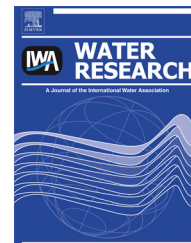


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# Application of fluorescence spectroscopy using a novel fluoroionophore for quantification of zinc in urban runoff

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## ABSTRACT

Fluorescence spectroscopy has great potential for on-site and real-time monitoring of pollutants in aquatic environments; however, its application to environmental aquatic samples has been extremely limited. In this study, a novel fluoroionophore based on a BODIPY-terpyridine conjugate was developed and applied to determine Zn concentrations in urban runoff. The fluoroionophore selectively bound to Zn<sup>2+</sup> in water, which led to an instant red-shift of the fluorescence peak of the fluoroionophore from 539 nm to 567 nm that could be seen by the naked eye. Zn concentrations could be quantified using the ratio of fluorescence intensities, and the detection limit was 9 µg/L, which is sufficiently low for environmental aquatic samples. To demonstrate applicability of the method to environmental samples, we measured Zn concentrations in urban runoff samples with a complex matrix (~60 mg/L dissolved organic carbon and ~20 mS/cm electrical conductivity). The total and dissolved fractions of Zn in the samples could be determined by fluorescence spectroscopy and its relative error was estimated to be less than 30% by inductively coupled plasma-atomic emission spectroscopy analysis. The proposed method is rapid and easy-to-use with simple pretreatment for Zn determination in environmental aquatic samples with complex matrices.

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## 1. Introduction

Rapid urbanization is a global phenomenon that is often associated with adverse environmental effects. In urban

environments, contaminants from vehicles and buildings accumulate on road surfaces until they are washed off into local aquatic systems by rainfall events, where they compromise water resources. In such areas, reuse and recycling of water may be needed to enable sustainable water

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management (Bischel et al., 2012). Accordingly, on-site and real-time monitoring technologies are necessary to measure contaminant levels and ensure water quality. Heavy metals are one of the most hazardous pollutants in aquatic environments. Zn is a common metal that is widely used for industrial applications in chemical and alloyed products, fabricated metal products, and paper products (Naito et al., 2010). In recent years, Zn has received increased attention owing to concerns about its toxic effects on aquatic life. In Japan, the environmental quality standard for Zn is 30  $\mu\text{g/L}$  in freshwater (Japanese Ministry of Environment, Environmental quality standards for water pollution). Urban runoff is considered to be one of the main sources of Zn found in surface water (Naito et al., 2010).

Currently, the most common analytical methods for heavy metals including Zn are atomic absorption spectrometry (AAS) and inductively coupled plasma (ICP) spectroscopy (Adeloju and Zhang, 2009; Majedi et al., 2012). Although these methods are precise, they are expensive and often require complex sample preparation. In addition, they are not applicable to continuous on-site monitoring and measure only the total concentration of heavy metals. Simple analytical methods such as colorimetric or electrochemical techniques have recently been developed for rapid detection of heavy metals (Yan and Indra, 2012; Gong et al., 2010). Among these methods, fluorescence spectroscopy has attracted a great deal of attention from environmental engineers owing to its high sensitivity, simplicity, and versatile instrumentation (Lakowicz, 2006). Although fluorescence excitation-emission matrix (EEM) measurements have been employed to monitor water quality, their application to detection of trace amounts of contaminants is limited to monitoring of dissolved organic matter, such as humic-like and protein-like matters (Henderson et al., 2009). In contrast, fluoroionophores are usually used for detection of heavy metals in biochemistry (Domaille et al., 2008). A fluoroionophore is an organic molecular indicator that exhibits quantifiable changes in fluorescence spectra upon binding a particular guest ion. The design and development of novel fluoroionophores remains an active area of research, and various fluoroionophores for heavy metal ions have been reported (Li et al., 2009, 2008; Weng et al., 2009). However, their application for environmental use has been extremely limited. Here, we developed a fluoroionophore for determination of total and dissolved Zn concentrations in urban runoff by fluorescence spectroscopy. The photo-physical properties of the fluoroionophore were also reported. This approach enabled screening of the Zn levels with no complicated pretreatment processes.

## 2. Materials and methods

### 2.1. Urban runoff sampling and testing

Urban runoff samples were collected from heavy traffic areas in four cities in March and April 2012 during rainfall events: Gifu (+35° 26' 54.88", +136° 44' 28.15"), East-Hiroshima (+34° 24' 4.40", +132° 43' 1.43"), Osaka (+34° 43' 50.46", +135° 32' 48.40"), and Tsukuba (+36° 3' 38.05", +140° 7' 11.92"). Samples were preserved in 500-mL polypropylene bottles at 4 °C. All

polypropylene bottles and glassware were previously soaked for at least 24 h in 2 M  $\text{HNO}_3$  and then rinsed thoroughly with Milli-Q water. Following filtration through a 0.45- $\mu\text{m}$ -pore-size membrane, the dissolved organic carbon (DOC) was measured by total organic carbon analyzer (TOC-VCSH; SHIMADZU Corporation, Kyoto, Japan). pH and electrical conductivity (EC) were measured by pH meter (D-54; HORIBA, Ltd., Kyoto, Japan) and EC meter (ES-51; HORIBA, Ltd., Kyoto, Japan). Additionally, 0.45- $\mu\text{m}$ -pore-size cellulose ester membrane was used to fractionate dissolved metals. Nitric acid digestion was performed before metal analysis by ICP/atomic emission spectrometry (AES) [ICPE-9000; SHIMADZU Corporation, Kyoto, Japan]. To accomplish this, each urban runoff sample (9 mL) and concentrated  $\text{HNO}_3$  (1 mL) were added into 10-mL test tubes and samples were then digested on an aluminum heating block with watch glasses at 95 °C for 2.5 h and cooled to room temperature. Following filtration through a 0.45- $\mu\text{m}$ -pore-size membrane, the concentrations of Zn, Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Sb were determined by ICP/AES. These metals were selected because they are generated by motor vehicles (Mahbub et al., 2010). All reported data are the averages of at least three replicates.

### 2.2. Fluorescence spectroscopic measurement

The fluoroionophore designed in our laboratory was synthesized according to a previously described method (Hafuka et al., 2013). Milli-Q water (18.25  $\text{M}\Omega\text{cm}$ ) was used to prepare all aqueous solutions. Stock solutions of fluoroionophore (40  $\mu\text{M}$ ) were prepared by dissolving the fluoroionophore in acetonitrile, while stock solutions of metal ions for calibration were prepared by dissolving appropriate amounts of perchlorate or chloride salts in Tris-HCl buffer. For analysis of total zinc (T-Zn) in actual urban runoff samples, the samples were acidified with HCl to dissolve the complexed Zn.  $\text{HNO}_3$  was not used in this experiment because Tris-HCl buffer was appropriate for our fluoroionophore in terms of fluorescence intensity. Each urban runoff sample (36 mL) and 1 M HCl (2 mL) were added into 50-mL beakers and vigorously mixed at room temperature for 15 min. After mixing, each sample solution was filtered through a 0.45- $\mu\text{m}$ -pore-size membrane to remove suspended solids, after which 1 M NaOH solution was added to neutralize the pH. To measure the dissolved Zn (D-Zn), samples were filtered through a 0.45- $\mu\text{m}$ -pore-size membrane as the sole pretreatment. All spectroscopic measurements were carried out in an aqueous acetonitrile solution ( $\text{CH}_3\text{CN}/\text{H}_2\text{O} = 1/1, \text{v/v}$ ). Test solutions were prepared by adding an appropriate aliquot of the fluoroionophore stock solution into a volumetric flask, followed by 4.5 mL of the pretreated urban runoff samples and 0.5 mL of a Tris-HCl buffer adjusted to pH 7.0, and finally by diluting the solution to 10 mL with acetonitrile. Quartz cells with a cross section of 1 cm  $\times$  1 cm were used for fluorescence and absorption spectroscopic measurements (FP-6600 and V-630; JASCO Corporation, Tokyo, Japan). The excitation and fluorescence slit widths were 5.0 and 6.0 nm, respectively. The detection limit (LOD,  $3\sigma/\text{slope}$ ) and quantification limit (LOQ,  $10\sigma/\text{slope}$ ) for  $\text{Zn}^{2+}$  were determined based on the standard deviation ( $\sigma$ ) of 11 blank solutions (Han et al., 2010). As a natural organic matter (NOM) standard, IHSS Suwannee River NOM (RO

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