

## Improving chemical cleaning of fouled membranes in a drinking water treatment plant

Susumu Hasegawa, Yasuhiro Tanaka, Naokazu Wake, Ryosuke Takagi and Hideto Matsuyama

### ABSTRACT

Recently, membrane filtration systems have become increasingly common in drinking water treatment plants. In this industry, preventing membrane fouling is of utmost importance. Many studies on the relationship between raw water components and membrane fouling have been performed in laboratory conditions. However, very few studies have analyzed the components of foulants on the fouled membrane as operated in actual drinking water treatment plants. By analyzing these components in plant-conditions, membrane fouling will be more effectively prevented. In this study, we analyzed the components of foulants extracted with 0.1 N NaOH from a fouled membrane operated in a drinking water treatment plant in Japan. Our analysis revealed that the main foulants were humic substances. In order to dissolve the accumulated humic substances, additional chemical cleaning was attempted with 500 ppm sodium hypochlorite. As a result, it was found that humic substances were dissolved and filtration resistance significantly decreased. Additionally, the removal of inorganic foulants was also greater after chemical cleaning with 500 ppm sodium hypochlorite, as inorganic foulants trapped within humic substances were released to the membrane surface as hydroxides by the additional sodium hypochlorite cleaning and were dissolved by the periodic citric acid cleaning.

**Key words** | citric acid cleaning, drinking water treatment plant, fouling, humic substances, liquid chromatography organic carbon detection (LC-OCD), sodium hypochlorite cleaning

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### INTRODUCTION

In drinking water treatment plants, membrane filtration systems have become increasingly common due to their ability to remove turbid materials (such as pathogenic microorganisms), reduce installation space, and provide automatic operation (Peter-Varbanets *et al.* 2009). Membrane fouling in such filtration systems is unavoidable due to the adsorption of foulants included in the filtrating water on the inside and surface of the membrane. To control membrane fouling, it is important to understand the fouling mechanisms and the substances involved. Recently, polyvinylidene difluoride (PVDF) or polytetrafluoroethylene (PTFE)

have been used as materials in microfiltration (MF) and ultrafiltration (UF) membranes, because of their resistance to chemical cleaning. Membrane fouling can thus be prevented by strong chemical cleaning. However, it is very important to select the appropriate chemicals to effectively prevent membrane fouling.

Many studies on foulants found in river water have been reported. Some studies have reported a relationship between the components of river water and membrane fouling in drinking water treatment plants (Fan *et al.* 2001; Peldszus *et al.* 2011; Hasegawa *et al.* 2018). Other reports have

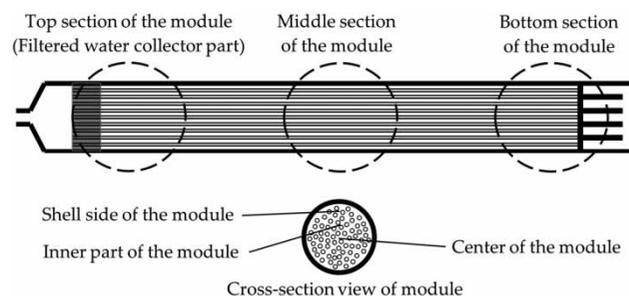
shown how river foulants affect filtration resistance under laboratory conditions (Hallé *et al.* 2009; Tian *et al.* 2013; Yamamura *et al.* 2014). However, few reports have investigated the components of foulants on and within membranes in actual plant conditions (Siembida-Lösch *et al.* 2016).

This study aimed to examine foulant substances in membranes used for filtering river water in actual plant conditions to suggest optimum cleaning methods and verify the impacts of these proposed methods. The Motoyama Purification Plant (hereafter Motoyama PP) in Kobe, Japan, replaced a rapid sand filtration system with an MF system, considering the merits of that system in providing safe drinking water, saving space, and being easy to maintain. This new system has been in service since 2010. The Motoyama PP has two trains, consisting of ten modules each. Each module has a 50 m<sup>2</sup> surface area of hollow fiber membrane made of PVDF. The pore size of the hollow fiber membrane is 0.08 µm. The planned flux of this membrane filtration is 2.0 m/d, providing 2,000 m<sup>3</sup>/d (2 × 10 × 50 × 2) of purified water. The real operating flux is about 1.9 m/d throughout the year. In the Motoyama PP, membrane modules are chemically cleaned using two methods: (1) backwashing every 30 minutes with 5 ppm sodium hypochlorite, which sterilizes the treated water pipeline and is thought to contribute to the removal of membrane organic foulants; and (2) bi-weekly chemical cleaning with 0.3% citric acid to remove inorganic foulants. Membranes are usually replaced every 3 years, or when the transmembrane pressure difference (TMP) exceeds 150 kPa. In the first two years of operation, the TMP gradually increased, in spite of the two chemical cleaning methods, and after three years in operation, just as planned, the modules of train No. 1 were replaced by new membrane modules. We then analyzed the foulants on the membranes of the discarded modules.

## METHODS

### Dismantling of membrane modules

Fouled membranes were taken from the used membrane modules operated for three years at a permeation flux of 1.9 m/d and for which TMP was predicted to become higher than



**Figure 1** | Sampling position of the used membrane module for foulant analysis.

150 kPa in the next winter season (initial TMP ~ 30 kPa). As shown in Figure 1, 12 samples of 12 cm length each were cut from the three parts of the module (center, inner, and shell side parts of the module radius) for each of the three sections (top, middle, and bottom) of the module length.

In total, 108 samples (12 × 3 × 3) were taken from the membrane module and washed slightly with ultrapure water to remove any foreign material from the membrane surface before carrying out the foulant analysis. Each of the 12 samples taken from each of the nine parts of the module were divided into four groups (3 samples × 4 groups). Each group was analyzed for the extraction of organic reversible foulants, organic irreversible foulants, inorganic reversible foulants, and inorganic irreversible foulants, respectively.

### Extraction of foulants

Three samples taken from each of the nine parts, totaling 27 samples (3 × 9), were immersed in 200 mL of 0.1 N NaOH to extract organic foulant. Another 27 samples were immersed in 0.3% citric acid to extract inorganic foulant. Next, the fouling materials were extracted from the membranes by shaking the vessel under the conditions of 20 mm stroke and 120 rpm for 12 h at 20 ± 0.2 °C. The amounts of organic and inorganic foulants extracted were measured using a total organic carbon (TOC) analyzer and an inductively coupled plasma optical emission spectrometry (ICP-OES) analyzer, respectively. The identification of organic foulants was performed with a liquid chromatography organic carbon detector (LC-OCD) and excitation emission matrix (EEM) fluorescence spectroscopy. The measured value is referred to as the total

foulant,  $Ft$  ( $\text{mg}/\text{m}^2$ ), that is, the sum of reversible foulants ( $Fr$ ) and irreversible foulants ( $Fir$ ) mentioned below.

For the remaining 54 samples, the outer surfaces of the membranes were lightly wiped with a sponge to remove any accumulated reversible foulant which might be removed by physical cleaning methods such as air bubbling or backwash cleaning. Next, each of the 27 samples was treated by chemical extraction in a similar manner as described above. The amount of foulant extracted after wiping with the sponge was referred to as the irreversible foulant,  $Fir$ . The reversible foulant,  $Fr$ , is given by Equation (1):

$$Fr = Ft - Fir \quad (1)$$

### Filtration resistance of fouled membranes

To measure the membrane filtration resistance (which indicates the degree of fouling), a single hollow fiber membrane test was performed (Hasegawa et al. 2018), using the single hollow fiber membrane test equipment as shown in the online Supplementary Data (Figure S1). The sampled membrane was set in an MF column with an interior diameter of 4 mm and a length of 100 mm, just after being cut off from the module or after wiping. Ultrapure water was injected into the column using a micro-tube pump, and the water permeated through the membrane (from outside to inside) was discharged at a constant flux of  $1.9 \text{ m}^3/\text{m}^2/\text{d}$ . TMP and cumulative weight of permeated water were monitored continuously and recorded in a data logger. The fouling degree of the sampled membrane was evaluated using filtration resistance  $R$  ( $1/\text{m}$ ), defined by Equation (2) derived from Darcy's equation (Zondervan & Roffel 2007):

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

where  $\Delta P$  is the TMP (Pa);  $J$  is the filtration flux ( $\text{m}/\text{s}$ ), fixed at  $1.9 \text{ m}/\text{d}$  for this study; and  $\mu$  is the viscosity ( $\text{Pa}\cdot\text{s}$ ) of feed water. A large  $R$  value indicates a higher degree of membrane fouling. The filtration resistance of the fouled membrane without wiping is known as the total filtration resistance  $Rt$  and that with wiping is known as the irreversible filtration resistance  $Rir$ . Therefore, the reversible

filtration resistance  $Rr$  is given by Equation (3):

$$Rr = Rt - Rir \quad (3)$$

### Analysis method

Howe & Clark (2002) reported that particulate matter exceeding  $0.45 \mu\text{m}$  had no significant fouling impact compared with dissolved matter. Particulate organic matter may greatly influence TOC. Therefore, prior to the measurements, all samples were filtered through a  $0.45\text{-}\mu\text{m}$  hydrophilic polytetrafluoroethylene membrane (DISMIC 13HP045AN, Advantec, Tokyo, Japan).

The TOC of the sampled water was measured with a TOC analyzer (TOC-V<sub>CSH</sub>, Shimadzu Corporation, Kyoto, Japan). Natural organic matter (NOM) was analyzed by LC-OCD (Model 8 DOC-Labor instrument, Karlsruhe, Germany). Dissolved organic matter (DOM) was analyzed with an EEM spectrometer (Aqualog, Horiba Advanced Techno Co. Ltd, Kyoto, Japan). For the inorganic analysis, we used an ICP-OES analyzer (SPS3100, SII Nanotechnology).

## RESULTS AND DISCUSSION

### Difference of fouling degree in the various parts of the module

The filtration resistances of the membrane samples taken from each part of the module are shown in Figure 2. The

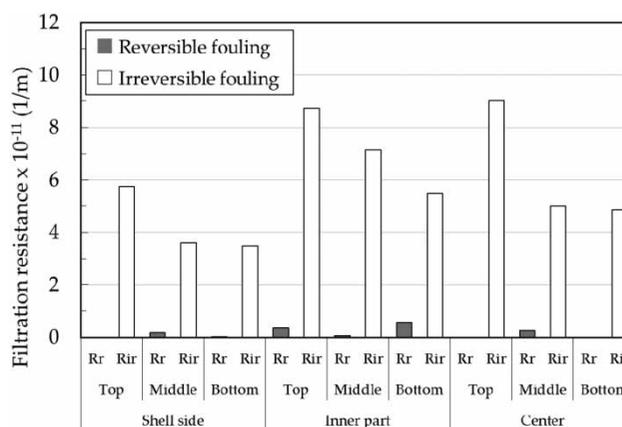


Figure 2 | Filtration resistance of each part in the membrane module.

reversible filtration resistance of the membrane is almost zero for every part of the module, suggesting that any reversible foulant might be almost completely removed by physical cleaning.

The irreversible filtration resistance in the top section of the module is larger than in the middle and bottom sections, and the irreversible filtration resistance of the shell side in the module is smaller than that of the inner and center parts. This means that fouling occurred most easily in the center/inner parts in the top part of the module, and hardly occurred on the shell side part in the bottom part of the module. From these results, it is presumed that fouling progressed from the center/inner part in the top part of the module to the shell side in the bottom part of the module.

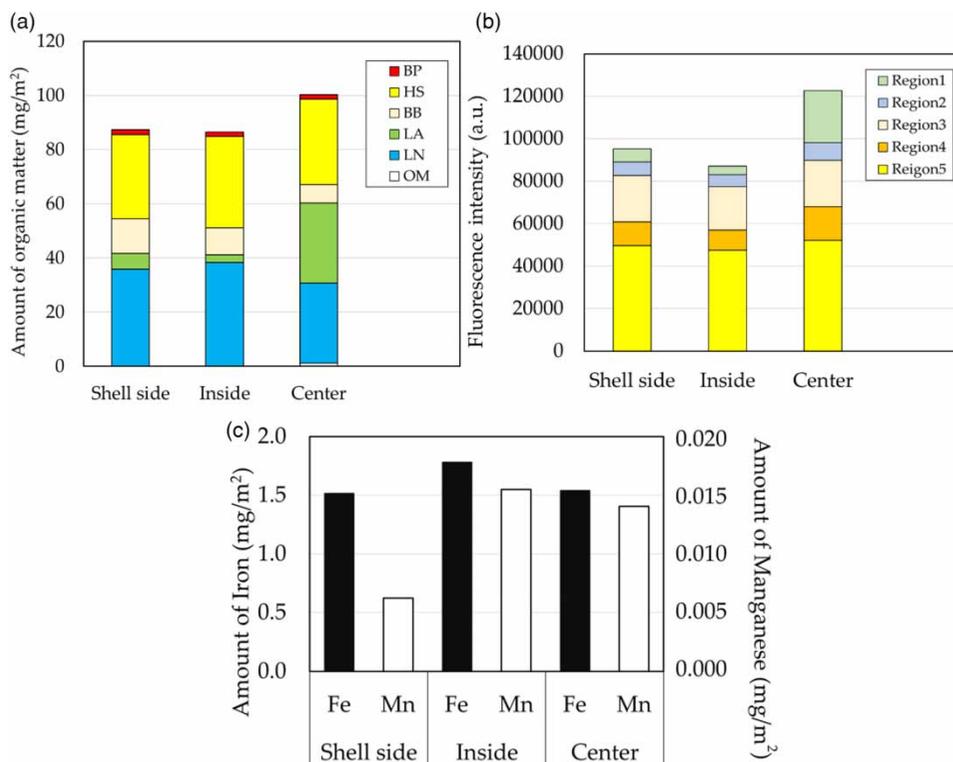
### The major foulant in actual plant conditions

Recently, membrane foulants in the treatment of river water have been studied by many researchers. They have revealed that the main foulants in river water treatment plants are

mainly DOM, such as biopolymers and humic substances (Kimura *et al.* 2014; Chon *et al.* 2017; Hasegawa *et al.* 2018).

Figure 3 shows the components of the irreversible foulant extracted from the fouled membrane used in the Motoyama PP (i.e., that remaining after wiping of the membrane surface). In Figure 3(a), biopolymers (BP), humic substances (HS), building blocks (BB), low molecular weight acids (LA), low molecular weight neutrals (LN) and other materials (OM) were detected by LC-OCD analysis (Huber *et al.* 2011). In Figure 3(b), the components of foulant measured by EEM are classified according to Chen's method as aromatic protein I (Region 1), aromatic protein II (Region 2), fulvic acid-like (Region 3), soluble microbial (Region 4) and humic acid-like (Region 5) (Chen *et al.* 2003). Figure 3(a) and 3(b) suggest that the ratio of components is similar for all samples taken from the three parts of the module.

Moreover, Figure 3(a) suggests that the concentration of BP (the foulant reported as most related to filtration resistance) was relatively low in each part of the module.



**Figure 3** | The amount of organic and inorganic matter extracted from the fouled membrane after wiping the membrane surface: (a) LC-OCD analysis (amount of organic matter in foulant), (b) EEM analysis (amount of protein-like components in foulant), (c) ICP-OES analysis (amount of inorganic matter in foulant).

On the other hand, a lot of HS – which also relate to the fouling (Jacquin *et al.* 2018) – were observed. Although other components such as BB, LA, LN, and OM, account for more than 50 wt%, it has previously been reported that they do not cause significant membrane fouling (Hasegawa *et al.* 2017). Therefore, the increase in filtration resistance in actual plant conditions in this case was caused by HS, not by BP. Additionally, Figure 3(b) reveals Region 5 to be the main component in the membrane foulant. Region 5 substances accumulated on the membrane, because humic acid cannot be dissolved by periodic citric acid cleaning. Region 3 substances are also recognized as HS, but these are dissolved by periodic citric acid cleaning and therefore do not accumulate on the membrane surface. It is clear from Figure 3(c) that the inorganic matter (mainly iron) of which the amount is 1/50 that of organic matter, is removed easily by the usual scheduled citric acid cleaning and does not accumulate on the membrane surface like DOM and HS.

### Modification of the chemical cleaning process

As mentioned above, the main foulants in this water treatment plant are HS. We have therefore modified the procedure for chemical cleaning. The main aspect of our modification was to use sodium hypochlorite instead of citric acid once every three cleanings to remove HS.

In the Motoyama PP, the membrane module of the No. 2 train was changed to a new membrane module in August 2014, because of the increase in TMP. As TMP depends on water temperature, it often reaches critical levels of 150 kPa during winter, which is the basis for changing the membrane after three years in operation.

We started the modified chemical cleaning with 500 ppm sodium hypochlorite once every three cleanings on Dec. 10, 2016. TMP dramatically decreased after this modification, as shown in Figure 4. This means our modified chemical cleaning process is useful for preventing membrane fouling.

### The effect of sodium hypochlorite cleaning on foulant removal

To evaluate the effects of the modified cleaning method, we analyzed the components of the wastewater from chemical cleaning. With regard to the analysis of organic foulants, citric acid is a dissolved organic compound, and the concentration of citric acid is very high as compared with the extracted foulant. Furthermore, in the LC-OCD analysis, the citric acid peak appears at the same retention time as HS and BB, which means it is difficult to detect the extracted organic foulant in citric acid cleaning wastewater. Therefore, we evaluated the organic foulant contained in sodium hypochlorite wastewater.

Figure 5(a) shows the components of foulant in the sodium hypochlorite cleaning wastewater after the first cleaning for each train. Almost the same components as those of the foulants extracted from the surface of the fouled membrane with 0.1 N NaOH (Figure 3(a)) were detected. The 500 ppm sodium hypochlorite would cause a similar effect with NaOH extracting, since its pH is about 12. This means that the foulant accumulated on the membrane surface was removed by hypochlorite cleaning. From the results shown in Figures 3(a) and 5(a), it was calculated that about 20% of foulants accumulated on the

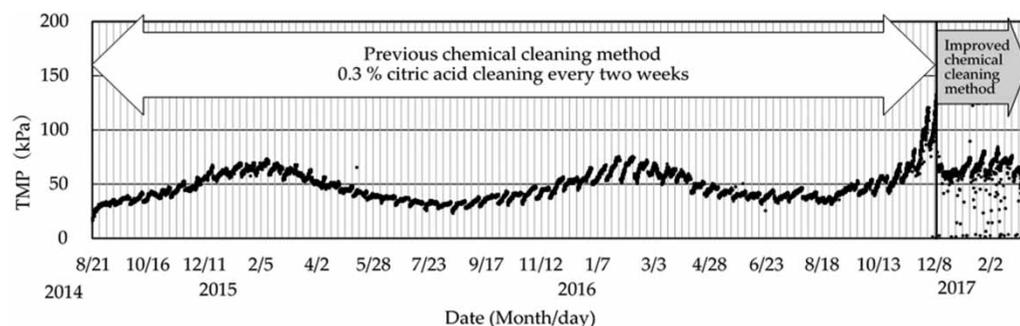
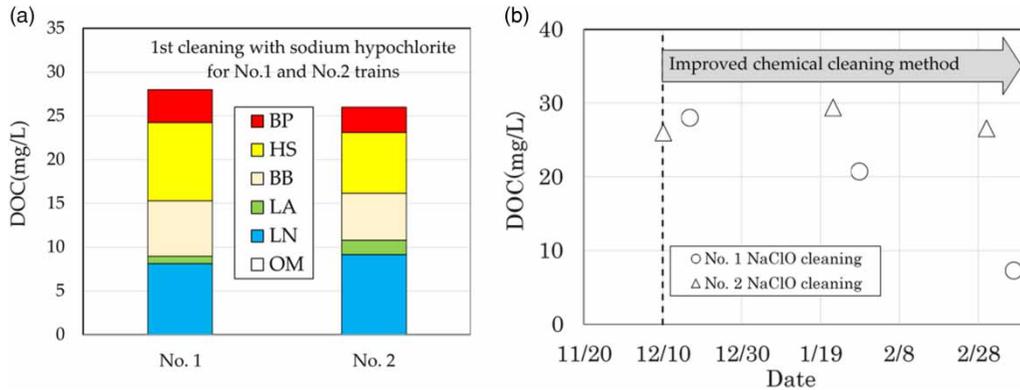


Figure 4 | Changes in TMP over time in the Motoyama PP.

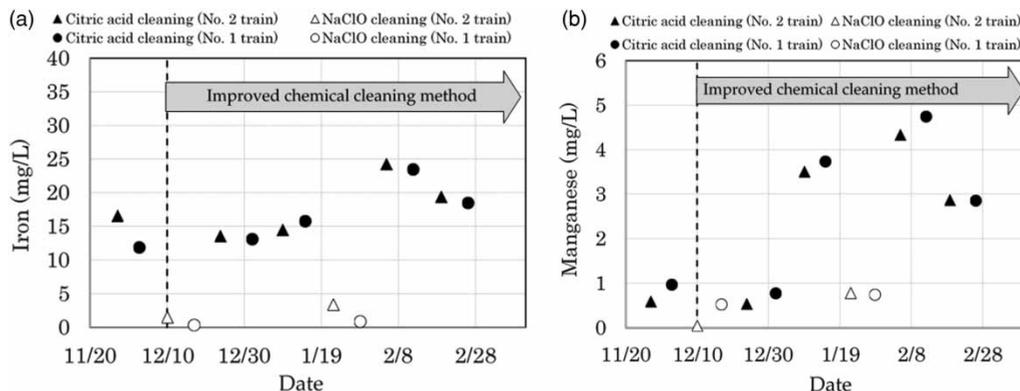


**Figure 5** | DOC concentration of the NaClO cleaning wastewater. The dashed line in (b) indicates the start of improved chemical cleaning.

membrane surface could be removed by one hypochlorite cleaning. Figure 5(b) shows the change of DOC in the wastewater of the sodium hypochlorite cleaning. DOC concentration of the No. 2 train was almost the same after three cleanings, suggesting that there were a lot of organic foulants remaining in the module. On the other hand, DOC concentration of the No. 1 train decreased gradually over three cleanings, suggesting that the foulant in the module might be completely cleared after three cleanings. The differential effect of hypochlorite cleaning between the No. 1 and No. 2 trains is thought to be due to the operating periods. The module of the No. 2 train accumulated organic foulant for more than two years of operation, whereas the module of the No. 1 train operated for only one year. The foulant accumulation of the No. 1 train is therefore lower than for the No. 2 train and requires earlier cleaning.

From the above discussion, it is clear that the additional sodium hypochlorite (500 ppm) cleaning to citric acid cleaning is effective for controlling membrane fouling in the drinking water treatment system. Speculating from this result, if we use the sodium hypochlorite at higher than 5 ppm for regular backwashing, the additional cleaning with 500 ppm sodium hypochlorite may not be necessary. However, at this moment, we do not have any data on this matter.

Figure 6 shows the change in iron and manganese concentrations in the chemical cleaning wastewater. Generally speaking, iron and manganese are removed more efficiently by acidic substances than by sodium hypochlorite (Gao et al. 2011; Shi et al. 2014). It is therefore interesting that the concentrations of both increased in the wastewater on citric acid cleaning after sodium hypochlorite cleaning. This phenomenon occurs because inorganic matter found within organic foulant is not dissolved by citric acid as it



**Figure 6** | The change of iron and manganese concentration in the chemical cleaning wastewater. The dashed line indicates the start of improved chemical cleaning.

is covered by organic foulants, and therefore remains on the membrane surface (Jermann *et al.* 2007). When the fouled membrane surface is then subsequently washed with sodium hypochlorite, inorganic substances are released alongside organic foulant and are deposited as hydroxides on the membrane surface if the pH is relatively high (around 12). The hydroxides will be dissolved by the next citric acid cleaning. For this reason, it is expected that periodic alkaline cleaning during the repeated acid cleaning cycle might also promote the removal of inorganic foulants.

## CONCLUSIONS

Foulant analysis of membrane modules that were operated to obtain drinking water from river water for more than three years, or up to a TMP of 150 kPa, was performed using LC-OCD, EEM, and IPC-OES analyzers. From the results, a modified chemical cleaning method was proposed and applied in the plant. The results are as follows:

- The main foulants were humic substances, which could not be removed by acid cleaning.
- Periodic chemical cleaning with sodium hypochlorite removed accumulated organic foulants and significantly decreased filtration resistance.
- The analysis of sodium hypochlorite cleaning wastewater revealed that about 20% of the organic foulant accumulated in a module can be removed in one cleaning.
- The inorganic foulant removal efficiency of citric acid is reinforced by periodic sodium hypochlorite cleaning.

## AUTHOR CONTRIBUTIONS

Susumu Hasegawa, Yasuhiro Tanaka and Naokazu Wake conceived and designed the experiments; Susumu Hasegawa and Yasuhiro Tanaka performed the experiments; Naokazu Wake provided the actual data of Motoyama PP; Susumu Hasegawa, Yasuhiro Tanaka and Ryosuke Takagi analyzed the data; Susumu Hasegawa, Ryosuke Takagi, and Hideto Matsuyama contributed to writing the manuscript.

## SUPPLEMENTARY DATA

The Supplementary Data for this paper are available online at <http://dx.doi.org/10.2166/ws.2019.114>.

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First received 27 March 2019; accepted in revised form 31 July 2019. Available online 12 August 2019