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Fouling prediction method using TOC and EEM analysis

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Abstract:

Many studies on membrane fouling have been made and reported, and it has been revealed, based on liquid chromatography organic carbon detection (LC-OCD), that biopolymer is the main foulant in the drinking water treatment process, in which the raw water is taken from a river or a dam. However, measurement by LC-OCD is time-consuming and costly. Therefore, continuous measurement of biopolymer concentration by LC-OCD is not feasible. For this reason, we have not been able to monitor the biopolymer continuously and control membrane fouling. The purpose of this study is to find a new fouling index (FR) to control membrane fouling without measuring the biopolymer concentration. Then, we tried to find a correlation between biopolymer and other water components by a multiple regression analysis. As the result, we have suggested the new fouling index (FR) which consists of the sum of the fluorescence intensity within the Region III domain measured by excitation emission matrix (EEM) fluorescence spectroscopy and the concentration of dissolved organic carbon measured by the total organic carbon (TOC) measurement. TOC and EEM are measured easily and continuously. Thus, we can control membrane fouling by monitoring the FR continuously.

Keywords: biopolymer, excitation emission matrix (EEM) fluorescence spectroscopy, fouling prediction, liquid chromatography organic carbon detection (LC-OCD), membrane fouling

1. Introduction

The drinking water treatment system using membrane has many advantages, such as complete removal of pathogenic bacteria and protozoa including *cryptosporidium*, downsizing of the process equipment, and easy maintenance. Particularly, the use of the membrane system has been high in small-scale water purification plants. On the other hand, membrane fouling is a serious problem associated with this system, which causes an increase in operational power and frequency of chemical cleaning, and subsequently increases operating cost. Therefore, reduction in operating cost using chemical cleaning optimization has been considered (Yoo 2018).

To control membrane fouling, we must identify the foulants, i.e. the materials that cause membrane fouling, and monitor them continuously. If we could measure the concentration of foulant in raw water continuously, we would be able to control membrane fouling by stopping the intake of raw water that has high fouling tendency or supplying chemicals to flocculate the foulants (Bogati 2015).

In the case of a drinking water treatment system using membrane, which takes raw water from surface sources such as rivers or dams, many researchers have reported that the main foulant must be a biopolymer related to biological metabolism on the membrane surface (Halle 2009; Peldszus 2011; Tian 2013). We have also succeeded in decreasing membrane fouling by reducing biopolymer concentration in raw water with a biological contact filter (Hasegawa 2017).

Recently, biopolymer concentration has been measured accurately using liquid chromatography organic carbon detection (LC-OCD), in which biopolymer is separated by a size-exclusion column (Chon 2017). However, LC-OCD analysis is not suitable for continuous measurement of foulants in raw water, because it takes as long as 130 min per sample measurement. On the other hand, a total organic carbon (TOC) analyzer and excitation emission matrix (EEM) fluorescence spectroscopy can measure components in raw water in a short time at low cost; thus, it is more suitable for continuous measurement. However, it is reported that TOC does not have a clear correlation with membrane fouling (Kimura 2014). Furthermore, though the correlation between membrane fouling and the components determined from EEM analysis using parallel factor analysis has been examined, a clear correlation between them has not been obtained (Shao 2014; Yu 2014).

In this study, we intend to establish a new fouling index that can be monitored continuously and predict membrane fouling. At first, we investigated the relationship between membrane fouling and raw water components for 13 water samples collected from 9 rivers, and confirmed that biopolymer concentration had the strongest correlation with membrane fouling. Then, we tried to find the correlation between biopolymer concentration and the TOC value and EEM analysis using the multiple regression analysis.

2. Materials and experimental methods

2.1. Water sample

In this study, 40 water samples were collected from 9 rivers (Akashi, Ikawa, Ikuta, Ishiya, Ina, Sumiyoshi, Toga, Mo, and Yodo) in the Hyogo and Osaka prefectures, Japan. They were collected from smooth flowing part of the river using a bucket, filled in 20L plastic container, transported within several hours, and stored in a refrigerator without any pretreatment. Within 2 days, components of the samples were analyzed, and 13 water samples were selected by random sampling and fed to the filtration test equipment.

2.2. Filtration test of sampled water

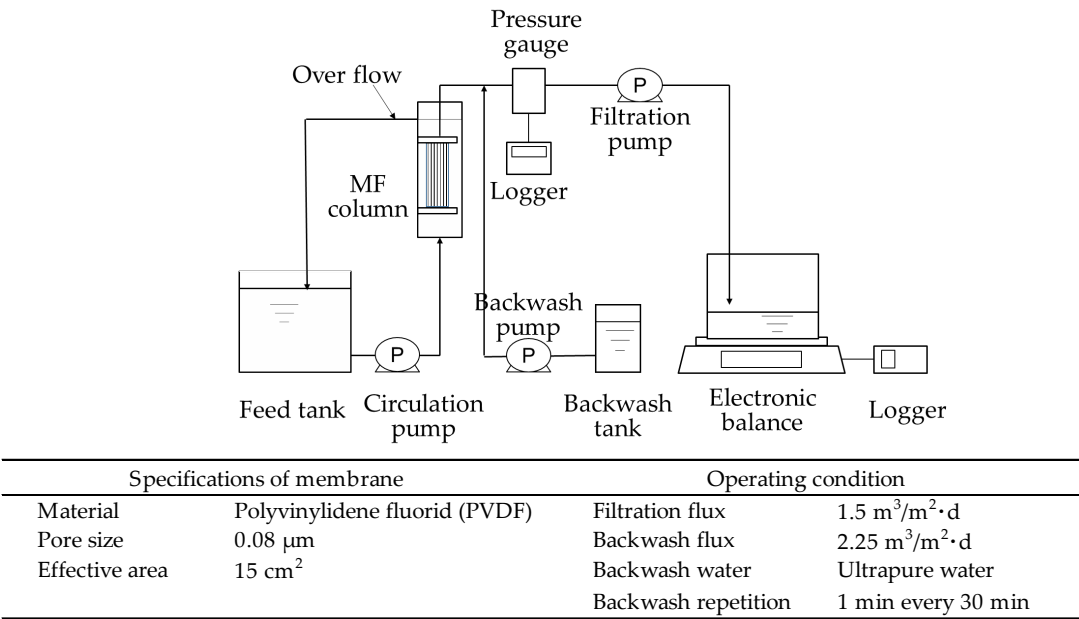
In order to evaluate the fouling potential of the water samples, i.e. the tendency to cause membrane fouling, a filtration test was performed using the mini micro filtration (MF) module test equipment (Figure 1). The sampled water was circulated through the mini MF column in which the mini MF module was set. The water temperature was controlled at $20 \pm 0.5^\circ\text{C}$ during the test period, using a heater and a cooler. The permeated water was drawn through the mini MF module at a constant velocity of $1.5 \text{ m}^3/(\text{m}^2\cdot\text{d})$. The mini MF module was backwashed with ultrapure water for 1 min every 30 min to reduce membrane fouling. The transmembrane pressure (TMP) was monitored until it exceeded 50 kPa. Specifications of the mini MF module and operating conditions are detailed in Figure 1.

The fouling potential of the sampled water was evaluated by the rate of increase of its membrane filtration resistance R_f ($1/\text{m}\cdot\text{d}$), hereafter referred to as “fouling rate (FR),” which is defined by Equation (1).

$$FR = R_f = \Delta R_t(t_f) / t_f \quad (1)$$

$$\Delta R_t(t_f) = \Delta(\Delta P(t_f)) / (\mu \cdot J) \quad (2)$$

where $\Delta R_t(t_f)$ is the increment in the membrane filtration resistance ($1/\text{m}$) during time t_f given by Equation (2); t_f is the operating time of the filtration test (d); $\Delta(\Delta P(t_f))$ is the increment in transmembrane pressure (Pa) during t_f ; J is the filtration flux ($\text{m}^3/\text{m}^2\cdot\text{s}$), which is fixed at $1.5 \text{ m}^3/\text{m}^2\cdot\text{d}$ for this study; and μ is the viscosity ($\text{Pa}\cdot\text{s}$) of the sampled water. Note that larger values of FR indicate a higher fouling potential of the sampled water.



94 2.3. Analytical method

95 2.3.1. Total organic carbon (TOC)

96 Prior to TOC measurement, sampled water was filtered through a 0.45-μm hydrophilic
97 polytetrafluoroethylene membrane (DISMIC 13HP045AN, Advantec, Tokyo, Japan). Generally,
98 TOC comprises dissolved organic carbon (DOC) and particulate organic carbon (POC).
99 However, in this paper, POC was removed by filtration and only DOC was measured. Thus,
100 the measured TOC is referred to as TOC-DOC.

101 The TOC of the sampled water was measured with a TOC analyzer (TOC-V_{CSH}, Shimadzu
102 Corporation, Kyoto, Japan). First, inorganic carbon was removed from the sampled water
103 injected into the TOC analyzer as carbon dioxide at pH less than 3. Then, the filtered sampled
104 water was burnt at 680 °C on a platinum catalyst. The burnt gas was cooled and dehumidified,
105 and then the CO₂ in the gas was detected with a non-dispersive infrared gas detector. Phthalate
106 hydrogen potassium was used as a standard for calibration.

107 2.3.2. Excitation emission matrix (EEM) fluorescence spectroscopy

108 To characterize the dissolved organic matter (DOM) in the sampled water, EEM
109 measurements were performed. Prior to the EEM measurements, all samples were filtered
110 through the same filter used in the TOC measurement. EEM fluorescence was measured with
111 an EEM spectrometer (Aqualog, Horiba Advanced Techno Co. Ltd, Kyoto, Japan). The
112 excitation light was set from 220 to 800 nm and was irradiated for 1 s at intervals of 3 nm. When
113 evaluating the three-dimensional fluorescence spectra, the spectra were divided into five
114 domains and the sum of the fluorescence intensity within each domain was calculated (Chen
115 2003). Hereafter, Reg. x indicates the sum of the fluorescence intensity within the Region x
116 domain.

117 2.3.3. Liquid chromatograph organic carbon detector (LC-OCD)

118 LC-OCD measurements were performed to analyze the concentration of natural organic
119 matter (NOM) in sampled water. Prior to the LC-OCD measurements, all samples were filtered
120 through the same filter used in the TOC measurement. The organic carbon content was
121 measured with a Model 8 DOC-Labor instrument (DOC-Labor, Karlsruhe, Germany). A
122 hydrophilic weak cation exchange resin (TOYOPEARL HW-50, Tosoh, Tokyo, Japan) was used
123 in the chromatographic column. The NOMs separated through the chromatographic column
124 were oxidized by UV in a thin film reactor. Then, the NOMs were converted to CO₂ with an
125 acidification liquid and removed from the feed. The concentration of NOMs was determined as

the concentration of CO₂ using a non-diffusion infrared detector. The mobile phase was a phosphorus acid buffer of pH 6.58, comprising sodium dihydrogen phosphate and disodium hydrogenphosphate (Sigma-Aldrich Japan, Tokyo, Japan). The acidification liquid was a phosphorus acid buffer of pH 1.5, comprising phosphoric acid and potassium peroxodisulfate (Sigma-Aldrich Japan, Tokyo, Japan). The mobile phase was injected at a flow rate of 1.1 mL/min, and the quantity of the sample injection was set at 1,000 µL. The total retention time was set at 130 min. The concentration of NOMs was calculated using the software chromCALC (DOC-Labor, Karlsruhe, Germany) customized to our system.

2.3.4. Multiple regression analysis

For multiple regression analysis, we used the regression analysis Excel pack from Microsoft corporation (Washington, USA). In the results of the multiple regression analysis, the effectiveness of the correlation was evaluated by a P-value (probability value) of 5%, that is, when the P-value was less than 5%, the correlation was estimated to have significance.

In Excel pack, the coefficient of determination R² is defined as Equation (3):

$$R^2 = \frac{\sum (\hat{y}_i - \bar{y})^2}{\sum (y_i - \bar{y})^2} \quad (3)$$

Where, y_i indicates one of criterion value y, \bar{y} indicates an average value of y, and \hat{y}_i indicates a predictive value of y_i. According to this definition, R² can be negative value as seen in Table 1 and Table 2.

3. Results and discussion

3.1 Components of river water which affect membrane fouling

The results of TOC, LC-OCD, and EEM measurements of water samples collected from 9 rivers are shown in the supplementary data (Table S.1). The coefficient of determination (R²) values (Table 1), obtained from the linear regression analysis of each component for fouling rate, show that only biopolymer concentration correlates strongly with fouling rate. The second strongest correlation is with TOC-DOC; however, R² of TOC-DOC (0.475) is much less than that for biopolymer concentration (0.928). Thus, if biopolymer concentration could be measured continuously, we could predict membrane fouling from the continuous monitoring of biopolymer concentration in raw water, and membrane fouling could be controlled automatically by chemical dosing or increasing the frequency of chemical cleaning before membrane fouling. However, unfortunately, the current LC-OCD analyzers cannot measure continuously, because it takes a long time (130 min) for one measurement and a dilution procedure is necessary to make the concentration lower than the upper limit of the LC-OCD measurement, and even then, analysis cost is high. Thus, a new parameter is required, which correlates with membrane fouling and can be measured continuously.

Table 1. The coefficient of determination of each component for fouling rate

TOC analysis		LC-OCD analysis		EEM analysis	
Components	R ²	Components	R ²	Components	R ²
TOC-DOC	0.475	LC-OCD-DOC	0.404	Reg. 1	0.268
		BP	0.928	Reg. 2	0.017
		HS	0.285	Reg. 3	0.083
		BB	0.089	Reg. 4	0.015
		LN	0.233	Reg. 5	0.023
		LA	-1.014		

R²: coefficient of determination; LC-OCD-DOC: sum of BP, HS, BB, LN and LA; BP: biopolymer, HS: humic substances, BB: building blocks, LN: low molecular weight nutrients, LA: low molecular weight acids

3.2 New parameter instead of biopolymer concentration

The correlations between biopolymer concentration and other components of sampled water analyzed by linear regression (Table 2) show that no component correlates with biopolymer concentration, because the R^2 value of each parameter is lower than 0.5. Thus, we need to consider the correlation between biopolymer concentration and a combination of other components.

Table 2. Relationship between biopolymer concentration and other components

TOC analysis		LC-OCD analysis		EEM analysis	
Components	R^2	Components	R^2	Components	R^2
TOC-DOC	0.387	LC-OCD-DOC	0.329	Reg. 1	0.441
		BP	1.000	Reg. 2	0.105
		HS	0.026	Reg. 3	0.103
		BB	0.069	Reg. 4	0.153
		LN	-0.767	Reg. 5	0.152
		LA	0.288		

R^2 : coefficient of determination

The concentration of biopolymer, [BP], is given by Equation (4):

$$[BP] = [LC-OCD-DOC] - ([HS] + [BB] + [LN] + [LA]) \quad (4)$$

where, HS indicates humic substances, BB building blocks, LN low molecular weight nutrients, and LA low molecular weight acids. [] indicates the concentration.

We conclude that [LC-OCD-DOC] has a correlation with [TOC-DOC], because both values show the DOC concentration of the same sampled water, even if the analytical method is different. The result of linear regression analysis between [LC-OCD-DOC] and [TOC-DOC] (Figure 2) shows that [TOC-DOC] has a strong correlation with [LC-OCD-DOC]. It means that the DOM of river water can be detected with an LC-OCD analyzer using a chromatographic column with a hydrophilic weak cation exchange resin. As a result, Equation (4) can be rewritten as Equation (5):

$$[BP] = 791.96 [TOC-DOC] - ([HS] + [BB] + [LN] + [LA]) \quad (5)$$

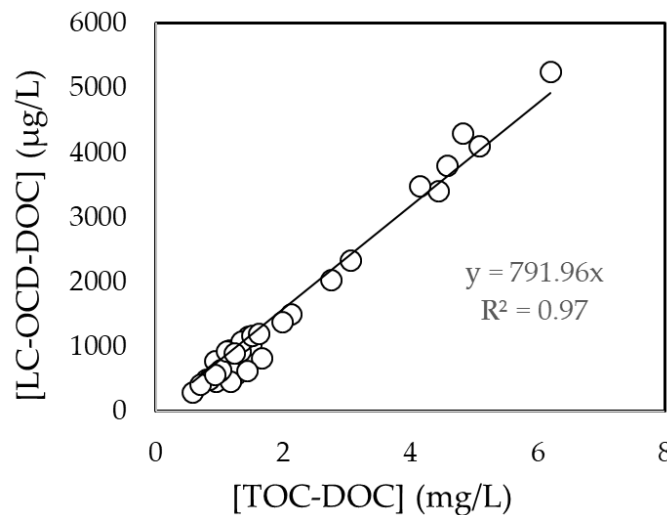


Figure 2. Correlation between [TOC-DOC] and [LC-OCD-DOC]

In Equation (5), it is reasonable to consider that [HS], [BB], [LN], and [LA] have a correlation with EEM results, because EEM also measures DOM by dividing it into 5 domains. Thus, we attempt multiple regression analysis for FR by rewriting Equation (5) as Equation (6):

$$FR = a \cdot [TOC-DOC] + b \cdot \text{Reg. 1} + c \cdot \text{Reg. 2} + d \cdot \text{Reg. 3} + e \cdot \text{Reg. 4} + f \cdot \text{Reg. 5} + g \quad (6)$$

where a, b, c, d, e, f, and g are constants.

The results of the multiple regression analysis for FR values, shown in Table S.1, with Equation (6) (Table 3(a)) show that Equation (6) fits with FR very well ($R^2 = 0.975$). However, the P-values of Regs. 2, 4, and 5 are higher than 0.05. Thus, we retried the analysis using Equation (7):

$$FR = h \cdot [TOC-DOC] + i \cdot \text{Reg. 1} + j \cdot \text{Reg. 3} + k \quad (7)$$

where h, i, j, and k are constants.

Table 3(b) shows the results of the multiple regression analysis for FR with Equation (7). Equation (7) fits very well with FR, though the R^2 for Equation (7) (0.910) is slightly less than that for Equation (6) (0.975). However, the P-value of Reg. 1 is higher than 0.05. Therefore, we retried the analysis using Equation (8):

$$FR = l \cdot [TOC-DOC] + m \cdot \text{Reg. 3} + n \quad (8)$$

where, l, m, and n are constants.

Table 3(c) shows the results of the multiple regression analysis for FR with Equation (8). It is found from Table 3(c) that the P-value of each term is less than 0.05. In addition, R^2 is 0.903, which means Equation (8) fits with FR well enough, even though R^2 at 0.903 is a little lower than 0.975 for Equation (6) and 0.910 for Equation (7). Equation (8) is rewritten as Equation (9) by inserting the coefficients shown in Table 3(c) into Equation (8):

$$FR = 3.10 [TOC-DOC] - 4.17 \times 10^{-6} \text{Reg.3} - 1.34 \quad (9)$$

Table 3. Multiple regression analysis for FR

(a) With Equation (6)

		Coefficient	P-value	R^2
TOC-DOC	a	2.77	6.16×10^{-5}	0.975
Reg. 1	b	9.99×10^{-6}	0.00742	
Reg. 2	c	-6.70×10^{-7}	0.821	
Reg. 3	d	-4.26×10^{-6}	0.0331	
Reg. 4	e	-4.28×10^{-6}	0.108	
Reg. 5	f	5.26×10^{-7}	0.326	
Intercept	g	-1.48	0.000345	

(b) With Equation (7)

Term		Coefficient	P-value	R^2
TOC-DOC	h	3.01	4.27×10^{-5}	0.910
Reg. 1	i	1.59×10^{-6}	0.412	
Reg. 3	j	-4.31×10^{-6}	0.000110	
Intercept	k	-1.34	0.00132	

(c) With Equation (8)

Term		Coefficient	P-value	R^2
TOC-DOC	l	3.10	1.31×10^{-5}	0.903
Reg. 3	m	-4.17×10^{-6}	6.17×10^{-5}	
Intercept	n	-1.34	0.000924	

Figure 3 shows the correlation between the experimental FR and the estimated FR with Equation (9). It is clear that FR is estimated well with Equation (9).

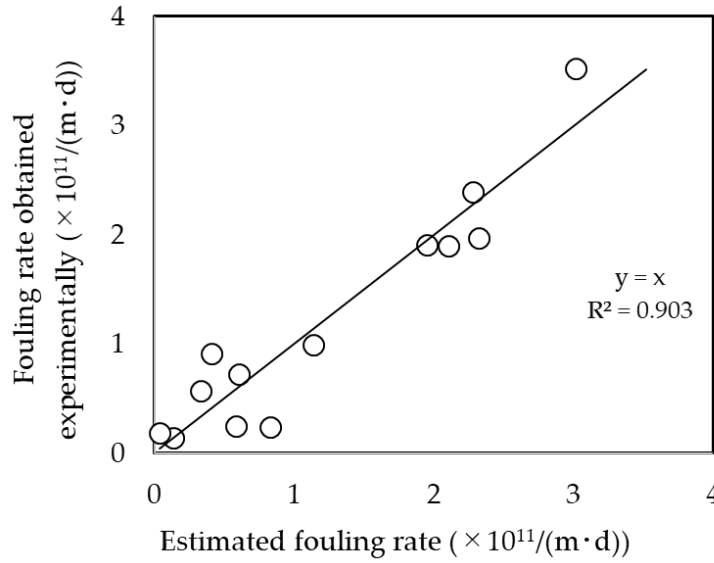


Figure 3. Correlation between FR obtained experimentally and the estimated FR in Eq. (9)

It will be possible to predict membrane fouling by consecutive measurement of the TOC and EEM and estimation of the FR with Equation (9). Figure 4 shows a flowchart of a fouling control system that uses an arithmetic unit for fouling prediction.

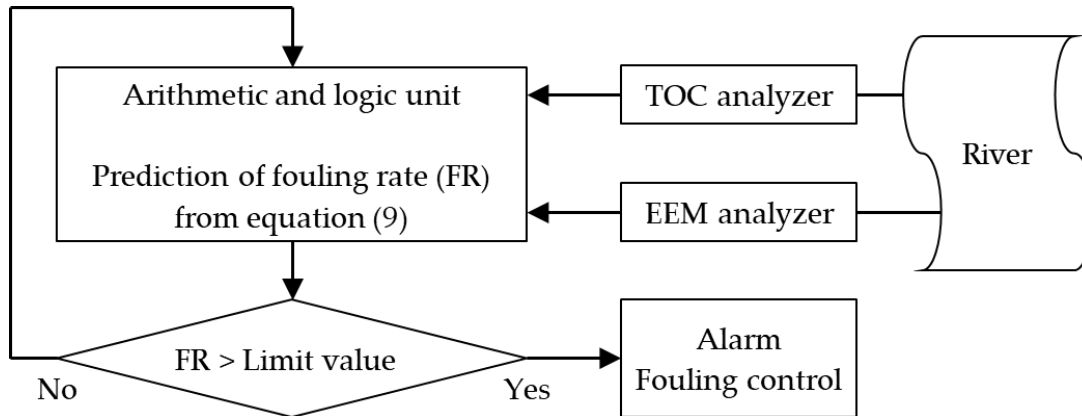


Figure 4. Image of fouling control system using arithmetic unit for fouling prediction.

3.3 Discussion on Equation (9)

From Equation (9), it is found that only Region 3 of the EEM has a correlation with FR. Other regions of the EEM have no correlation with FR. Table 4 shows the correlation of linear regression between each component of EEM analysis and LC-OCD analysis. Humic substances ([HS]) and building blocks ([BB]) have a very strong correlation with Reg. 3, and low molecular weight nutrients ([LN]) and acids ([LA]) with Reg. 1. Therefore, Equation (5) can be rewritten as Equation (10), which is similar to Equation (7):

$$\begin{aligned}
 [\text{BP}] &= 791.96 [\text{TOC-DOC}] - ([\text{HS}] + [\text{BB}] + [\text{LN}] + [\text{LA}]) \\
 &= 791.96 [\text{TOC-DOC}] - (p \cdot \text{Reg. 3} + q \cdot \text{Reg. 3} + r \cdot \text{Reg. 1} + s \cdot \text{Reg. 1}) + t \\
 &= 791.96 [\text{TOC-DOC}] - ((p+q) \cdot \text{Reg. 3} + (r+s) \cdot \text{Reg. 1}) + t
 \end{aligned}
 \tag{10}$$

where, p, q, r, s and t are constants.

As seen in Table S.1, [HS]+[BB] is higher than [LN]+[LA]. Thus, the contribution of Reg. 3 to the difference between [LC-OCD-DOC] and [BP] is probably stronger than that of Reg. 1. Therefore, FR correlates with only [TOC-DOC] and Reg. 3, as given by Equation (9).

233 Table 4. R² values in correlation between each component of EEM and LC-OCD analysis

LC-OCD analysis	EEM analysis									
	Reg. 1		Reg. 2		Reg. 3		Reg. 4		Reg. 5	
BP	○	0.441		0.105		0.103		0.153		0.152
HS		0.601		0.798	○	0.934		0.777		0.877
BB		0.718		0.883	○	0.936		0.882		0.908
LN	○	0.630		0.328		0.337		0.395		0.373
LA	○	0.137		0.106		0.100		0.126		0.094

234 ○ : Component of EEM analysis that has the strongest correlation with each component
235 of LC-OCD analysis

236 R²: coefficient of determination

237 Of course, soluble BOD and COD may be usable in substitution for TOC-DOC
238 because they are associated with TOC-DOC. But in case of applying enzymatic reaction or
239 ultraviolet absorbance method for the consecutive measurement of BOD or COD, they
240 would be unsuitable because the value is influenced by water compositions. Also regarding
241 other water quality index, for example, Effluent Quality index (EQI) explained by
242 Pathnayake and Tanyimboh (Pathnayake and Tanyimboh 2015), as it includes various
243 compositions other than dissolved organic matters, it will be unusable in substitution for
244 TOC-DOC

245 4. Conclusion

246 This study examined a foulant monitoring method with low cost and easy operation. We
247 found good correlation between fouling rate and two components of the sampled water, viz.
248 TOC and Reg. 3, measured by EEM. The following equation was derived to predict fouling rate:

$$249 \text{FR} = 3.10 [\text{TOC-DOC}] - 4.17 \times 10^{-6} \text{Reg.3} - 1.34$$

250 TOC-DOC and Reg. 3 can be measured continuously and with little effort. By measuring
251 TOC-DOC and Reg. 3, and estimating FR using the above equation, we can predict the tendency
252 of membrane fouling and control it.

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256 **Author Contributions:** Susumu Hasegawa and Taro Miyoshi conceived and designed the
257 experiments; Susumu Hasegawa and Taro Miyoshi performed the experiments; Susumu
258 Hasegawa, Taro Miyoshi, and Ryosuke Takagi analyzed the data; Susumu Hasegawa, Ryosuke
259 Takagi, and Hideto Matsuyama contributed to writing the manuscript.

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294 Table S.1. The analysis data of TOC, LC-OCD and EEM obtained from each river water sample

Name of river	Collecting date	TOC analysis (mg/L)	EEM analysis (-)					LC-OCD analysis (µg/L)						Fouling rate
		TOC -DOC	Reg. 1	Reg. 2	Reg. 3	Reg. 4	Reg. 5	LC [*] -OCD -DOC	BP ^{**}	HS ^{**}	BB ^{**}	LN ^{**}	LA ^{**}	
Akashi	2016/2/2	3.058	156177	371787	1482452	532908	4286632	1920	205	1439		276	0	1.91
Akashi	2016/2/2	4.436	439669	897637	2428318	1515305	8512909	3403	272	1646	792	639	54	2.39
Akashi	2016/2/9	4.152	501584	1042961	2259194	1530525	7471950	3491	311	1788	643	749	0	1.90
Ikawa	2016/2/2	6.207	444197	1459833	3702731	2076486	10038708	5259	280	3214	956	728	81	
Ikawa	2016/2/2	4.572	227500	715247	2326945	1041676	6597818	3797	215	2354	709	476	43	
Ikawa	2016/2/9	4.814	454438	1308825	2796828	1816590	7211699	4299	185	2230	1118	699	67	
Ikuta	2016/1/3	0.935	58999	153958	339643	258279	811363	468	30	214	104	120	0	
Ikuta	2016/1/21	0.787	102226	196525	373784	311414	876192	486	27	224	93	142	0	
Ikuta	2016/2/2	1.244	104987	168280	377900	288269	940095	566	28	271	133	134	0	
Ikuta	2016/2/17	1.152	142169	191830	502101	309998	1342632	951	26	428	190	307	0	0.14
Ikuta	2016/2/26	1.221	100334	216901	385793	342737	1019975	599	37	240	174	148	0	0.24
Ishiya	2016/1/13	1.499	47930	100064	427526	191429	1260841	1043	325	388	159	171	0	
Ishiya	2016/1/21	1.323	147241	167434	433032	240710	1301467	936	231	402	137	166	0	
Ishiya	2016/1/27	2.122	220112	231979	530463	369855	1596269	1509	450	635	169	255	0	3.53
Ishiya	2016/2/2	1.662	111524	172424	467414	263574	1396857	820	229	393	137	61	0	
Ishiya	2016/2/17	1.446	139328	194810	579497	273805	1708849	1161	199	527	190	245	0	
Ishiya	2016/2/19	1.346	124971	154526	463018	222400	1356542	1080	166	397	178	339	0	
Ina	2016/1/26	5.078	669844	1401532	2899486	2238833	9595513	4109	529	1623	819	1075	63	
Ina	2016/2/9	1.505	186895	353439	698520	406137	1846646	1166	181	528	249	208	0	0.92
Ina	2016/1/26	2.757	386398	808772	1539151	1061417	4215412	2035	320	936	327	442	10	
Sumiyoshi	2016/1/13	0.828	20145	12140	153193	27927	495309	485	64	238	78	105	0	0.25
Sumiyoshi	2016/1/21	0.568	28582	40574	165179	57118	533445	300	28	153	55	64	0	
Sumiyoshi	2016/1/21	0.690	62228	51715	180720	72932	503466	413	34	215	68	96	0	0.19
Sumiyoshi	2016/2/2	1.173	62362	71227	209882	94326	605761	459	54	235	80	90	0	
Sumiyoshi	2015/10/2		214370	159656	304803	337280	882178	1799	353	271	167	729	279	
Sumiyoshi	2015/10/21		4382	19448	199196	63100	724952	457	8	203	70	176	0	
Sumiyoshi	2015/11/13		214429	96737	281597	189614	712193	537	36	277	58	166	0	
Sumiyoshi	2016/2/17	0.927	70451	68149	287624	115247	863028	772	39	319	135	279	0	0.58
Sumiyoshi	2016/2/19	0.981	88153	82185	235275	107135	725522	615	28	258	126	203	0	
Toga	2016/1/13	1.025	11880	15414	167038	62458	646399	643	149	259	100	135	0	1.00
Toga	2015/11/13		67830	75832	266057	128050	838192	563	28	234	119	182	0	
Toga	2015/12/2		75937	62078	216537	117846	675842	800	50	289	75	386	0	
Toga	2016/1/21	0.929	98821	80766	222775	122446	659784	564	120	236	100	108	0	0.73
Toga	2016/2/2	1.424	65182	87324	249329	136986	813688	622	90	271	123	138	0	
Toga	2016/2/17	1.103	59513	96644	386727	149739	1214952	937	57	454	175	251	0	
Toga	2016/2/19	1.233	79844	94256	338911	132973	1020314	901	59	381	169	292	0	
Mo	2016/1/26	1.608	221660	318367	738906	501661	2165389	1203	188	520	199	296	0	
Yodo	2015/11/12		72650	66398	234358	112686	739852	831	48	292	92	399	0	
Yodo	2015/12/1		208839	322713	898017	498519	2610883	2031	80	938	180	833	0	
Yodo	2016/1/26	1.985	172400	318294	595799	429700	1724573	1389	221	564	165	439	0	1.97

295 * LC-OCD-DOC is the sum of BP, HS, BB, LN and NA

296 ** BP: biopolymer, HS: humic substances, BB: building blocks, LN: low molecular weight nutrients,

297 LA: low molecular weight acids