

Date of Submission（month day, year）： July 9, 2021

Department of Architecture and Civil Engineering	Student ID Number	D189503
Applicant's name	Pertiwi Andarani	

Supervisors	Kuriko Yokota Takanobu Inoue Shigeru Kato

Abstract（Doctor）

Title of Thesis	Spatio-temporal variation assessment of zinc concentrations and loads and its source identification in rivers

Approx. 800 words

Zinc (Zn) is crucial for life and plays a vital part in organisms' biological activities (humans, animals, and plants). Zn, the fourth-most frequent metal in usage, is widely used in the industrial sector to create products. Zn is the third-most produced non-ferrous metal in Japan and the third-most released chemical in water bodies. Zn has become one of the most critical considerations concerning worldwide water quality, including in Japan, with the role of preserving aquatic life. Since 2003, the Japanese Ministry of the Environment has established an environmental quality standard (EQS) for Zn in surface water (0.030 mg/L) to conserve aquatic life. However, multiple Japanese rivers still could not comply with the EQS in 2019. Therefore, this study aimed to assess the spatial and temporal variation and the source identification of Zn in near-neutral rivers.

This study was conducted in two rivers, affected mainly by urban areas (manufacturing industries) and agriculture located in the vicinity of Aizumame River and the Umeda River, Aichi, Japan. This study consisted of three survey types, i.e., monthly baseflow survey (on sunny days), hourly baseflow survey (on sunny days during weekday and weekend), and hourly stormflow survey (during a rain event). The monthly baseflow survey and the hourly baseflow survey were undertaken in the Aizumame River and the Umeda River. Because a further investigation of the possible Zn source and the underlying factors of the Zn variability was needed, more detailed water parameter measurement was conducted in the Umeda River. Water parameters [Zn, Fe (iron), particulate organic carbon (POC), temperature, pH, electroconductivity, cations, and anions] and riverbed sediments (Zn, Fe, and POC in fine sand, medium sand, and coarse sand) were measured accordingly. The metal content was measured using atomic absorption spectrometry. Hierarchical cluster analysis (HCA), flow analysis, pearson correlation, principal component factor loading analysis (PCFA), load and discharge curve (L-Q model), and end member mixing analysis (EMMA) were performed to assess the association among the parameters and to identify the potential Zn sources.

In the Aizumame River, at the two downstream sampling stations (A4 = 0.059 mg/L; A5 = 0.055 mg/L), the EQS was breached in 2017. Zn levels considerably varied from undetected to 0.139 mg/L. Throughout the year, Zn concentrations along the Umeda River fluctuated in spatial and temporal, ranging from 0.002 to 0.090 mg/L. At the most downstream part of the Umeda River, the annual mean concentration value of 0.031 mg/L exceeded the EQS. Anthropogenic activities have likely influenced the riverine Zn levels in

Umeda River.

Most of the Zn concentrations in the river water and wastewater were presented in a dissolved phase in the Umeda River. Seasonal variation also affected the Zn fluctuation in water, in which the highest level was found during the winter and spring. By contrast, in summer and autumn, the Zn concentrations in the riverbed sediment were relatively higher than in other seasons.

The HCA of observation revealed that the middle-lower reach of the Aizumame River and Umeda River has been polluted by Zn. Based on the flow analysis, the industrial area at the downstream section contributed 44% (in summer) to 88% (in winter) of total Zn loading in the Aizumame River. However, in the Umeda River, the industrial Zn input (61%) was clearly observed only in spring. A further data analysis of water parameters in the Umeda River was thus conducted to whether the variability was affected by the water parameters. According to the HCA of variable in the Umeda River, the cations and anions presence are generally less significant in term of metal transport and behavior compared to parameters such as pH, organic matter, and the particulate Fe. The dissolved Zn was grouped together with pH, POC, and HCO_3^-. Furthermore, results of cluster variable analysis were verified by PCFA, which shows that the dissolved Zn (together with pH, Na^+, Cl^-, HCO_3^-, POC, Ca^{2+}, and Mg^{2+}) contributed to a varifactor (industrial point sources) which explains about 15% of the total variance. Meanwhile, particulate Zn participated in the varifactor (agricultural sources), representing 17% of total variance. Moreover, particulate Zn and Fe were also involved in the varifactor (inorganic fraction of SS), constituting 8% of the total variance.

The source identification was also confirmed by the hourly survey. The hourly survey conducted in the baseflow during weekday and weekend revealed that the Zn levels were remarkably higher during weekday, indicating that the industrial point sources contributed to the riverine Zn levels both in the Aizumame River (57%) and the Umeda River (67%). The Fe was potentially originated from natural occurrences. During the stormflow, the Fe concentrations were mainly governed by the suspended solids. The Zn concentrations remained high following the discharge fluctuation in the stormflow and had four subsequent peaks indicating the sources were ubiquitous. Nevertheless, at the end of the stormflow, the Zn source might have been relatively reduced, as shown by lower concentrations. Although the Zn was likely from non-point sources according to the L-Q model, several data points did not fit the prediction interval of the regression line. Using the baseflow and stormflow loads comparison and the EMMA, approximately 74% of the Zn loadings were released from point sources and the rest was originated from non-point sources. Not only industrial discharges but also anthropogenic non-point sources should be adequately managed in order to maintain the Zn level below the toxic threshold level to the aquatic organisms.