

Application of Laser-Induced Fluorescence for EDC monitoring in aquatic system

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Abstract

In order to monitor the levels and seasonal variations of EDCs, samples of the discharged effluent from sewage & wastewater treatment plants and river waters were collected. The target EDCs including bisphenol A and alkylphenols were determined by Laser-induced fluorescence(LIF) as in-situ monitoring technique. The category of EDCs showed similar fluorescence spectra and nearly equal decay time. This point makes it hard to distinguish each EDCs from the EDCs mixture by LIF and LIF results were expressed only by the total EDCs. However, LIF monitoring results and GC-MS results was comparable. The correlation coefficient between EDCs concentration acquired from GC-MS and fluorescence intensity from LIF was significant. This study supports the feasibility of the application of LIF into EDCs monitoring in aquatic system.

Key Words: Endocrine Disrupting Compounds (EDCs), Effluent and river water samples, GC-MS, Laser-induced Fluorescence (LIF)

1. Introduction

For the past several decades, human activities have increased the production of many xenobiotics indicating unknown fates in the natural water system. These chemicals including endocrine disrupting chemicals (EDCs) and persistent organic pollutants (POPs) have been introduced into the aquatic system and organisms through the discharge from industries, manufactures and waste waters. Subsequently it accumulated directly or indirectly in soil and aquatic environment.

As there is a growing interest in the fast, selective and sensitive *in situ* contaminants monitoring in the aquatic environment, fluorescence spectroscopy with laser as light sources has been recognized as a promising analytical tool for in-situ environmental analysis. Several classes of chemical contaminants can be detected at high level of sensitivity by using laser induced fluorescence (LIF) technique in combination with fiber optic guidance of the exciting laser beam and of the induced fluorescence light [1-3]. The

LIF monitoring techniques provide significant advantages; reduced time and cost, bypass of the complicate experimental procedures and portable power independent system. It makes it possible to achieve continuous *in-situ* monitoring.

The objectives of this study are to monitor the environmental EDC levels including bisphenol A and alkylphenols in water samples using LIF and to investigate the feasibility of the LIF application into *in-situ* monitoring of EDCs in the aquatic environment. For the validation of the LIF application to EDC monitoring, the relationship between analytical results of EDC concentrations by GC-MS and LIF intensity was examined for the 15 water samples from sewage & wastewater treatment plants and river system.

2. Materials and methods

Aquatic samples were collected from fifteen sites. Five water samples were collected from local rivers (Youngsan, Geugrak, Hwangryoung River and Watan-chun). Six samples were collected from local sewage treatment plants (Gwangju, GIST, Songdae, Jangsung, Damyang and Hwasoon), and Four samples were also collected from local wastewater treatment plants (Youngam, Gumsung, Dongmeon and Sochon)

The LIF system used in this study is comprised of four part: pulsed UV laser, a fiber-optic probe, a detection unit for time-and spectrally resolved detection of the fluorescence light, and the control and data acquisition unit. A diode laser pumped Nd:YAG laser deliver 7ns pulses at 266nm with energies 40μJ at 100Hz repetition rate. The detection unit is basically an optical multi-channel analyzer with a time resolution of 5ns, which consists of a spectrograph, a gateable image intensifier and a CCD camera. The spectral resolution is determined over a spectral range from 270 to 600nm. The fiber was designed with four 400μm detection fibers around one 600μm excitation fiber. In order to compare the laboratory results from GC-MS with LIF monitoring results, analysis of EDCs was also performed by the GC-MS which consists of a HP 6890 series GC system with a mass selective detector and a HP Vectra XM PC.

In order to acquire the characteristic decay time, wavelength coverage of each EDC, as well as the calibration curve, fluorescence spectra was obtained from single phenol solution and all mixtures solution with 0,0.2, 0.5, 1, 2, 5 mg/l. EDC stock solutions were prepared by dissolving each EDC in dichloromethane. The detection limits of each EDC and total EDCs were calculated from this linear regression. The absolute detection limits were calculated as the sum of the triple standard deviation of the blank(n=8) and the intercept of the calibration plot. Five measurement per each sample from fifteen sites were recorded and averaged to get total fluorescence intensity.

3. Results

The each EDC and total EDCs were measured with LIF sensor. we encounter the some complications in the interpretation of the results. First reason is that the wavelength coverage of each EDC is very similar showing characteristic spectra range from 285 to 355nm with maximum around 308nm. Generally, the difference in fluorescence lifetimes to

distinguish spectrally similar PAHs analytically could be used, but only minor differences were observed in the fluorescence decay times (2.0–2.5ns). Therefore, the EDCs of interest in this study was expressed only the total EDCs intensity including Bisphenol A and alkylphenols in which chlorophenol was not considered because of their negligible fluorescence

The fluorescence spectra of each EDC after 266nm excitation via optical fiber showed quantum yield was definitely different according to phenol type and smaller molecules produce higher quantum yield as alkyl substitution on the aromatic ring induced the change in the extinction coefficient(Fig.1).

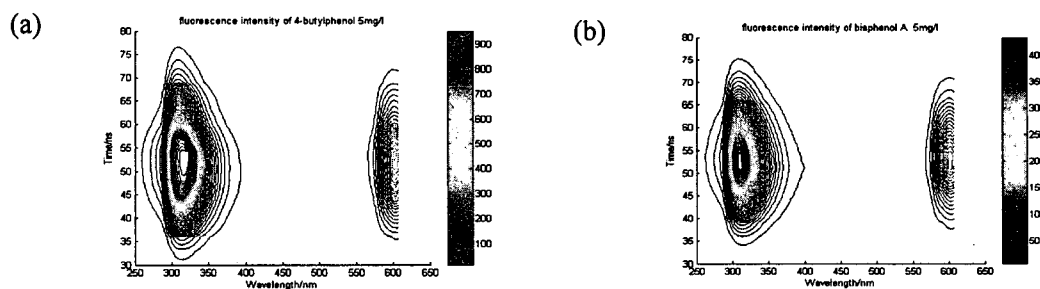


Fig. 1. Fluorescence spectra of (a)4-butylphenol 5mg/l and (b) Bisphenol A 5mg/l

For the calibration and spectra recognition of total EDCs, the wavelength coverage range from 285 to 355nm was considered and the fluorescence intensity was integrated over this wavelength range. The linear correlation of the fluorescence intensity and the concentration were satisfactory for each EDC solution and total mixture solution including 10 phenol of interest in this study($R=0.99$). The detection limit was 31.02 $\mu\text{g/l}$.

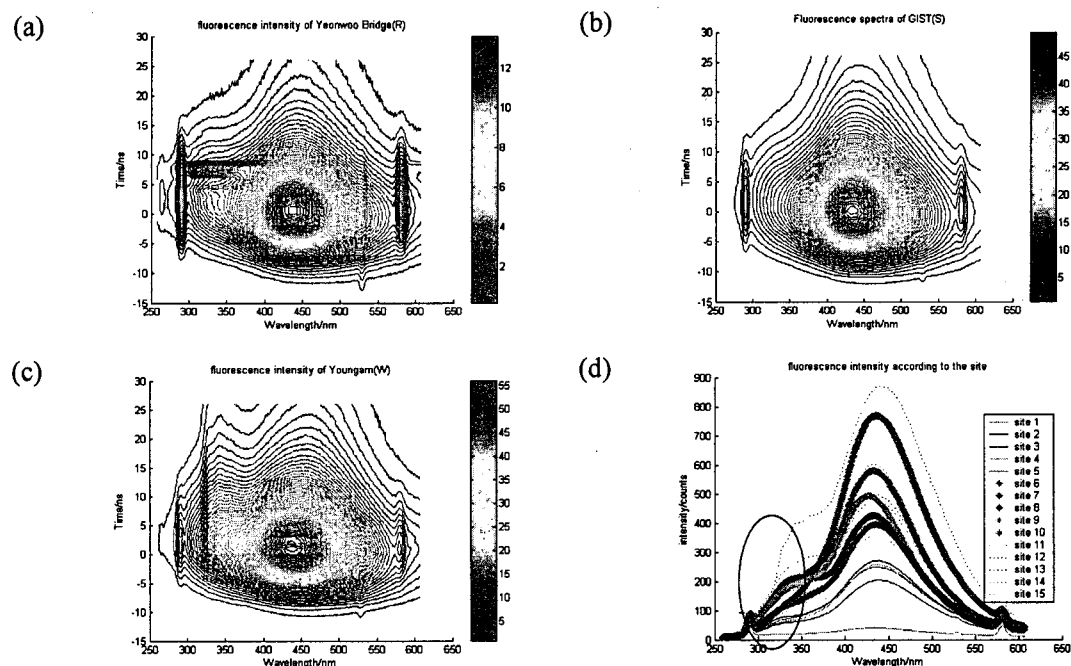


Fig. 2. Fluorescence spectra of EDCs compounds from (a) sample from river, (b) effluent sample from sewage treatment plant, and (c) effluent sample from wastewater treatment plant(d) fluorescence intensity ($I_{F, 285-355}$) according to 15 field sites (2004. 2)

The fluorescence spectra of the water sample from river, sewage and wastewater treatment plant was shown in Fig.2. It revealed short wavelength fluorescence from 285 to 355nm together with rather unstructured fluorescence from 355 to 550nm which was broad and high background fluorescence resulted from humic substance which is also excited by the UV-laser light.. The fluorescence intensity of the total EDCs according to the site categories and seasonal variation was given in Fig.3. Samples in Feb. and Aug.2004 were examined using LIF system. The effluent sample had higher fluorescence intensity implying high EDCs level compared to the river sample. The seasonal variation of EDCs by LIF monitoring supports that the concentration of EDCs in summer was lower than that in winter. The y axis, fluorescence intensity was calculated by subtracting spectra area due to humic substance from total integrated intensity(area) over wavelength coverage(285-355nm).

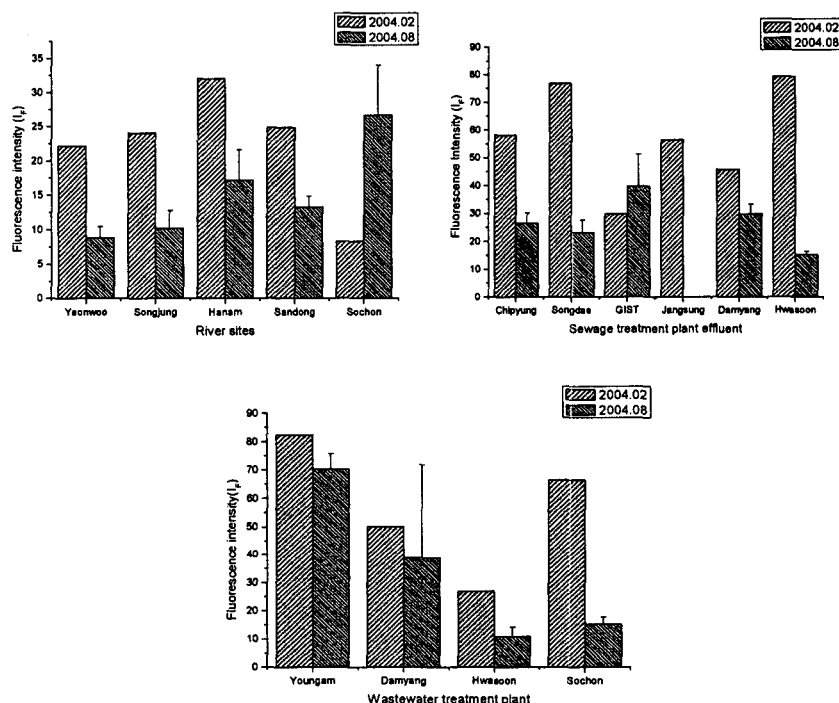


Fig. 3. Seasonal LIF intensity variation of EDCs compounds from fifteen sampling sites.(a) sample from river, (b) effluent sample from sewage treatment plant, and (c) effluent sample from wastewater treatment plant

All data are compared with results of the chemical analysis of the same samples. The relationship between total EDCs concentration and total fluorescence intensity was plotted showing relatively moderate R value(=0.73739). As a further study, semi-quantification with weighting factor for specific EDC having the higher quantum yield will be evaluated, and indicator showing the existence of EDCs in the aquatic system may also be considered as pyren implying the PAH existence in the environmental sample.

4. Conclusions

The monitoring of EDCs including alkylphenols and bisphenol-A from rivers and sewage & wastewater treatment plants was conducted with Laser-induced Fluorescence

(LIF). The concentrations of targeted compounds in most effluent samples were relatively higher than those of river samples. The seasonal variation of target compounds from river and effluent samples showed a lower levels of EDCs in summer than those in winter. Mixtures of EDCs showing similar fluorescence spectra and nearly equal decay times are difficult to be discriminated into the single EDCs components. However, the results of LIF are comparable to the results of GC-MS. Therefore the development of the representative indicator showing EDCs existence can be helpful to assess the EDCs in the water system. The LIF will be used for the potential real-time in-situ monitoring technique of EDCs in the water system

5. Reference

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