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Characterization of Humic Compounds in the Surface-Water of Lake Kojima*

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Abstract: *Humic compounds are one of the major substances that affect the COD value of the surface water of Lake Kojima. The humic compounds in the lake water were studied with a spectrofluorophotometer. The 3-dimensional fluorescence spectrum suggests that two kinds of fluorescent substances exist in the lake water. One shows an fluorescence excitation maxim (Ex) at about 240 nm and an emission maxim (Em) at 413 nm. The other has an Ex at 330 nm and an Em at 418 nm. The former peaks are associated with humic acid and the latter peaks are associated with fulvic acid. These peak intensities are proportional to the COD values. The fulvic acid in the lake water may be enriched by the effluent from domestic water treatment plants.*

Keywords: *3-dimensional fluorescence spectrum, humic acid, fulvic acid, Lake Kojima*

1. Introduction

Lake Kojima in southern Okayama Prefecture was built about 40 years ago in Kojima Bay to obtain fresh water for agricultural use (Fig.1). Sasagase and Kurashiki Rivers feed into the lake. At present, the quality of water has depreciated due to the urbanization along the rivers. Despite a great deal of effort, the average chemical oxygen demand (COD) value of the lake water still remains at approximately twice the value allowed by the Japanese environmental standard ($5\ \mathrm{mg \cdot kg^{-1}}$).

The COD value is proportional to the sum of organic substances transferred from outside the lake and those produced inside. In the case of Lake Kojima, the contribution to COD by the sum outside the lake than the sum inside (Ashitani, K., 1988). The COD is divided into particulate and dissolved CODs. The dissolved COD value is thought to depend on the amount of organic substances transferred from outside, because umic compounds affect the dissolved COD value (JIS K0102, 1993).

The humic compounds in the surface water of L. Kojima were analyzed with a spectrofluorophotometer. The relationship between fluorescence intensities of the humic compounds in the

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lake water and its COD values was ecamined, and the source of the humic compounds was researched.

2. Materials and method

The surface water of Lake Kojima was sampled monthly at three points : the center of the lake, and the mouths of Kurashiki and Sasagase Rivers. The samples were filtrated through a glass

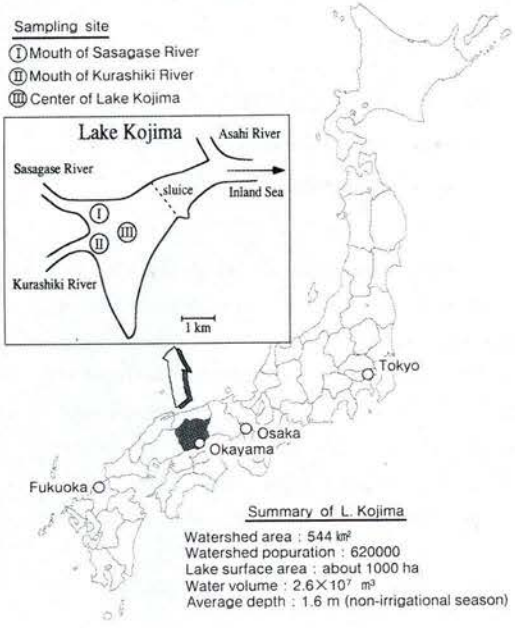


Fig. 1 Sampling site at Lake Kojima and humic acids from the soil

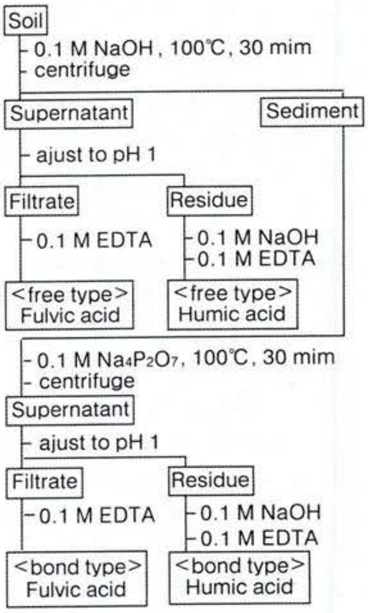


Fig. 2 Extraction procedure of fulvic

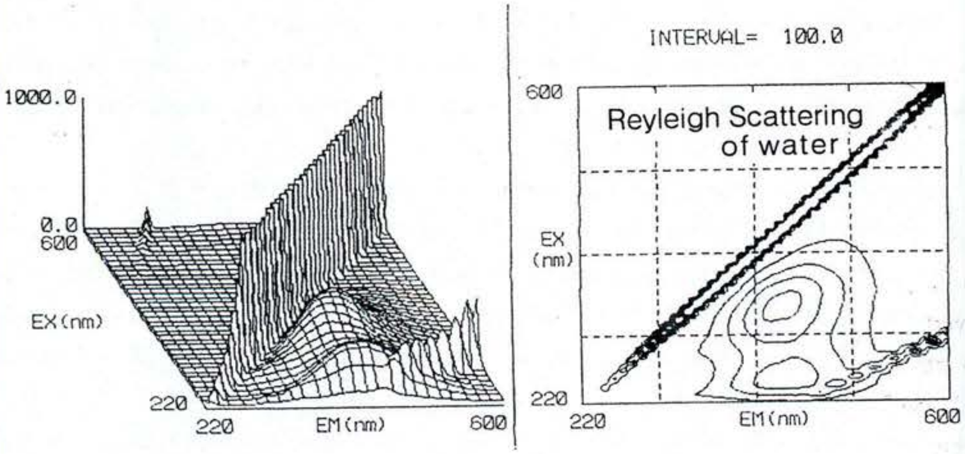


Fig. 3 An example of 3-dimensional fluorescent spectrum of humic substance in Lake Kojima; (Sampling Site: Center of Lake Kojima)

fiber filter (ADVANTEC GS25). It is known that humic compounds consist of free and bond types of humic and fulvic acids. Figure 2 shows the procedures to separate the two types of acid from the soil. The types of the humic compound in the lake water were identified by these acids.

It is considered that humic compounds have both natural and antholopogenic sources of emission. Natural humic compounds are made in soil by bio-degradation, and then washed out by rain water. The antholopogenic humic compounds are made in domestic waste water treatment plants along the rivers.

Two samples were used to elucidate the source of fulvic and humic acids in the lake water: 1) extracts from the soil with distilled water, and 2) effluents of the domestic waste water treatment plants.

We performed correlation analysis between the COD values of the extracts and fluorescence peak intensities. The same analyses were also done for the lake water. Semi-quantitative analyses of the fulvic and humic acids in water in which the humic compounds consist were carried out with a spectrofluorophotometer (Hitachi F-3010). The COD values of the extracts and the lake water were measured with chemical grade $KMnO_4$).

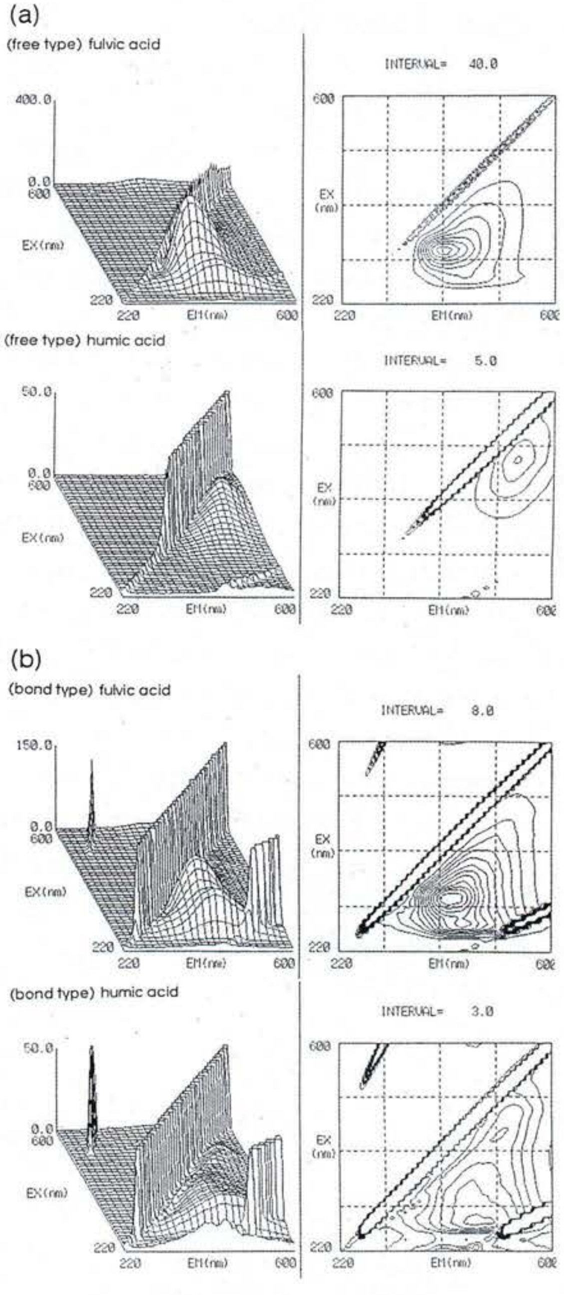


Fig. 4 3-dimensional fluorescent spectra of humic substance extracted from the soil around Lake Koj; (a) fulvic and humic acid extracted with 0.1M NaOH (free type); (b) fulvic and humic acid extracted with 0.1M $Na_4P_20_7$ (bond type)

3. Results and discussion

Fig. 3 shows an example of the 3-dimensional fluorescence spectrum of the humic compounds in the lake water sampled at the center of Lake Kojima. The spectrum suggests that two kinds of fluorescent substance exist in the sample. One is shown by a fluorescence excitation maxim (Ex) at about 240 nm and an emission maxim (Em) at 413 nm, and the other by an Ex at 330 nm and an Em at 418 nm. These peak positions agree well with the results reported by Ashitani for humic compounds. These peaks were also observed in the surface water at the mouths of Kurashiki and Sasagase Riveres.

Figure 4(a) shows the fluorescent spectra of the substances extracted with NaOH solution from the soil around Lake Kojima. Two peaks are observed at Ex 310 nm, Em 400 nm and at Ex 480 nm, Em 440 nm. The former is associated with free type fulvic acid and the latter with free type humic acid. These peak positions do not coincide with those for the lake water, however, the spectra of the bond type fulvic and humic acids extracted with $Na_4P_2O_7$ solution from the soil are similar to the spectrum of the lake water (Fig.4 (b)). The mechanism for explaining the absence of the free type acids will be investigated in a later study.

We extracted the humic compounds from the soil with distilled water to elucidate the sources of the fulvic and humic acids in the lake water. The fluorescent spectrum of the extract is shown in Fig. 5. Two peaks are shown, and are associated with bond type fulvic and humic acids. The peak intensity of the latter is higher than that of the former. Fig. 6 shows the fluorescence spectra of the influent, the water in an aeration tank, and the effluent of the domestic waste water plants. According to these spectra, the peak intesity of the bond type fluvic acid in the water of the tank is very high, as it is formed in the tank due to bio-degradation. However, the peak intensity of the bond type humic acid is very low. No free type fulvic and humic acids were observed in the effluent from the domestic waste water plants.

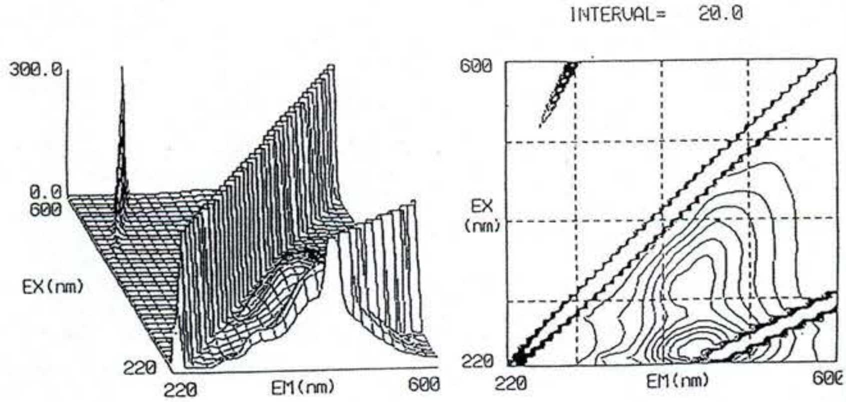
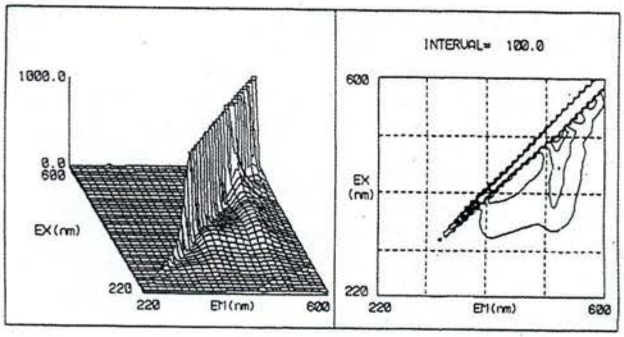


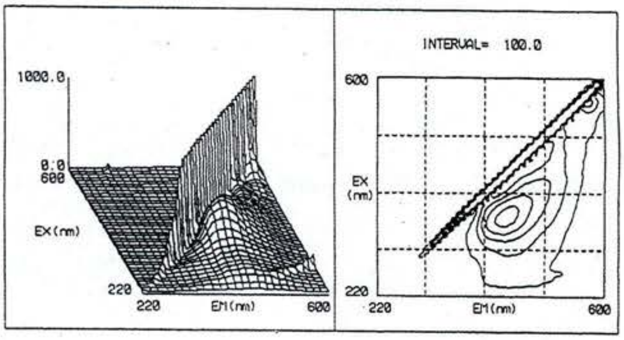
Fig. 5 3-dimensional fluorescent spectrum of water-extract from the soil around L.Kojima (right)

According to these results, the humic acid in the lake water is from the soil, and the fulvic acid from the effluent of the domestic waste water plants. The relationship between the COD values of the extract from the soil and the peak intensities is shown in Fig. 7. The COD values increase proportionally with increasing the peak intensities of fulvic and humic acids. Figure 8 shows the relationship between the COD and the sums of the peak intensities of the fulvic and humic acids of the lake water. The sums of the peak intensities were the simple summation of the two peaks. The data analyzed were obtained during the period during 1995 to 1996. The COD values and the peak intensities show a positive correlation ($r = 0.726$, $n = 17$, $p < 0.001$). Generally, COD values of the lake is the sums of COD values of humic compaounds and another substances that are reducible, therefore futher quantitative study is desirabale to confirm the results of the lake water.

Influent



Aeration tank



Effluent

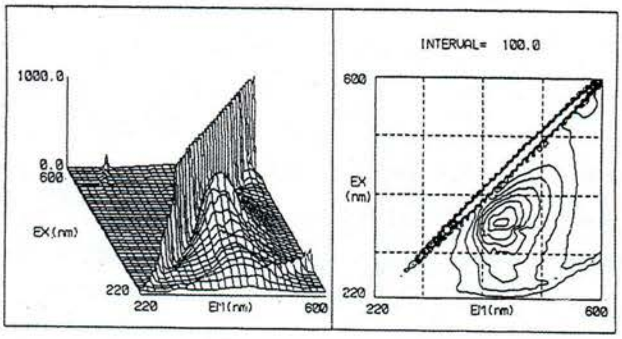


Fig. 6 3 - dimensional fluorescent spectra of the influent, the water in the aeration tank and effluent from the waste water treatment plant

4. Conclusion

We found a relationship between the COD value and the fluorescence intensities of humic compounds by means of 3-dimentional fluorescence analysis. Humic compounds were detected in the soil around the lake and in the effluent of the domestic waste water treatment plants. We also found that humic compounds are formed in the domestic waste water plant.

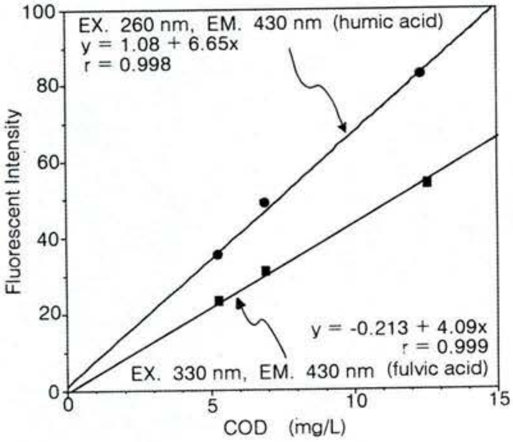


Fig. 7 Relationship between COD and peak intensity of fulvic and humic acids

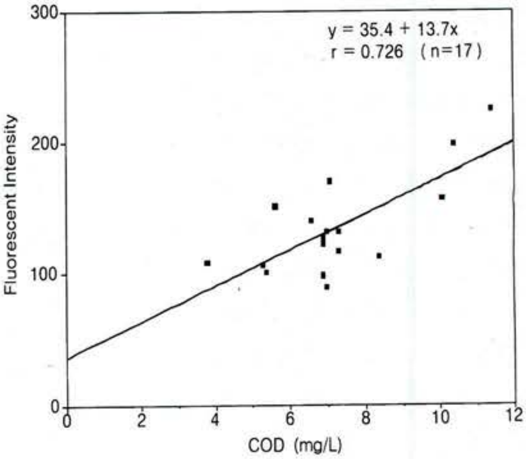


Fig. 8 Relationship between COD and the sums of peak intensities of fulvic and humic acids at the mouth of the Kurashiki River

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