Study on the characterization of the water-soluble fluorescent substances in rainwater and airborne particulate matter by using three-dimensional excitation emission spectrometry.

Yuzuru Nakaguchi* and Takashi Tanaka**

**Research Institute for Science and Technology, Kinki University*
***Graduate School of Science and Technology, Kinki University*
Kowakae Higashi-Osaka, 577-8502, Osaka Japan

(Received December 23, 2005)

Abstract

Three-dimensional excitation emission spectrometry was applied to the characterization for the water-soluble fluorescent substances (WSFS) in rainwater and airborne particulate matter. The contour plots of EEM spectra of WSFS in rainwater showed one sharp peak at an excitation wavelength 300-305 nm/emission wavelength 405-415nm.

The fluorescence intensity of WSFS in rainwater decreased with rainfall amount. The peak position of the WSFS in airborne particulate matter was in good agreement with the peak position of WSFS in rainwater. The fluorescent intensity of the water-soluble component was affected by the extraction operating conditions. The fluorescent substances in the water-soluble components of airborne particulate matter were defined as the filtrate obtained using a 0.45 μm membrane filter after immersion in ultrasonic wave irradiation for 20 minutes. The spectrum patterns of rainwater and WSFS in airborne particulate matter were almost coincided with WSFS in the NIES standard reference material.

Keywords: water-soluble fluorescent matter, rainwater, airborne particulate matter, three dimensional excitation-emission spectrometry

1. Introduction

Suspended particulate matter (SPM) from anthropogenic sources such as soot and exhaust fumes has a bad affect on human health. A portion of airborne particles and gaseous matter is eliminated from the atmosphere by rainfall via rainout and/or washout. Thus, rainfall greatly affects the transport of substances from the atmosphere to the land. In recent years, many investigators have reported acid rain. On the other hand, there are few reports on the organic matter in rainwater such as aldehyde and organic acid[1,2], volatile organic compounds[3-5] and lipids[6]. The behavior and source of the organic matter in the atmosphere have not been discussed in detail.

Enrichment factor (EF) have been

applied source analysis for the target element (e.g. Al as a crustal enrichment factor[7-9] and Na as a sea enrichment factor[10,11]. On the other hand, an indicator substance for industrial soot and diesel exhaust particulate sources still has not been decided.

In this study, three-dimensional excitation emission spectrometry was applied to characterization of WSFS in airborne particulate matter. The photochemical properties and origin of the fluorescent substances in the samples were investigated. The possibility of WSFS as an indicator for anthropogenic source was discussed.

2. Experimental

Apparatus and reagent

Three dimensional excitation emission spectra (3D-EEMS) were directly measured in the samples using a Hitachi Model F-4500 scanning spectrofluorometer with a high sensitive cell holder. Dissolved organic carbon (DOC) in the sample solution was analyzed with a Shimadzu TOC-5000 analyzer. A 100 mg dm^{-3} of quinine sulfate stock solution was prepared by dissolving 0.1000g of quinine sulfate in 1000 cm^3 of 0.1 mol dm^{-3} sulfuric acid. A standard solution for the correction of fluorescent intensity was obtained by diluting the stock solution before use. One thousand mgC dm^{-3} of glucose stock solution was prepared by dissolving 0.5004g of glucose in 200 cm^3 of Milli-Q TOC water. The standard solutions for calibration were obtained by diluting the stock solution before use. Milli-Q TOC water was used throughout.

Measurement of 3D-EEMS

Fluorescence measurements were made by making emission scans from 250 to 400 nm, at excitation wavelengths every 5 nm from 300 to 500 nm, with a 5 nm slit width, a PMT voltage of 700 V and scanning speed of 2400 nm min^{-1}. The spectra were corrected for instrumental bias according to the manufacturer's instructions. The relative fluorescent intensities of the samples were expressed in terms of standard quinine sulfate units (QSU). Ten QSU corresponds to the fluorescent intensity of standard quinine sulfate (10 μ g dm^{-3} in 0.1 mol dm^{-3} sulfuric acid solution) at Ex.345nm/ Em.465nm.

Determination of dissolved organic carbon

The sample solution was filtered through a precombusted glass fiber filter (Whatman GF/F). The filtrates were placed in 5 cm^3 glass ampules. The filtrated samples for DOC analysis were acidified by addition of 50 mm^3 of 6 mol dm^3 and bubbling with high purity air for 10 mins at 100 cm^3 min^{-1} to displace any dissolved inorganic carbon. Then, the treated solution was injected into a TOC 5000 analyzer.

Sampling

Rainwater and airborne particulate matter were collected from the roof of Kinki University building. The rainwater was collected in Pyrex glass beakers and the acid rain sampler "Raingoround" (HORIBA). The airborne particulate matter was collected with a GF/F set on the plastic filter holder (ADVANTEC PP047) by suction with an air pump at a constant flow rate 10 L min^{-1} for 5 hr

3. Results and discussion

3.1 Rainwater 3D-EEMS

The rainwater 3D-EEMS were measured directly using the samples collected from the roof of the university. After sampling, rainwater samples were filtered as soon as possible by 0.7 μm glass fiber filter (Whatman GF/F), then it analyzed by spectrofluorometer. The contour plots are shown in Fig.1. One sharp peak was observed at Ex.305/Em.405nm.

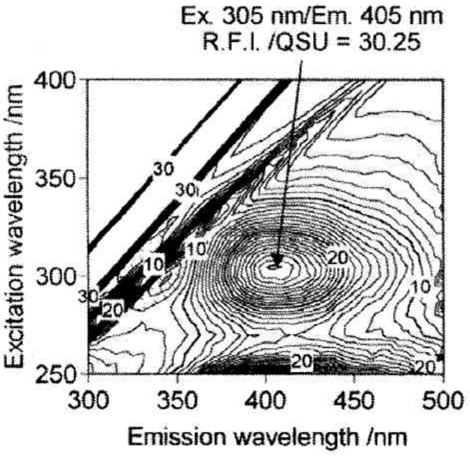

Fig.1 Contour plots of EEM spectra for the rainwater collected at Kinki University

3.2 Effect of pH on the rainwater 3D-EEMS

The fluorescent properties such as relative fluorescent intensity (RFI) and peak position (maximum excitation-emission wavelength) may be affected by the pH. Then, the effect of pH on the spectrum and RFI of rainwater sample were investigated. The initial pH value of rainwater sample was 5.2. The pH was adjusted from 1 to 12 by addtion 6M-HCl and/or 6M-NH_4OH to the samples. Below pH 3, the RFI decreased slightly with decreasing pH, and over pH 11, the RFI increased slightly with increasing pH. Significant differences about fluorescent properties were not recognized between pH 3 to 11.

3.3 Effect of rainfall amounts on the rainwater RFI

The rainwater was collected on May, June and November in 1999. The excitation-emission wavelength of each rain water samples was almost same. The changes of RFI with rainfall amount are shown in Fig.2. The initial RFI showed highest value, then it decreased with the rainfall amount. These results showed that the fluorescent substances may be derived from the dissolution from airborne particulate matter.

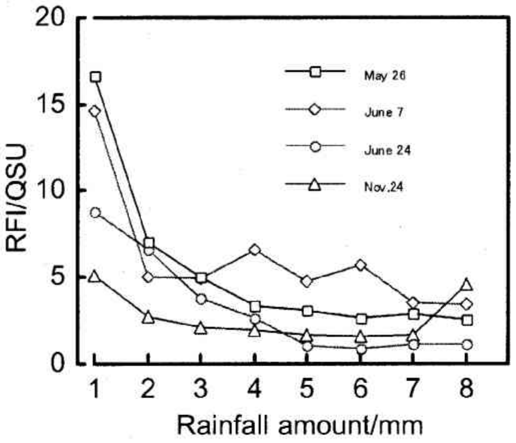

Fig.2 Changes of RFI of rainwater with rainfall amounts

3.4 The relationship between the RFI and DOC in rainwater..

We also determined DOC concentration in rainwater. Figure 3 shows the relationship between the RFI and DOC concentration in. Obviously, a positive strong relationship was shown between the RFI and DOC concentration (r=0.9). This result suggested that the fluorescent substance which has excitation wavelength 300nm/ emission wavelength 400 nm is some water-soluble organic compounds in rainwater.

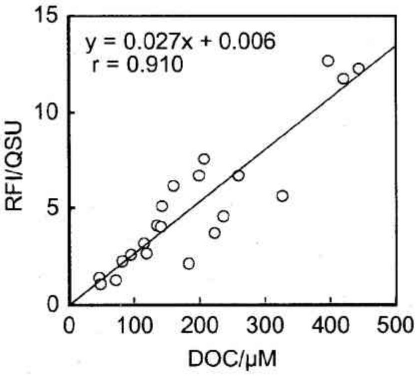

Fig.3 Relationship between RFI and DOC in rainwater

3.5 The extraction of water-soluble fluorescent substances from the airborne particulate matter.

The fluorescent substances in rain water might be derived from the dissolution of airborne particulate matter. Then the dissolution of fluorescent substances from particulate matter was examined. Airborne particulate matter was collected on the glass fiber filter by air pump. After collection, a 10mm diameter hole was punched on the glass fiber filter. Ten mm diameter filter samples were placed in teflon beaker and 20 mm^3 of distilled water was added. Then the following operations were done; (a) non treatment (left alone), (b) after filtration of (a) with a 0.45 μm membrane filter, (c) ultrasonic wave irradiation and (d) after filtration of (c) with a 0.45 μm membrane filter.

The contour plots of EEM spectra for water-soluble substances (a) are shown in Fig.4. The spectrum pattern was in good agreement with that of rainwater. The same spectrum patterns were observed for (b), (c) and (d). The effect of immersion time on the extraction was investigated (n=3). As shown in Fig.5, the fluorescent intensity of (a) after 10 minutes was set at 100. The fluorescent intensity of (a) increased with immersion time. The fluorescent intensity of (c) decreased with time. The standard deviation of (c) was larger than that of (a). On the other hand, the fluorescent intensity after filtration of (b) and (d) showed low values compared with before filtration of (a) and (c). The lowest standard deviation was observed after 20 minutes for (b) and (d).

These results suggested that the fluorescent intensity of water-soluble components was affected by the operating conditions for the extraction. In addition, a definition was necessary to express the fluorescent substances in the water-soluble components. The fluorescent substances in the water-soluble components of airborne particulate matter were defined as the components which were immersed in ultrasonic wave irradiation for 20 minutes and filtered with a 0.45 μm membrane filter.

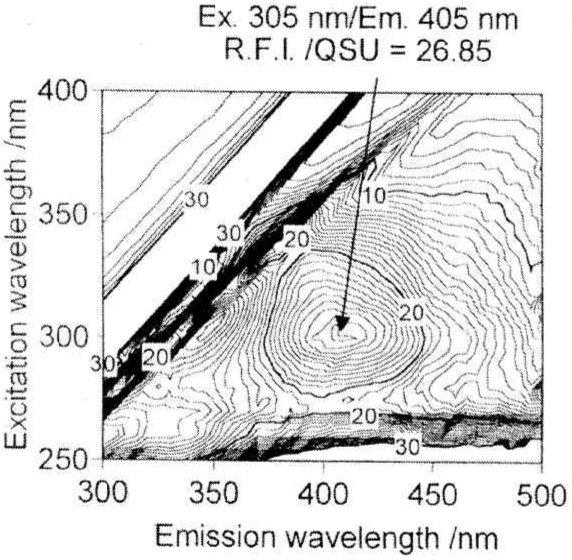

Fig.4 Contour plots of EEM spectra for water-soluble substances of non-treated (a) collected at Kinki University

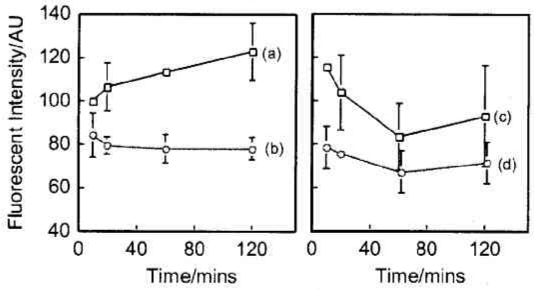

Fig.5 Effect of immersion time on the extraction of fluorescent substances from airborne particulate matter under the following conditions;(a) non treatment (leave alone), (b) after filtration of (a) with 0.45 μm filter, (c) ultrasonic wave irradiation and (d) after filtration of (c) with 0.45 μm filter

3.6 The sources of the fluorescent substances in the rainwater and airborne particulate matter

The sampling point at the university was in the east of Osaka prefecture adjoining the Kinki expressway, the central loop road and Hansin expressway. The color of airborne particulate matter was brown and/or black which suggested that it might be originated from soot and smoke from industry and car exhaust fumes. Then the three dimensional excitation-emission spectrum of the water-soluble component in vehicle exhaust particulate was investigated.

The contour plots of the spectrum of the standard reference material for trace metal analysis (NIES No.8 Vehicle Exhaust Particulates) are show in Fig.6. One sharp peak (Ex.305nm/Em.420nm) was observed in the reference material. The spectrum pattern was almost coincided. These results suggested that WSFS in rainwater and airborne particulate matter might be derived from diesel exhaust cars.

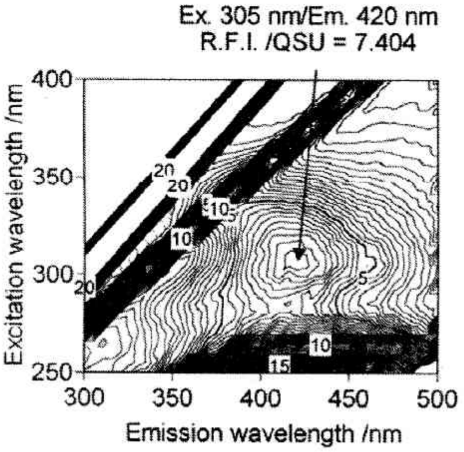

Fig.6 Contour plots of EEM spectra for the water soluble substances in vehicle exhaust particulates of NIES standard reference material

References

1. Sakugawa, H., Takeno, R., Matuki, K., Miyake, T., Takeda, K. and Fujiwara, K. (1995), Degradation of synthetic water soluble polymers with L-ascorbic acid/oxygen, The Chemical Society of Japan, **1995**, 823-829.
2. Sakugawa, H., and Kaplan, I.R. (1993) Measurements of H_2O_2, aldehydes and organic acids in Los Angels rainwater: Their sources and deposition rates, Atmos. Environ., **27B**, 203-219.
3. Kawamura K. and Kaplan, I.R. (1983) Organic compounds in the rainwater of Los Angels Environ. Sci. Technol., **17**, 497-501.
4. Hart, K.M., Tremp, J., Molnar, E. and Giger W. (1993) The occurrence and the fate of organic pollutions inn the atmosphere, Water. Air, Soil Pollut., **68**, 91-112.
5. Igawa M., Nakada, N. and Okochi, H., J. Jpn. Soc. Atmos. Environ., **34**, 211-218 (1999).
6. Peltzer, E. T. and Gagosian, R. B. (1987) Sampling and quantitation of lipids in aerosols from the remote marine atmosphere, Anal. Chim. Acta, **198**, 125 -144.
7. Zoller, W. H., Gladney, E. S. and Duce, R.A. (1974), Atmospheric concentrations and sources of trace metals at the South Pole, Science, **183**, 198-200
8. Wiersma, B. and Davidson, C. I. (1986) Trace metals in the atmosphere of remote areas, Adv. Environ. Sci. Technol., **17**, 201-266..
9. Milford, J. B. and Davidson, C. I. (1985)The sizes of particulate trace elements in the atmosphere-a review, J. AirPollu. Assoc. **35**, 1249-1260.
10. Duce, R. A. , Hoffman G. L., Ray, B. J., Fletcher, I. S., Wallace, G.T., Fasching, J. L., Plotrowlcz, S.R., Walsh, P.R., Hoffman, E. J., Miller, J. M. and Heffter, J. L.(1976) "Trace metals in the marine atmosphere sources and fluxes", ed. Windom, H. and Duce, R., Marine Pollutant Transfer. D.C. Heath and Co., Lexington, MA, p.77-119,
11. Piotrowicz, S. R., Duce, R. A., Fasching, J.

L. and Weisel, C. P. (1979) Bursting bubbles and their effect on the sea-to-air transport of Fe, Cu and Zn, Mar. Chem., **7**, 307-324.