

Application of EEM-PARAFAC for characterizing dissolved organic matter in a wastewater treatment plant having four types of advanced treatment processes

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Excitation emission matrices (EEM) coupled with parallel factor (PARAFAC), EEM-PARAFAC analysis has been used for characterizing dissolved organic matter (DOM) in aquatic environments. This technique has come into use to assess the water quality in the wastewater treatment plant (WWTP). In this study, we were to collect water samples from the WWTP operating four types of advanced treatment processes (Type-A: Activated sludge process with addition of coagulant, Type-B: Anaerobic/Anoxic/Aerobic process [A2O], Type-C: Recirculating denitrification process with addition of coagulant, Type-D: Modified Bardenpho process with addition of carriers) and then characterize the changes in fluorescence properties of DOM by EEM-PARAFAC. Furthermore, the same analysis was applied to the water samples of a river into which the WWTP effluent was discharged, and then the effect of the effluent on the river water quality was evaluated. The number of the WWTP and river samples were 96 in total.

Fluorescence spectra were measured with a multiwavelength fluorescence spectrophotometer (F-7000, Hitachi) equipped with a quartz flow-cell in an autosampler (AS-3000, Hitachi). The fluorescence intensity was recorded at an excitation wavelength ranging from 200 to 600 nm and an emission wavelength ranging from 200 to 600 nm. The spectra were corrected for instrument biases and standardized by using integrated Raman scattering data for Milli-Q water, as suggested by Matthews et al. (1996), and Mostafa et al. (2005).

On EEM, one unique peak at excitation/emission wavelengths (Ex./Em.) of 490/520 nm was observed as well as humic/fulvic acid-like and protein-like peaks as shown in Fig. 1. The fluorescence intensities of tyrosine-like peaks were extraordinary high in the WWTP influent samples as compared with those in the effluents. By PARAFAC, in this study, five fluorescent components were identified in the EEM spectra. These components showed a peak at an Ex./Em. of 280/350 nm (C1), 330/385 nm (C2), 360/440 nm (C3), 420/480 nm (C4), and 490/520 nm (C5). Based on the previous studies, C1 is likely to be originated from protein-like, and C2-C4 are from humic/fulvic acids-like; however, C5 is unknown in its origin but seems to be related with the characteristics of WWTP.

The concentration scores of fluorophores (PARAFAC components) were found to be $C5 > C3 \geq C1 > C4 > C2$ in the influent, whereas those were $C5 > C3 \geq C4 > C2 > C1$ in the effluent. The removal ratio, calculated by comparing the score of each component between influent and effluent, was 85-91% as C1, 20-31% as C2, 47-52% as C3, 3-25% as C4, and 40-53% as C5. It is suggested that the fluorophore of protein-like (C1) is easily removed and those of humic-like (C2, C3, and C4) are hardly done. The scores of C1, C2, and C3 were decreased steadily as the treatments in series at the WWTP were progressed. On the other hand, the score of C4, which removal ratio was substantially low, was increased through the anaerobic /anoxic treatment but decreased through the aerobic treatment. The elevated C4 fluorophores might be something to do with the transformation of DOMs associated with C1, C2, C3 and C5. Humic-like components (C2 and C3) appeared

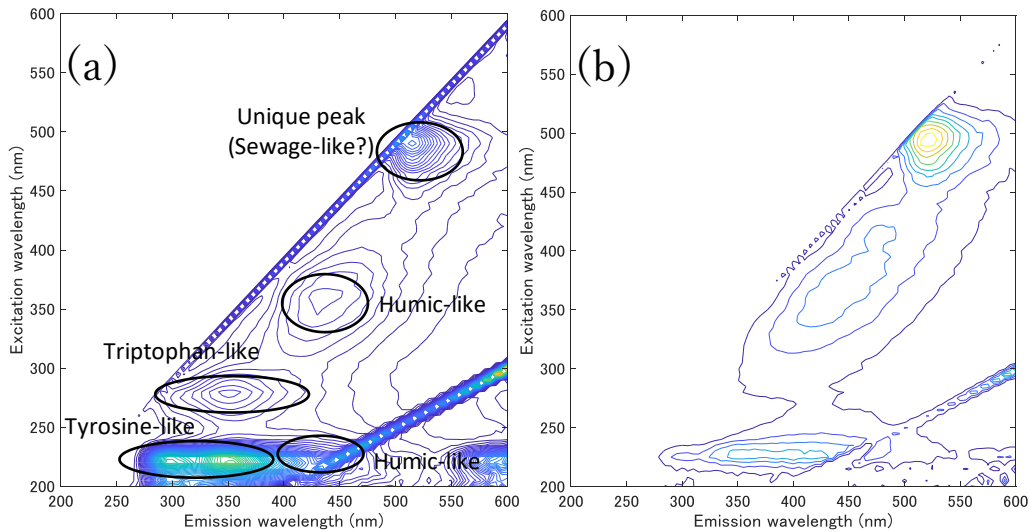


Fig.1: Examples of EEM spectra

(a) Influent of WWTP (b) Effluent of WWTP

to be effectively removed in the coagulation process installed in Type-A and Type-C.

In the river water samples, the concentration scores were decreased compared to the effluent of WWTP. Near the discharging site of the WWTP, artificial thermocline was formed especially in winter, and the ratios of PARAFAC component scores between surface and bottom (surface/bottom) were the highest in C5 (ex. 1.44 as C1, 1.73 as C2, 1.77 as C3, 1.75 as C4, and 3.19 as C5 in winter). In the surface water of the river near the WWTP, the C1-C4 components were suggested to be from the upstream water as well as the WWTP effluent, whereas the C5 originated almost exclusively from the WWTP effluent. It has been suggested that C5 is not detected in the waters of aquatic environments such as river, lake, and coastal sea (Galapate et al., 1998; Komatsu et al., 2005). However, in this study, C5 was also detected in the surface water of river within the distance of a few hundred meters from the outlet of WWTP. The origin of C5 has not been clearly identified by the previous studies because of its unique position on EEM; however, our results indicate that C5 may be effective in acting a tracer of artificial wastewater in freshwater environments.

References

- Galapate R. P., Baes A. U., Ito K., Mukai T., Shoto E. & Okada M. (1998) Detection of domestic wastes in Kurose River using synchronous fluorescence spectroscopy, *Wat. Res.*, **32**(7), 2232-2239.
- Komatsu K., Nakajima F., Furumai H. & Miki O. (2005) Characterization of dissolved organic matter (DOM) removed by iron coagulation using spectrofluorimetry and pyrolysis GC/MS analysis, *J. Water Supply*, **54**(3), 157-163.
- Matthews B. J. H., Jones A. C., Theodorou N. K. & Tudhope A. W. (1996) Excitation-emission-matrix fluorescence spectroscopy applied to humic acid bands in coral reefs, *Mar. Chem.*, **55**, 317-332.
- Mostofa K. M. G., Yoshioka T., Konohira E., Tanoue E., Hayakawa K. & Takahashi M. (2005) Three-dimensional fluorescence as a tool for investigating the dynamics of dissolved organic matter in the Lake Biwa watershed, *Limnology*, **6**, 101-115.