



Title	Identifying, counting, and characterizing superfine activated-carbon particles remaining after coagulation, sedimentation, and sand filtration
Author(s)	Nakazawa, Yoshifumi; Matsui, Yoshihiko; Hanamura, Yusuke; Shinno, Koki; Shirasaki, Nobutaka; Matsushita, Taku
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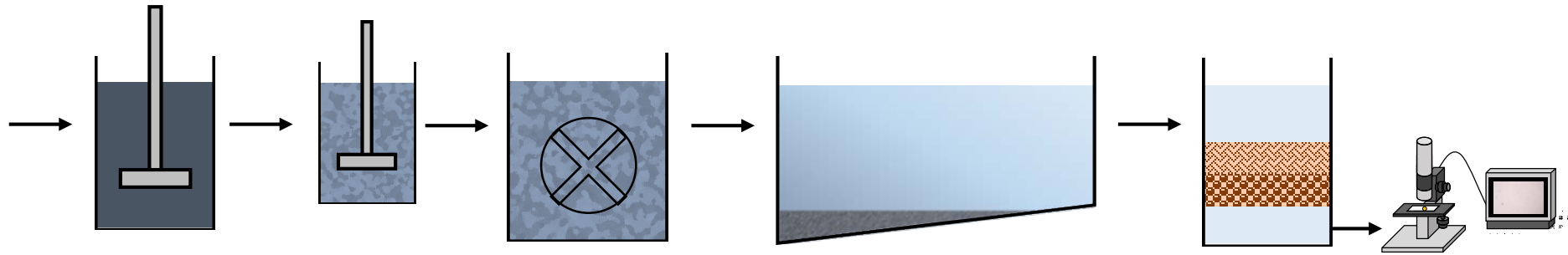
## **Research Highlights**

- Removals of superfine PAC (SPAC) and conventionally-sized PAC were examined.
- Novel image analysis method allowed visualization of particles with diameter  $> 0.2 \mu\text{m}$ .
- Conventional water treatment process produced a 5-log decrease in particle number.
- SPAC remained in sand filtrate at same concentration as PAC at equivalent doses.
- Smaller carbon particles were neutralized less during coagulation.

### SPAC

7.5 mg/L =  $\sim 5 \times 10^7$  particles/mL

$D_{50} = 1 \mu\text{m}$



### PAC

30 mg/L =  $\sim 1 \times 10^7$  particles /mL

$D_{50} = 14 \mu\text{m}$



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**Identifying, counting, and characterizing superfine activated-carbon particles remaining after coagulation, sedimentation, and sand filtration**

*Yoshifumi Nakazawa<sup>a</sup>, Yoshihiko Matsui<sup>b,\*</sup>, Yusuke Hanamura<sup>a</sup>, Koki Shinno<sup>a</sup>, Nobutaka Shirasaki<sup>b</sup>, Taku Matsushita<sup>b</sup>*

*<sup>a</sup> Graduate School of Engineering, Hokkaido University, N13W8, Sapporo 060-8628, Japan*

*<sup>b</sup> Faculty of Engineering, Hokkaido University, N13W8, Sapporo 060-8628, Japan*

*\* Corresponding author. Faculty of Engineering, Hokkaido University, N13W8, Sapporo 060-8628, Japan. Tel./fax: +81-11-706-7280*

E-mail address: matsui@eng.hokudai.ac.jp (Y. Matsui)

20 ABSTRACT

21 Superfine powdered activated carbon (SPAC; particle diameter  $\sim 1 \mu\text{m}$ ) has greater adsorptivity  
22 for organic molecules than conventionally sized powdered activated carbon (PAC). Although  
23 SPAC is currently used in the pretreatment to membrane filtration at drinking water purification  
24 plants, it is not used in conventional water treatment consisting of coagulation–flocculation,  
25 sedimentation, and rapid sand filtration (CSF), because it is unclear whether CSF can  
26 adequately remove SPAC from the water. In this study, we therefore investigated the residual  
27 SPAC particles in water after CSF treatment. First, we developed a method to detect and  
28 quantify trace concentration of carbon particles in the sand filtrate. This method consisted of 1)  
29 sampling particles with a membrane filter and then 2) using image analysis software to  
30 manipulate a photomicrograph of the filter so that black spots with a diameter  $> 0.2 \mu\text{m}$   
31 (considered to be carbon particles) could be visualized. Use of this method revealed that CSF  
32 removed a very high percentage of SPAC: approximately 5-log in terms of particle number  
33 concentrations and approximately 6-log in terms of particle volume concentrations. When  
34 waters containing 7.5-mg/L SPAC and 30-mg/L PAC, concentrations that achieved the same  
35 adsorption performance, were treated, the removal rate of SPAC was somewhat superior to that  
36 of PAC, and the residual particle number concentrations for SPAC and PAC were at the same  
37 low level (100–200 particles/mL). Together, these results suggest that SPAC can be used in  
38 place of PAC in CSF treatment without compromising the quality of the filtered water in terms  
39 of particulate matter contamination. However, it should be noted that the activated carbon  
40 particles after sand filtration were smaller in terms of particle size and were charge-neutralized  
41 to a lesser extent than the activated carbon particles before sand filtration. Therefore, the  
42 tendency of small particles to escape in the filtrate would appear to be related to the fact that  
43 their small size leads to a low destabilization rate during the coagulation process and a low  
44 collision rate during the flocculation and filtration processes.

45 *Keywords:*

46 SPAC

- 47 PAC
- 48 image analysis
- 49 filtrate
- 50 zeta potential
- 51

## 52 **1. Introduction**

53 Recent developments in milling technology now enable the production of superfine powdered  
54 activated carbon particles (SPAC) down to micron and submicron dimensions. SPAC has an  
55 extremely fast rate of adsorption and higher capacity to adsorb dissolved organic contaminants  
56 compared with conventionally sized powdered activated carbon (PAC) (Ando et al. 2010,  
57 Bonvin et al. 2016, Dunn and Knappe 2013, Jiang et al. 2015, Matsui et al. 2015, Matsui et al.  
58 2012, Partlan et al. 2016). To date, the majority of research dealing with SPAC has focused on  
59 its use as part of membrane filtration processes (Amaral et al. 2016, Ellerie et al. 2013, Heijman  
60 et al. 2009, Matsui et al. 2007). In membrane filtration processes, SPAC is used as an adsorbent  
61 for the removal of dissolved organic contaminants before the water is treated by membrane  
62 filtration, which removes the SPAC entirely. SPAC is already used in full-scale water treatment  
63 plants that use membrane filtration processes because dosage costs are lower for SPAC than for  
64 PAC (Kanaya et al. 2015).

65 SPAC may also be useful as part of conventional treatment, which consists of the following  
66 unit processes: coagulation–flocculation, sedimentation, and rapid sand filtration (CSF).  
67 However, it is possible that SPAC will be inefficiently removed in the conventional treatment  
68 compared with the treatment including membrane filtration; that is, SPAC particles might not  
69 be adequately removed during the treatment process and could then enter the distribution  
70 system.

71 In addition to contributing to the removal of dissolved organic contaminants, adsorbents such  
72 as PAC may affect floc formation in coagulation and flocculation processes. Younker and  
73 Walsh (2016) have reported that the addition of PAC prior to the addition of a coagulant ( $\text{FeCl}_3$ )  
74 reduces floc size but has little impact on the final turbidity after sedimentation. Aguilar et al.  
75 (2003) have reported that the use of PAC decreases the number of particles remaining after

76 coagulation-flocculation and sedimentation. In a coagulation-membrane filtration study, the  
77 addition of SPAC or PAC enhanced floc formation, and at the same dose, larger, more  
78 permeable floc particles were formed with SPAC than with PAC because of the fractal effect  
79 and the increased frequency of particle–particle collisions with SPAC (Matsui et al. 2009).  
80 These results thus suggest that the addition of SPAC may have positive effects on the  
81 coagulation–flocculation process because the carbon particles serve as nuclei for flocculation.  
82 However, if carbon particles are to serve as nuclei, their high negative charge must be  
83 neutralized; non-neutralized carbon particles do not flocculate and would pass through the sand  
84 filter into the treated water.

85 The effects of the addition of PAC on the turbidity of treated water after CSF were reported  
86 more than 25 years ago. Some studies reported that PAC at concentrations up to 30 mg/L did  
87 not compromise the quality of the treated water in terms of particulate matter contamination  
88 (Carns and Stinson 1978, Gifford et al. 1989). However, in those studies the quality of the  
89 filtered water was evaluated via a naked-eye visual assessment. Therefore, the number of PAC  
90 and SPAC particles remaining in treated water at concentrations below the limit of visual  
91 detection remains unknown, despite the fact that PAC in treated water at concentrations below  
92 the limit of visual detection can lead to complaints from customers such as food-processing  
93 companies and photo-finishing stores (American Society of Civil Engineers and American  
94 Water Works Association 1998, Bureau of Waterworks Tokyo Metropolitan Government 2014).  
95 Therefore, the removal of SPAC, which has a much smaller particle diameter than PAC, is a  
96 critical issue that must be addressed before SPAC is used in CSF water treatment plants.

97 In the present study, we developed a method for identifying and quantifying very low  
98 concentrations of SPAC ( $<1 \mu\text{g/L}$ ,  $<1000$  carbon particles/mL) in treated water, and we  
99 determined the concentration and characteristics of the carbon particles remaining after CSF.



## 100 **2. Materials and methods**

### 101 *2.1. Carbon particles and coagulant*

102 A commercially available wood-based PAC (Taiko W; Futamura Chemical Co., Ltd., Nagoya,  
103 Japan) was prepared as a slurry in pure water (Milli-Q water; Millipore, Billerica, MA, USA)  
104 and then pulverized to produce SPAC slurries of different particle sizes (Table 1). SPAC<sub>L</sub> was  
105 produced with a closed-chamber ball mill (Nikkato, Osaka, Japan) with 5- and 10-mm-diameter  
106 balls. SPAC<sub>S1</sub> and SPAC<sub>S2</sub> were produced using a bead mill with a re-circulation system  
107 (LMZ015, Ashizawa Finetech, Chiba, Japan) and 0.3-mm-diameter ZrO<sub>2</sub> beads (Pan et al.  
108 2017). Standard carbon particle suspensions with predetermined mass concentrations were  
109 prepared by diluting a SPAC/PAC slurry with Sapporo City tap water filtered through a PTFE  
110 (polytetrafluoroethylene) membrane (nominal pore diameter, 0.1 μm; φ90 mm; Toyo Roshi  
111 Kaisha, Ltd., Tokyo, Japan). Membrane-filtered tap water without the addition of carbon  
112 particles was used as blank water. The particle size distributions of the carbons were determined  
113 by using a laser light diffraction and scattering method (Microtrac MT3300EXII, Nikkiso Co.,  
114 Tokyo, Japan). To measure the true particle size distribution of the carbon particles, a sample  
115 of the slurry was pretreated by the addition of a dispersant (Triton X-100; Kanto Chemical Co.,  
116 Tokyo, Japan; final concentration, 0.08% w/v) and subjected to ultrasonic dispersion before  
117 determination of the particle size distribution via the laser light diffraction and scattering  
118 method. The apparent particle size distributions of the carbon particles were measured via the  
119 same method but without dispersant addition or ultrasonic dispersion.

120 Poly-aluminum chloride with a basicity of 50% and sulfate content of 3% (Taki Chemical Co.,  
121 Ltd, Hyogo, Japan), a coagulant widely used in water treatment plants, was used as the  
122 coagulant in this study.

123

124 *2.2. Coagulation–flocculation, sedimentation, and rapid sand filtration*

125 Tap water in Sapporo city was filtered through a membrane filter (nominal pore diameter, 0.1  
126  $\mu\text{m}$ ; Toyo Roshi Kaisha, Ltd.) and then added with one of the carbon slurries to 30-mg/L SPAC,  
127 7.5-mg/L SPAC, or 30-mg/L PAC to prepare raw waters. Most CSF experiments were  
128 conducted with these waters, but two CSF experiments were conducted with water from the  
129 Toyohira River (Hokkaido) after supplementing the water with SPAC at 7.5 mg/L. The river  
130 water was sampled at the location where it becomes the raw water source for the Moiwa Water  
131 Purification Plant (Sapporo, Japan).

132 A schematic of the experimental setup and procedure is shown in Fig. 1S (SI, Supplementary  
133 Information). The coagulation–flocculation and sedimentation steps were conducted in a 4-L  
134 rectangular beaker. After a predetermined volume of HCl or NaOH (0.1 N) was added to adjust  
135 the coagulation pH to 7.0, the coagulant (poly-aluminum chloride) was injected into the beaker  
136 to a final concentration of 4 mg-Al/L. The water was stirred rapidly for 20 s (coagulation;  $G =$   
137  $600\text{ s}^{-1}$ , 197 rpm) and then slowly for 20 min (flocculation; 5 min at  $50\text{ s}^{-1}$ , 38 rpm; 5 min at  
138  $20\text{ s}^{-1}$ , 20 rpm; 10 min at  $10\text{ s}^{-1}$ , 13 rpm). The water was then left at rest for 1 h until the floc  
139 particles settled. Next, the top three liters of the water (supernatant) were transferred to another  
140 beaker for the determination of turbidity (2100Q portable turbidimeter; Hach Co., USA) and  
141 for rapid sand filtration. The rapid sand filtration was conducted for 40 min at a rate of  $90\text{ m}$   
142  $\text{d}^{-1}$  in the down-flow direction using a column ( $\phi 4\text{ cm}$ ) filled to a depth of 50 cm with sand  
143 (effective diameter, 0.6 mm; uniformity, 1.3). The sand filtrate was collected from 13 to 40 min  
144 after the start of filtration, and the turbidity and particle count of the filtrate were determined.

145 After each filtration run, the sand filter was backwashed with tap water for 1 h. Next, pure water  
146 (Milli-Q water) was passed through the sand filter for 1 h in the down-flow direction, followed  
147 by 3 L of membrane-filtered tap water, also in the down-flow direction. After the 3 L of  
148 membrane-filtered tap water was passed through the sand filter, the sand filtrate was collected.  
149 The particle count of the sand filtrate was always low ( $< 6$  particles/mL), but this count was  
150 subtracted from the particle count of the filtrate collected in the filtration experiments to yield  
151 the net count of particles that had passed through the filter. The filter was then used for the next  
152 filtration experiment.

### 153 *2.3. Membrane filtration and microscopic image analysis*

154 To sample the carbon particles in the water, the water was filtered through a PTFE membrane  
155 filter (nominal pore diameter,  $0.1\ \mu\text{m}$ ;  $\phi 25\ \text{mm}$ ; Millipore) supported by a glass filter holder  
156 (KG-25; Toyo Roshi Kaisha, Ltd.) (Fig. 2S, SI). After drying the filter, color digital  
157 photomicrographs were captured for nine predetermined observation zones (microscope view  
158 area,  $247 \times 330\ \mu\text{m}$ ) per filter (Fig. 3S, SI) with a digital microscope (VHX-2000; Keyence,  
159 Japan) at  $1000\times$  magnification. The photomicrographs were analyzed by using the image  
160 analysis software supplied with the microscope.

161 Figure 1 shows two representative image analysis series. Series A shows the image analysis of  
162 a membrane through which 100 mL of standard suspension containing  $1\text{-}\mu\text{g/L}$  SPAC<sub>S1</sub> was  
163 filtered. Series B shows an image analysis of a membrane through which a sample of sand  
164 filtrate was filtered at a pilot-scale plant where surface water was treated by CSF after the  
165 addition of PAC (Yamaguchi et al. 2016). Panels A1 and B1 are the original photomicrographs  
166 of the surface of the membranes. In the photomicrographs, the black and dark gray spots in the  
167 background of the membrane texture are presumably carbon particles; very few of these colored  
168 spots were observed in the present study. After removal of the membrane texture, the images

169 were converted to grayscale (Panels A2 and B2). The black and dark gray spots in the images  
170 were identified as carbon particles based on their lightness, with the cut-off value being  $195 \pm$   
171 15 in the range 0–255, because the maximum lightness of carbon particles in these photographs  
172 was  $\sim 195$ . Touching or overlapping spots were separated from each other by using a shrink-  
173 and-blow process in the software. Spots with a diameter  $> 0.2 \mu\text{m}$  were individually identified.  
174 Panels A3 and B3 show detected spots, which appear black in these panels. The original  
175 photomicrograph was then checked to confirm that the spots were present in both the  
176 photomicrograph and the processed image: false spots were removed through this process.  
177 Panels A4 and B4, which show the verified spots, were then obtained. Note that if many spots  
178 with colors but not black-and-white had been observed in the photomicrographs, more  
179 advanced image processing would have been required to identify the carbon particles (see Figs.  
180 4S and 5S, SI). However, because the raw waters used in the present study were made by adding  
181 carbon particles to membrane-filtered water or low-turbidity river water, colored spots were not  
182 observed (Fig. 1). This was true even in the photomicrographs of the samples collected at the  
183 pilot-scale water treatment plant. In principle, however, it is hard to distinguish between carbon  
184 particles and black mineral particles, but the interference due to black mineral particles would  
185 be small because of its very low concentration compared with carbon particle concentration  
186 (Figs. 6S, SI).

187 For each filter, the spot counts for the nine observation zones (Figs. 7S and 8S, SI) were  
188 summed to give the total spot count for the nine observation zones. The spot count for each  
189 whole filter was obtained by multiplying the total count by the ratio of the filtration area to the  
190 total area of the nine observation zones.

191 The filtration and counting processes were conducted three times for each water sample. The  
192 spot counts for the three filters were then averaged and corrected by subtracting the spot count

193 of the blank water. Dividing the average-minus-blank count by the volume of the water sample  
194 gave the carbon particle number concentration.

195 The volume of each particle was calculated by assuming the particle to be spherical with a  
196 diameter equal to the projected area diameter of its spot on the photomicrograph. The number  
197 concentration was converted to a volume concentration by using Eq. (1):

$$198 \quad \varnothing = C_N \int_0^{\infty} \frac{\pi}{6} d^3 f_N(d) dd \quad (1)$$

199 where  $\varnothing$  is the volume concentration (dimensionless),  $C_N$  is the number concentration ( $\text{cm}^{-3}$ ),  
200  $d$  is the particle diameter (cm), and  $f_N(d)$  is the particle size distribution by number ( $\text{cm}^{-1}$ ).

201 When determining the volume concentration and the particle size distribution by volume, a  
202 blank correction was not performed. Not performing a blank correction did not substantially  
203 increase the analytical error, because the black spots observed for the blank water were very  
204 small in size and number compared to the black spots determined to be carbon particles in the  
205 water samples.

#### 206 *2.4. Measurement of zeta potential*

207 The zeta potential of the carbon particles in the water samples after each stage of the water  
208 treatment process (i.e., coagulation, sedimentation, and rapid sand filtration) was determined  
209 by using a zeta electrometer (Zetasizer Nano ZS; Malvern, United Kingdom). Before the zeta  
210 potentials of the sand filtrate samples were determined, the samples were concentrated by a  
211 factor of 15.6. The zeta potentials of the other samples were measured without concentration.

212 To concentrate the sand filtrate samples, a tube containing 38.5 mL of sample water was  
213 centrifuged at 32,000 rpm (170,000 g) for 35 min at 25 °C (Ultracentrifuge L-80 XP; Beckman  
214 Coulter, USA). After centrifugation, the upper 26 mL of water in the tube was carefully  
215 removed, the tube was replenished with another 26 mL of sample water, and the tube was  
216 centrifuged again. This series of operations was repeated six times.

#### 217 *2.5. Fractionation of SPAC and PAC according to particle size*

218 The SPAC in suspension (8.3 g/L) was fractionated by means of centrifugation. A tube  
219 containing 30 mL of the SPAC suspension was centrifuged for 60 min at 0, 500, 1500, or 4000  
220 rpm (himac CT6E; Hitachi Koki Co., Ltd., Tokyo, Japan). The upper 20 mL of the sample in  
221 the tube was then withdrawn, and the particle size distribution (Microtrac MT3300EX II ) and  
222 zeta potential (Zetasizer Nano ZS) of the carbon particles remaining in the upper 20 mL of the  
223 sample were determined. Before measurement of the zeta potential, the turbidity of the sample  
224 was adjusted to 30 nephelometric turbidity units (NTUs) by diluting the sample with filtered  
225 tap water. Particle size distributions were determined without the addition of a dispersant or the  
226 use of ultra-sonication.

227 PAC in suspension (33 g/L) was fractionated by means of gravity settling. An aliquot (40 mL)  
228 of the PAC suspension was left at rest in a beaker for 0, 6, 120, or 720 min. The upper 4 mL of  
229 the sample was then withdrawn, and the zeta potential and particle size distribution were  
230 determined as described above.

### 231 **3. Results and Discussion**

#### 232 *3.1. Identification and enumeration of carbon particles on the filter*

233 The particle concentrations in the blank water and standard suspensions (0.1, 1.0, and 10  $\mu\text{g/L}$ )  
234 were determined by using the membrane-filtration and microscopic-image-analysis method  
235 (Fig. 9S, SI). The particle counts for the three blank water samples were very low, and the  
236 counts likely included false positives arising from the texture of the membrane filter and  
237 contamination. The counts in the 100-mL blank water samples were  $<6$  particles/mL. The  
238 counts for the same standard suspensions were comparable between filters. Particle  
239 concentrations  $\gg 6$  particles/mL in a 100-mL filtered water sample could therefore be easily  
240 measured.

241 Normalized standard deviations (coefficients of variation,  $C_V$ ) of particle number  
242 concentrations were calculated for the counts of the three filters for each water sample. The  $C_V$   
243 values for all of the measurements were collected and plotted against the mean particle number  
244 concentrations. Figure 2 shows the results for a filtration volume of 100 mL (the results for  
245 filtration volumes of 500 and 10 mL are shown in Fig. 10S, SI). The  $C_V$  decreased with  
246 increasing particle number concentration, roughly in agreement with the theoretical relationship  
247 calculated by Eq. (4), which was derived by assuming the particle count to be a Poisson-  
248 distributed random variable. The expected value and variance of a Poisson-distributed random  
249 variable are equal. Therefore, the coefficient of variation is

$$250 \quad C_V = 1/\sqrt{\lambda}, \quad (2)$$

251 where  $C_V$  is the coefficient of variation and  $\lambda$  is the mean particle count.

252 The particle number concentration was calculated from the mean particle count by using

$$253 \quad C_N = \frac{\lambda \times a_f/a_o}{V}, \quad (3)$$

254 where  $C_N$  is the number concentration ( $\text{cm}^{-3}$ ),  $a_f$  is the filtration area ( $\text{cm}^2$ ),  $a_o$  is the total area  
255 of the nine observation zones ( $\text{cm}^2$ ), and  $V$  is the filtration volume ( $\text{cm}^3$ ).

256 Substituting Eq. (3) into Eq. (2) gives

$$257 \quad C_V = \sqrt{\frac{a_f/a_o}{C_N V}}. \quad (4)$$

258

259 The observed  $C_V$  values were all less than 0.4, with the exception of one sample for which the  
260 particle number concentration was 3 particles/mL. The  $C_V$  values were  $<0.2$  for all the samples  
261 with particle number concentrations  $> 200$  particles/mL, which is equivalent to a SPAC  
262 concentration of  $> 0.07 \mu\text{g/L}$ , but the  $C_V$  values varied between samples. The  $C_V$  values of  
263 some particle number concentrations were higher than predicted by the Poisson distribution,  
264 perhaps because sintered glass filter holder (nominal pore diameter, 30–50  $\mu\text{m}$ , according to  
265 the manufacturer; Fig. 11S, SI). As a result, the filtration velocity across the membrane was  
266 uneven at the microscopic level, and the volumes of water passing through the filter at the  
267 observation zones were not exactly equal. Nevertheless, the fact that the number concentrations  
268 of the standard suspensions obtained by the membrane-filtration and microscopic-image-  
269 analysis method were linearly correlated with the mass concentrations ( $R^2 = 1.00$ ; Fig. 12S, SI)  
270 supports the validity of the method.

271 Figure 3 compares the volume-based particle size distributions of the standard carbon  
272 suspensions obtained by using our membrane-filtration and microscopic-image-analysis  
273 method with those obtained by using the laser light diffraction and scattering method. The  
274 median diameter obtained by our method was in agreement with that by the laser light



275 diffraction and scattering method. However, the ranges of the particle size distributions were  
276 not in good agreement. The poor agreement in particle size distribution could be due to the error  
277 generated when a number distribution of a wide distribution was converted into a volume  
278 distribution (Allen 2013). Our method measures number distribution so that it could not be  
279 accurate for large particles, which influence the volume-based size distributions to a much  
280 greater extent than small particles, because they are small in number. On the other hand, the  
281 laser light diffraction and scattering method could not be accurate in measuring small particles  
282 because smaller particles scatter light with weaker intensity.

### 283 *3.2. Comparison of SPAC and PAC remaining after treatment*

284 The turbidities, carbon particle number concentrations, and carbon particle volume  
285 concentrations for raw waters and sand filtrates are shown in Fig. 4 (the turbidities of the  
286 supernatants are shown in Fig. 13S, SI). The raw waters contained 30-mg/L PAC, 30-mg/L  
287 SPAC<sub>S2</sub>, or 7.5-mg/L SPAC<sub>S2</sub>. The turbidities of the sand filtrates were all very low (~0.05  
288 NTU); the turbidities were almost the same as the turbidity observed for Milli-Q water (0.05  
289 NTU). The false turbidity due to stray light in the turbidity measurement is < 0.02 NTU,  
290 according to the specifications of the turbidity meter. Turbidity measurements could therefore  
291 not differentiate carbon particle concentrations in the filtrates possibly containing SPAC and  
292 PAC. However, clear differences were observed in the particle number and volume  
293 concentrations determined by the membrane-filtration and microscopic-image-analysis method.  
294 A comparison of the results for raw waters containing 30 mg/L of carbon particles revealed that  
295 the SPAC number concentrations in the sand filtrate were 600–1000 particles/mL, about five  
296 times higher than the PAC number concentrations of 100–200 particles/mL. For the raw waters,  
297 the SPAC number concentrations were one order of magnitude higher than the PAC number  
298 concentrations. Therefore, the removal rates in terms of number concentration were comparable  
299 for SPAC and PAC, and that removal rates were roughly 5-log. The volume concentrations in

300 sand filtrates were higher for SPAC than for PAC. The removal rates in terms of volume  
301 concentration were around 6-log for SPAC, but they were somewhat lower for PAC.

302 It has been reported that the dose of SPAC is 25% of the PAC dose needed to provide a given  
303 adsorptive removal rate of a target compound, such as 2-methylisoborneol (Kanaya et al. 2015,  
304 Matsui et al. 2007, Matsui et al. 2005, Matsui et al. 2013). We therefore compared the  
305 experimental results obtained for raw waters containing 7.5-mg/L SPAC with those obtained  
306 for raw waters containing 30-mg/L PAC. The comparison revealed that the particle number  
307 concentrations in the sand filtrates were comparable (100–200 particles/mL). The particle  
308 volume concentrations were also comparable ( $\sim 100 \mu\text{m}^3/\text{mL}$ ), although the removal rate in  
309 terms of particle volume concentration was lower for SPAC than for PAC. Moreover, the  
310 removal rate in terms of particle number concentration was somewhat higher for SPAC than  
311 for PAC, but the difference was small (5.3-log for 7.5-mg/L SPAC and 5.0-log for 30-mg/L  
312 PAC). Therefore, the concentration of carbon particles that pass through a sand filter would be  
313 no higher in practice if SPAC were used instead of PAC.

314 The above-described high removals of SPAC particles were obtained in the experiments that  
315 involved the use of raw waters made from filtered tap water. When the raw water of CSF  
316 experiment was made from river water, the removal rate of carbon particles was similarly high,  
317 5.3-log (Fig. 14S, SI). The natural suspended solids and the organic matter contained in the  
318 river water before adding SPAC did not substantially affect the removal rate of SPAC particles,  
319 but this result could reflect the fact that the concentrations of natural suspended solids and  
320 organic matter were low (turbidity 5.7 NTU, dissolved organic carbon 0.9 mg-C/L). SPAC of  
321 7.5-mg/L, by way of comparison, resulted in a turbidity of 54 NTU.

322 If the principal mechanism responsible for carbon particle removal via coagulation is charge  
323 neutralization (Letterman and Yiacoumi 2011), the coagulant dosage required to remove all of

324 the carbon particles is determined by the total external surface area of the carbon particles  
325 (Dentel 1988, Stumm and O'Melia 1968). The total external surface area of 7.5-mg/L SPAC  
326 was similar to that of 30-mg/L PAC (Table 1S, SI). The similarity of the particle number  
327 concentrations in raw waters treated with 7.5-mg/L SPAC and 30-mg/L PAC may be due to the  
328 similarity of the total external surface areas. However, further studies are needed to better  
329 understand the effect of carbon particle size on the carbon particle concentrations in the treated  
330 water.

### 331 *3.3. Characteristics of carbon particles remaining in the sand filtrate*

332 Figure 5 shows the particle size distributions of carbon particles in raw water and sand filtrate.  
333 Compared to the raw water, the particle size distribution of SPAC in the sand filtrate was shifted  
334 toward smaller particles, an indication that smaller particles were less efficiently removed by  
335 CSF and therefore tended to pass through the filter. This tendency was more apparent for PAC.  
336 This tendency is also consistent with the observation that more SPAC than PAC remained in  
337 the sand filtrate when the raw waters with the same mass concentration of SPAC and PAC were  
338 treated, as described in section 3.2 (Fig. 4). Because particles of smaller size tended to be less  
339 efficiently removed, the particle size distributions of PAC and SPAC in the sand filtrates would  
340 eventually become similar.

341 Turbidity is quantified based on the amount of light scattered by particles. Specific turbidity  
342 (turbidity normalized to volume concentration) is inversely proportional to the average particle  
343 diameter calculated from the ratio of the volume to the surface area of particles with diameters  
344 larger than the wavelength of light (Kissa 1999). The implication is that turbidity is proportional  
345 to particle concentration quantified by external surface area (external surface area  
346 concentration), which is the total external surface area of the particles divided by the volume of  
347 the suspension. For standard suspensions of PAC and SPAC, turbidities were well correlated

348 with external surface area concentrations (Fig. 15S, SI). The external surface area concentration  
349 of the carbon particles remaining in the sand filtrate was calculated from the data obtained for  
350 the carbon particles remaining in the sand filtrate by using the membrane-filtration and  
351 microscopic-image-analysis method. When the turbidity resulting from the carbon particles  
352 remaining in the sand filtrate was estimated from the regression equation (Fig. 14S, SI) and the  
353 calculated external surface area concentration, the turbidity ranged from  $2 \times 10^{-5}$  to  $3 \times 10^{-4}$   
354 NTU (Table 2S, SI). These values were much smaller than the turbidities actually observed for  
355 the sand filtrates (~0.05 NTU, Fig. 4). It is therefore reasonable that turbidity measurement  
356 could not differentiate carbon particle concentrations in sand filtrates, as described in section  
357 3.2.

#### 358 *3.4. Mechanisms for lower removal rate of smaller carbon particles*

359 The main mechanism underlying rapid sand filtration is interception. When particles follow  
360 streamlines which lie very close to the surface of sand grains, the particles contact the surface  
361 of the sand grains and are captured. The probability of particles coming into contact with sand  
362 grains decreases as particle size decreases (Ives 1975). According to orthokinetic aggregation  
363 theory, particle–particle collisions during flocculation occur less frequently as particles become  
364 smaller (Ives 1978). Therefore, the lower removal efficiency of small carbon particles during  
365 CSF can be explained by the interception and orthokinetic aggregation mechanisms.

366 To determine whether the lower removal efficiency of small carbon particles was due solely to  
367 the interception and orthokinetic aggregation or was also related to other characteristics of the  
368 carbon, a further investigation was conducted. Even if carbon particles are transported to the  
369 surface of sand grains, they are not captured if there are strong electrokinetic repulsive forces  
370 between the sand grains and the carbon particles. Particle–particle collisions do not result in  
371 aggregation if significant repulsion exists. We therefore examined the zeta potential of the

372 carbon particles, a commonly used index of the electrokinetic potential in colloidal dispersions  
373 or aggregations that is correlated with coagulation and filtration performance. Figure 6 shows  
374 the zeta potential of carbon particles in raw water, water sampled after coagulation, supernatant  
375 after sedimentation, and sand filtrate. The zeta potential of the carbon particles in the raw water  
376 was approximately  $-23$  mV, but it increased to  $-4 \pm 8$  mV after coagulation, an indication that  
377 the charge on the carbon particles had been almost fully neutralized during the coagulation  
378 process. However, the particles remaining in the supernatant had a higher negative charge ( $-9$   
379  $\pm 5$  mV) than the particles after coagulation. The particles in the sand filtrate, which were smaller  
380 in size than the particles before CSF, had a higher negative charge ( $-15 \pm 5$  mV) than those in  
381 the supernatant.

382 The zeta potentials of the untreated SPAC and PAC particles did not vary as a function of  
383 particle size. Figure 7 shows the zeta potentials of the carbon particles as a function of carbon  
384 particle size. SPAC and PAC were separated by particle size based on the differences in  
385 the settling velocities of the particles. The original SPAC and PAC particles had a similar zeta  
386 potential of  $-20$  to  $-25$  mV. The negative charge was slightly higher for particles with a  
387 diameter of  $3 \mu\text{m}$ , and it then decreased with decreasing particle size, although the decrease was  
388 small. The reason for this small change in charge is unclear; however, the data indicate that the  
389 smaller carbon particles were not intrinsically higher negatively charged than the larger carbon  
390 particles, and the surface charges were not very different between the large and small carbon  
391 particles. However, the small carbon particles that remained in the sand filtrate had a higher  
392 negative charge than the carbon particles after coagulation. Therefore, the small carbon particles  
393 were charge-neutralized and destabilized at a lower rate than large carbon particles during the  
394 coagulation process. A possible explanation for the weak neutralization of the small particles  
395 during the coagulation process is that the adsorption of aluminum hydroxide species onto  
396 particles is a transport-limited process that depends on the particle size, and the rate of

397 adsorption onto small particles is low (Elimelech et al. 1995, Gregory 1988). Finally, we  
398 conclude that the low destabilization rate during the coagulation process, the low frequency of  
399 particle–particle collisions during flocculation, and the low probability of the particles coming  
400 into contact with sand grains during the sand filtration process could collectively make it  
401 difficult for small carbon particles to be removed by CSF, the result being that small carbon  
402 particles tended to remain in the sand filtrate.

#### 403 **4. Conclusions**

404 We developed a method to detect and measure the number of carbon particles remaining in sand  
405 filtrate. The method used membrane filtration, digital microscopy, and image analysis. We used  
406 this method to identify carbon particles with diameters  $> 0.2 \mu\text{m}$  at a concentration as low as  
407  $0.1 \mu\text{g/L}$ . By using this method, we were able to determine the trace concentration of residual  
408 carbon particles in sand filtrates, concentrations far below the limit of detection by turbidity  
409 measurements.

410 The residual concentration of SPAC was similar to that of PAC when the SPAC was used at  
411 25% of the PAC mass concentration, a percentage that resulted in comparable adsorption of  
412 dissolved organic contaminants by SPAC and PAC (SPAC mass dose is 25% of the PAC mass  
413 dose, but the SPAC enables comparable adsorptive removal to PAC). This result suggests that  
414 when SPAC is used instead of PAC, the risk that some activated carbon particles may pass  
415 through the CSF processes and remain in the treated water would not substantially increase.  
416 The number concentrations in the sand filtrate were 100–200 particles/mL when 7.5 mg/L  
417 SPAC and 30 mg/L PAC were treated. Reductions of approximately 5-log in terms of particle  
418 number concentrations and 6-log in terms of particle volume concentrations were attained via  
419 CSF.

420 Carbon particles remaining after CSF treatment were smaller in size than were the carbon  
421 particles before treatment. The small carbon particles remaining after CSF treatment had a  
422 higher negative charge than the carbon particles after coagulation treatment. The tendency of  
423 smaller particles to appear in the sand filtrate was therefore related to their lower destabilization  
424 rate during the coagulation process as well as their lower collision rates in the flocculation and  
425 filtration processes.

426

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430

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516

517 **List of Table and Figure**

518

519 Table 1. Carbon particle size. The median diameters are based on the particle size distribution  
 520 as determined by the laser light diffraction and scattering method.

521

522

523 Figure 1. Representative image analysis series. Series A begins with a photomicrograph  
 524 captured of a filter through which 100 mL of standard suspension containing 1- $\mu\text{g/L}$   
 525  $\text{SPAC}_{\text{S1}}$  was passed. Series B begins with a photomicrograph of a filter through  
 526 which a sand filtrate of unknown carbon particle concentration was passed (the  
 527 water was treated by a CFS after the addition of 20-mg/L PAC). Panels A2 and B2  
 528 are grayscale conversions of the original photomicrographs. The grayscale images  
 529 were converted to a binary image (Panels A3 and B3) in which the spots were  
 530 detected according to lightness. Panels A4 and B4 are images after visual  
 531 verification that all of the black spots in Panels A3 and B3 were included in the  
 532 original photomicrograph (panels A1 and B1); spots not found in the original  
 533 photomicrograph were eliminated. The yellow circles indicate dots that were  
 534 verified as not being carbon particles, which were removed during image  
 535 processing. The brown circles indicate dots eliminated by checking the original  
 536 photograph (Panels A1 and B1).

537

538 Figure 2. Mean particle number concentration versus coefficient of variation for a filtration  
 539 volume of 100 mL/filter. The line was calculated by using equation (4), which was  
 540 derived from the Poisson distribution.

541

542 Figure 3. Comparison of volume-based particle size distributions determined by means of our  
 543 membrane-filtration and microscopic image analysis process and by using a  
 544 Microtrac MT3300EXII instrument (laser light diffraction and scattering method;  
 545 Nikkiso Co., Tokyo, Japan) without the addition of a dispersant or the use of  
 546 ultrasonication. Panel A, PAC; panel B,  $\text{SPAC}_{\text{L}}$ ; panel C,  $\text{SPAC}_{\text{S1}}$ ; panel D,  
 547  $\text{SPAC}_{\text{S2}}$ .

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Figure 4. Reduction of carbon particles by the CSF treatment. Panels A1–C1, 30-mg/L PAC; panels A2–C2, 30-mg/L SPAC<sub>S2</sub>; panels A3–C3, 7.5-mg/L SPAC<sub>S2</sub>. Experiments were conducted twice for each experimental condition (Run 1 and Run 2). Error bars indicate standard deviations of measurement for each experiment.

Figure 5. Particle size distributions before and after treatment. Panels A1 and B1, 30-mg/L PAC (Run 1); panels A2 and B2, 30-mg/L SPAC<sub>S2</sub> (Run 1). Particle size distributions were obtained by means of membrane-filtration and microscopic image analysis.

Figure 6. Changes in the zeta potential of PAC and SPAC<sub>S2</sub> during coagulation-flocculation, sedimentation, and rapid sand filtration. The carbon particle concentration of the initial suspension was 30 mg/L. Error bars indicate standard deviations.

Figure 7. Zeta potential and median diameter of carbon particles remaining after sedimentation (PAC) or centrifugation (SPAC<sub>S2</sub>). Error bars indicate standard deviations.

Table 1. Carbon particle size. The median diameters are based on the particle size distribution as determined by the laser light diffraction and scattering method.

Activated carbon		Median diameter ( $\mu\text{m}$ )
PAC		13.7
SPAC	SPAC <sub>L</sub>	2.54
	SPAC <sub>S1</sub>	0.91
	SPAC <sub>S2</sub>	0.96

Note: SPAC<sub>L</sub>, SPAC with a large particle size; SPAC<sub>S1</sub> and SPAC<sub>S2</sub>, the first and the second, respectively, batch of SPAC with a small particle size.

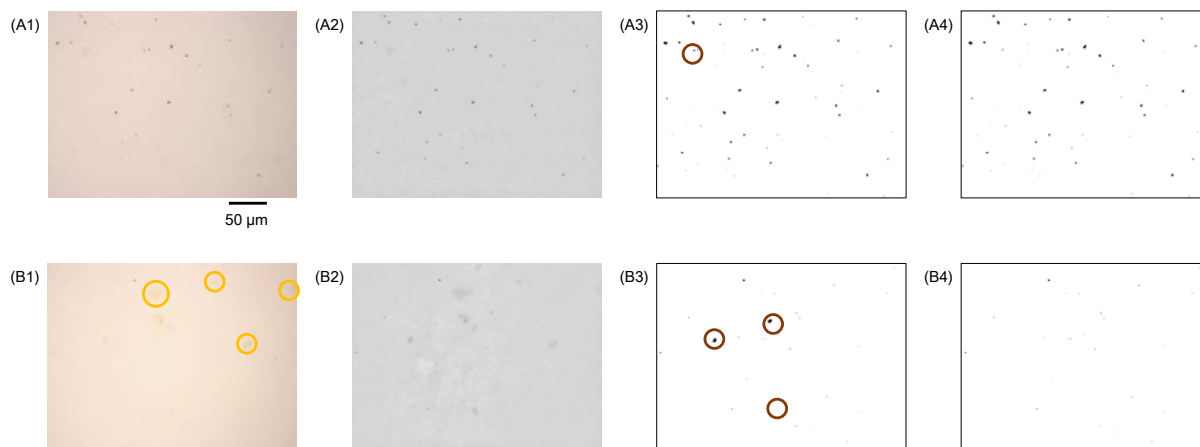


Figure 1. Representative image analysis series. Series A begins with a photomicrograph captured of a filter through which 100 mL of standard suspension containing 1- $\mu\text{g/L}$  SPAC<sub>S1</sub> was passed. Series B begins with a photomicrograph of a filter through which a sand filtrate of unknown carbon particle concentration was passed (the water was treated by a CFS after the addition of 20-mg/L PAC). Panels A2 and B2 are grayscale conversions of the original photomicrographs. The grayscale images were converted to a binary image (Panels A3 and B3) in which the spots were detected according to lightness. Panels A4 and B4 are images after visual verification that all of the black spots in Panels A3 and B3 were included in the original photomicrograph (panels A1 and B1); spots not found in the original photomicrograph were eliminated. The yellow circles indicate dots that were verified as not being carbon particles, which were removed during image processing. The brown circles indicate dots eliminated by checking the original photomicrograph (Panels A1 and B1).

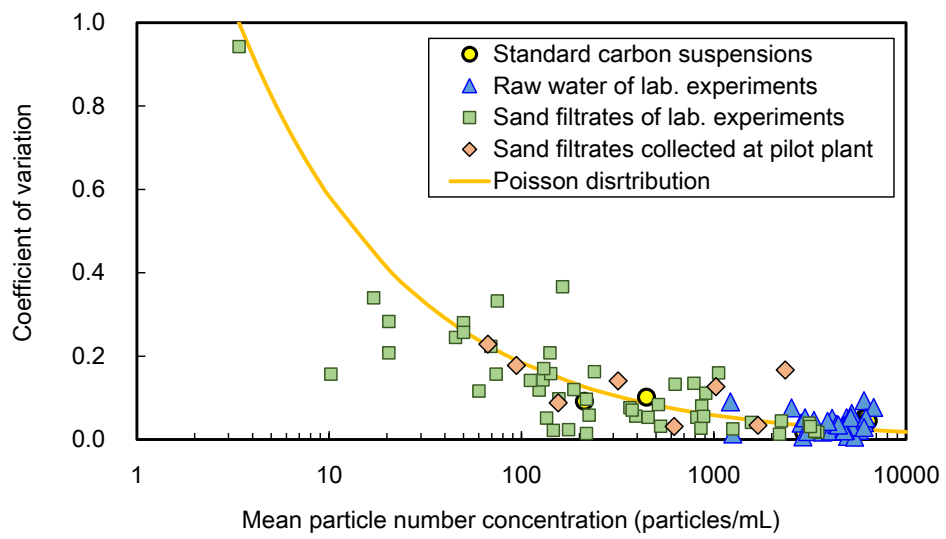


Figure 2. Mean particle number concentration versus coefficient of variation for a filtration volume of 100 mL/filter. The line was calculated by using equation (4), which was derived from the Poisson distribution.

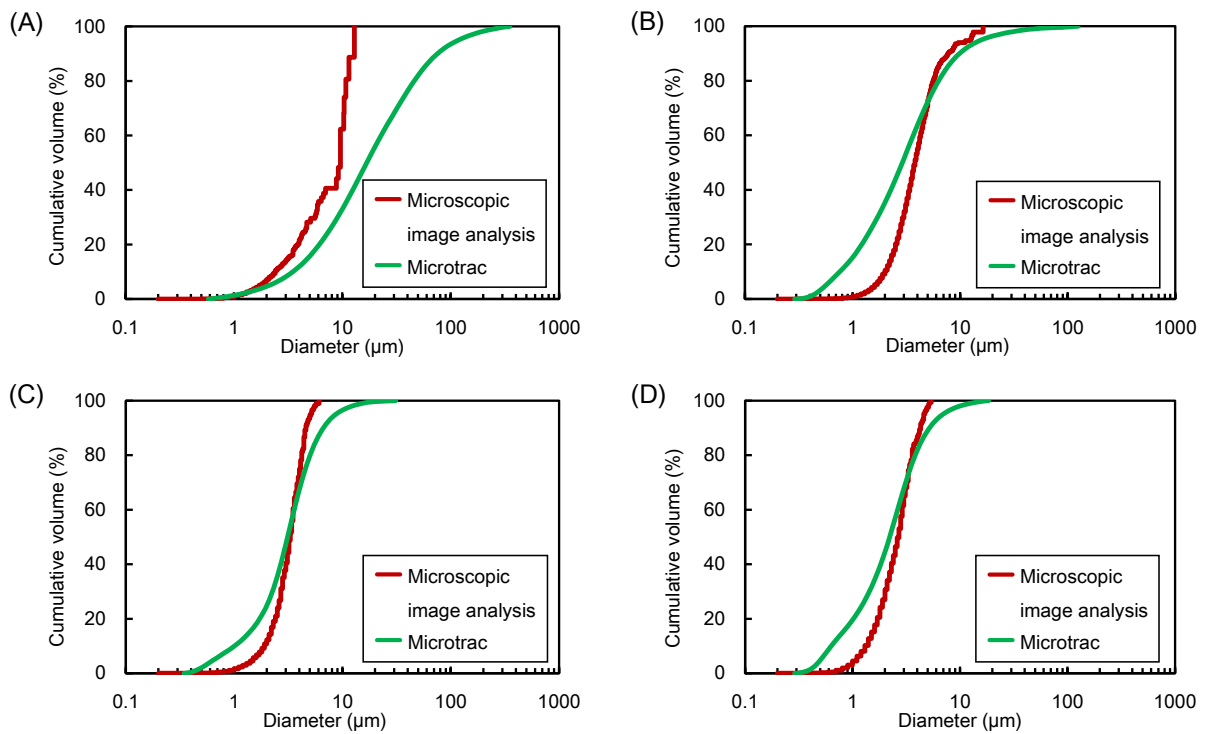


Figure 3. Comparison of volume-based particle size distributions determined by means of our membrane-filtration and microscopic image analysis process and by using a Microtrac MT3300EXII instrument (laser light diffraction and scattering method; Nikkiso Co., Tokyo, Japan) without the addition of a dispersant or the use of ultrasonication. Panel A, PAC; panel B, SPAC<sub>L</sub>; panel C, SPAC<sub>S1</sub>; panel D, SPAC<sub>S2</sub>.

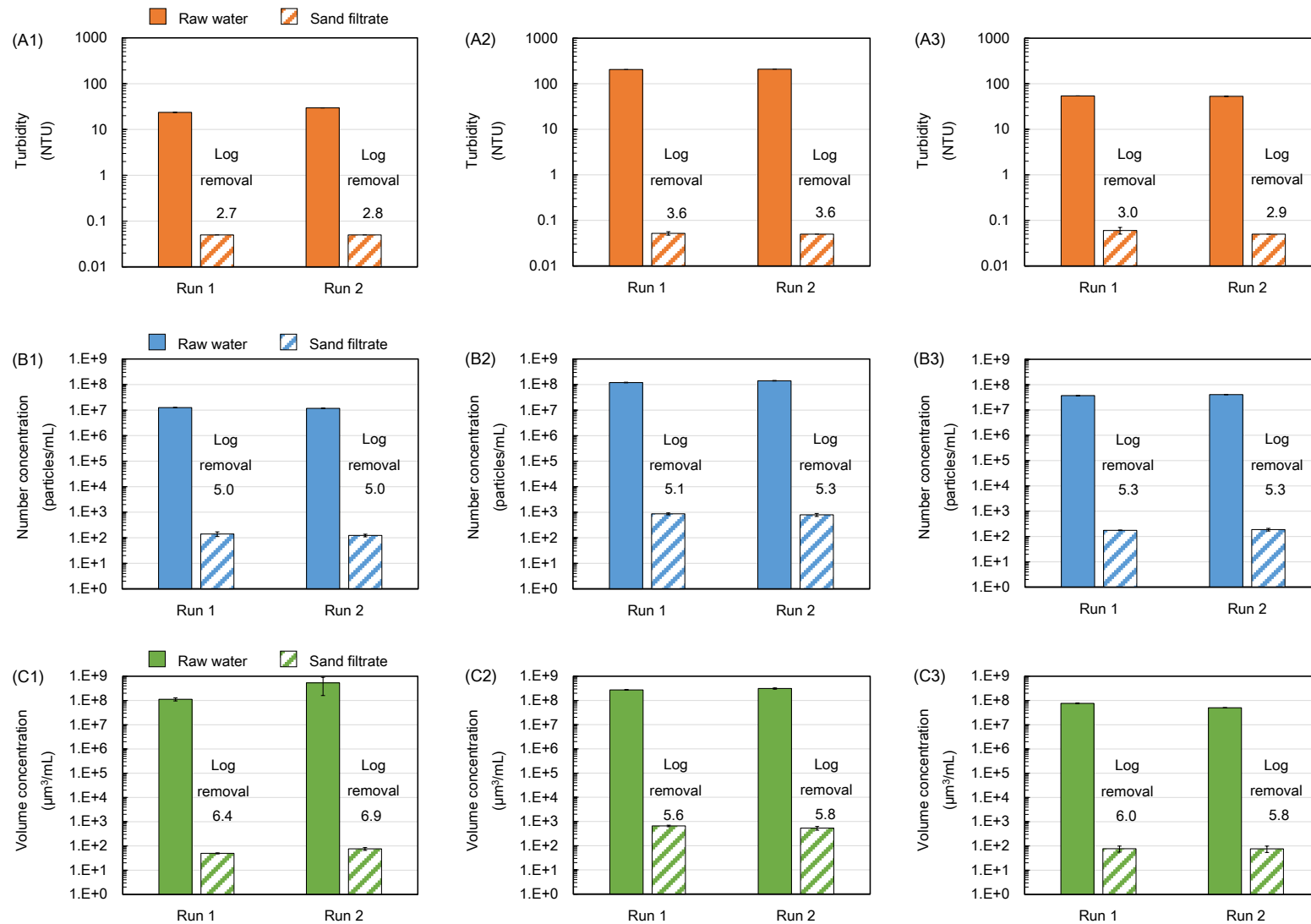


Figure 4. Reduction of carbon particles by the CSF treatment. Panels A1–C1, 30-mg/L PAC; panels A2–C2, 30-mg/L SPAC<sub>s2</sub>; panels A3–C3, 7.5-mg/L SPAC<sub>s2</sub>. Experiments were conducted twice for each experimental condition (Run 1 and Run 2). Error bars indicate standard deviations of measurement for each experiment.

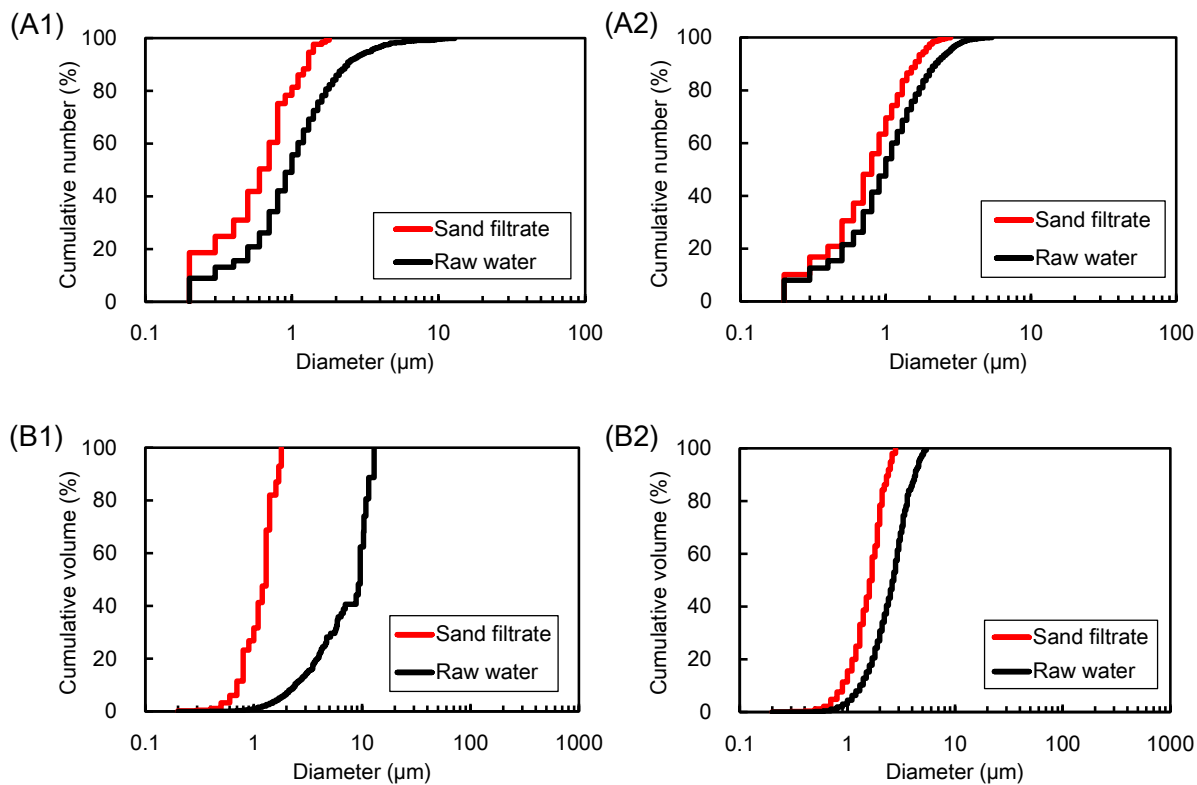


Figure 5. Particle size distributions before and after treatment. Panels A1 and B1, 30-mg/L PAC (Run 1); panels A2 and B2, 30-mg/L SPACs<sub>2</sub> (Run 1). Particle size distributions were obtained by means of membrane-filtration and microscopic image analysis.



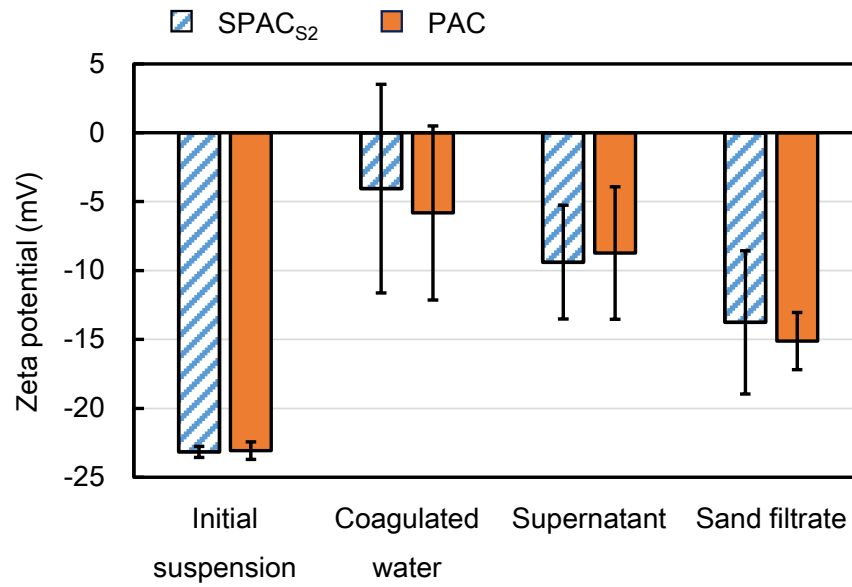


Figure 6. Changes in the zeta potential of PAC and SPAC<sub>S2</sub> during coagulation-flocculation, sedimentation, and rapid sand filtration. The carbon particle concentration of the initial suspension was 30 mg/L. Error bars indicate standard deviations.

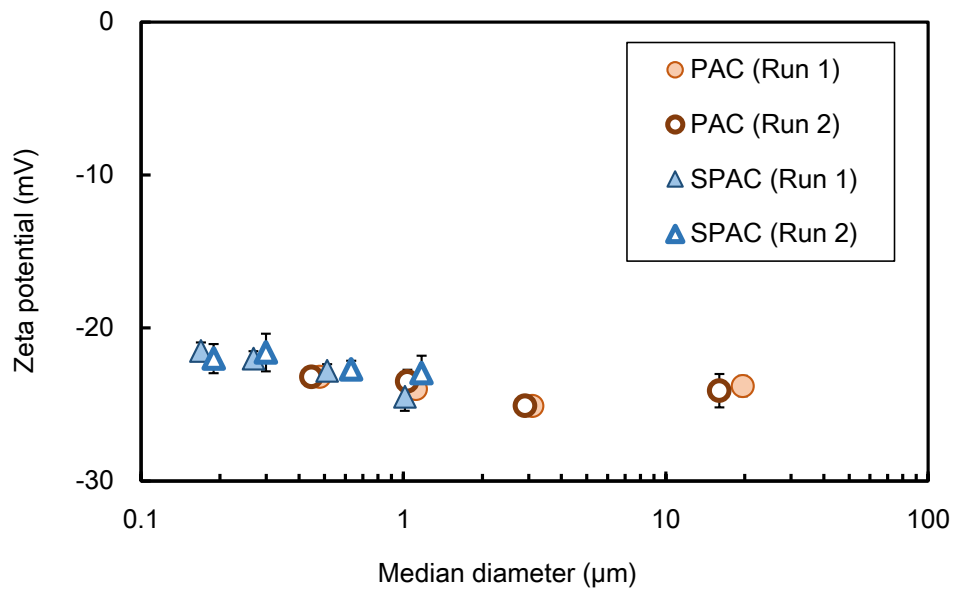


Figure 7. Zeta potential and median diameter of carbon particles remaining after sedimentation (PAC) or centrifugation (SPAC<sub>S2</sub>). Error bars indicate standard deviations.

## Supplementary Information

### **Identifying, counting, and characterizing superfine activated-carbon particles remaining after coagulation sedimentation and sand filtration treatment**

Yoshifumi Nakazawa <sup>a</sup>, Yoshihiko Matsui <sup>b\*</sup>, Yusuke Hanamura <sup>a</sup>, Koki Shinno <sup>a</sup>, Nobutaka Shirasaki <sup>b</sup>, and Taku Matsushita <sup>b</sup>

<sup>a</sup> Graduate School of Engineering, Hokkaido University, N13W8, Sapporo 060-8628, Japan

<sup>b</sup> Faculty of Engineering, Hokkaido University, N13W8, Sapporo 060-8628, Japan

\* Corresponding author. Tel./fax: +81-11-706-7280

E-mail address: matsui@eng.hokudai.ac.jp

Table 1S. External surface area concentration.

Activated carbon	Mass concentration (mg/L)	External surface area concentration (cm <sup>2</sup> /L)	
		Microscopic image analysis	Microtrac
PAC	30	$1.4 \times 10^3$	$2.5 \times 10^2$
SPAC <sub>S2</sub>	7.5	$2.0 \times 10^3$	$3.3 \times 10^2$
SPAC <sub>S2</sub>	30	$7.9 \times 10^3$	$1.3 \times 10^3$

Table 2S. Estimation of turbidity arising from carbon particles remaining in the sand filtrate.

Raw water			Sand filtrate			
Activated carbon	Mass concentration	Turbidity	Turbidity	Number concentration of carbon particles	External surface area concentration of carbon particles	Turbidity attributable to carbon particles
		Turbidity meter	Turbidity meter	Microscopic image analysis	Microscopic image analysis	Estimation from external surface area concentration
	mg/L	NTU	NTU	mL <sup>-1</sup>	cm <sup>2</sup> /L	NTU
PAC	30	27	0.05	$1.3 \times 10^2$	$3.1 \times 10^{-3}$	$1.9 \times 10^{-5}$
SPAC <sub>S2</sub>	7.5	54	0.06	$1.8 \times 10^2$	$3.9 \times 10^{-3}$	$2.4 \times 10^{-5}$
SPAC <sub>S2</sub>	30	207	0.05	$8.3 \times 10^2$	$2.5 \times 10^{-2}$	$1.9 \times 10^{-4}$

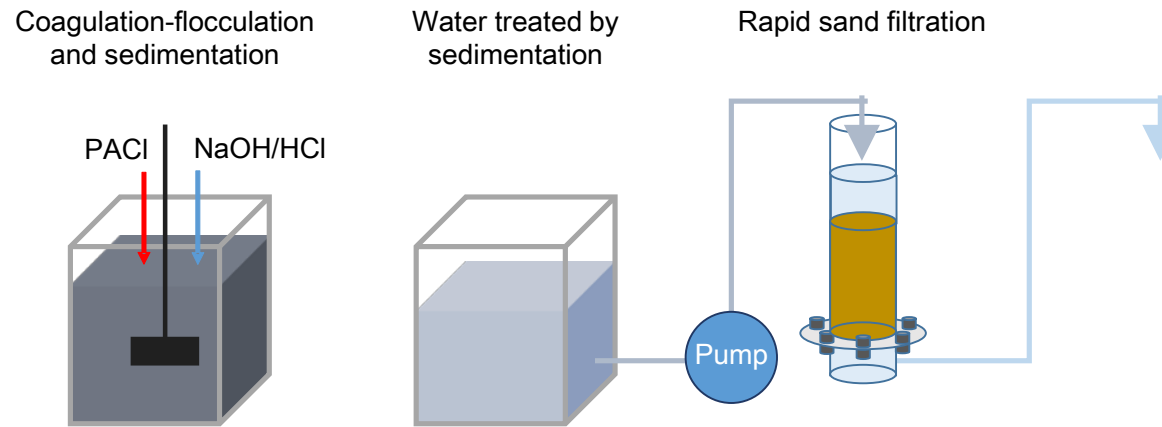


Figure 1S. Schematic diagram of the experimental setup for the coagulation-flocculation, sedimentation, and sand filtration experiment.

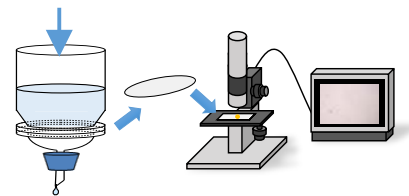


Figure 2S. Schematic diagram of the experimental setup for membrane filtration and microscopic image analysis.

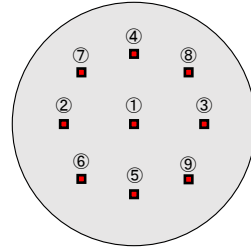


Figure 3S. Observation zones on a single membrane filter ( $\phi 25$  mm).

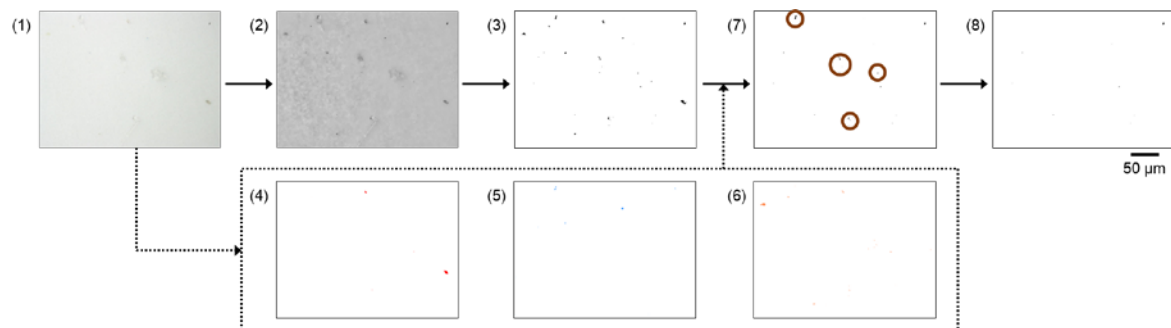


Figure 4S. Representative image analysis series showing the process when many colored spots were observed in the photomicrograph. Panel 1 is a photomicrograph of a filter through which 100 mL of water containing 0.1- $\mu\text{g/L}$  SPAC<sub>S2</sub> and 30  $\mu\text{g/L}$  of powdered mineral pigments (10  $\mu\text{g/L}$  each of Iwaaka241 [red], Gunjo342 [blue], Yamabuki121 [yellow]; Nakagawa Gofun Enogu Co., Ltd., Kyoto, Japan) was passed. Panel 2 is a grayscale conversion of the original photomicrograph. The grayscale image was converted to a binary image (Panel 3) in which the spots were detected according to lightness. Panels 4, 5, and 6 are binary images in which red, blue, and yellow spots, respectively, were extracted according to their HSL (hue, saturation, and lightness). Panel 7 is the image after comparison with Panels 3 to 6 during which spots that were verified as not being black particles were eliminated. Panel 8 is the image after visual verification that all of the black spots in Panel 7 were included in the original photomicrograph (Panel 1); spots not found in the original photomicrograph were eliminated. The brown circles indicate spots that were eliminated by the visual examination.

When black and colored spots were both observed on the membrane, it was difficult to distinguish the black particles from the color particles using only lightness, particularly to distinguish black particles from blue particles, which resulted in an increase in the number of false positives. Therefore, black and colored particles were identified with the image in the HSL color model (Panels 3–7), and black particles could be distinguished from colored particles (Panel 4–7) by comparing the images (Figure 5S).



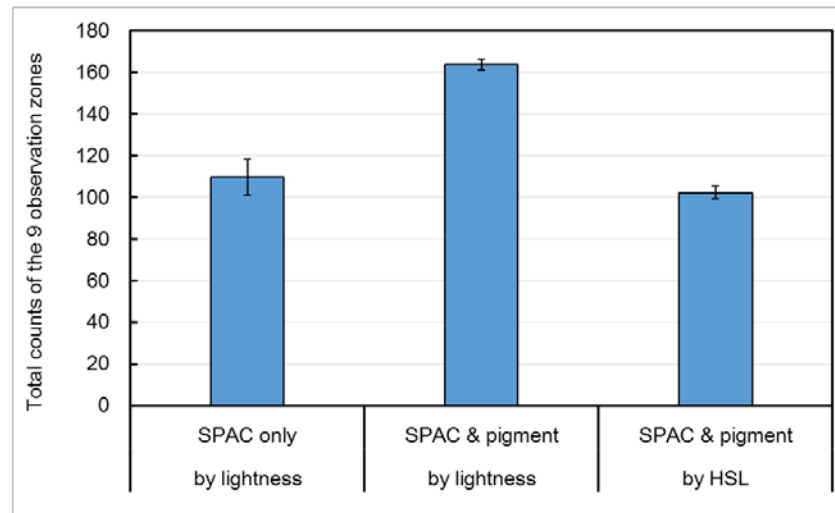


Figure 5S. Comparison of particle counts obtained for treated water originally containing 0.1- $\mu\text{g/L}$  SPAC<sub>S2</sub> and 30- $\mu\text{g/L}$  powdered mineral pigment particles (10  $\mu\text{g/L}$  each of Iwaaka241 [red], Gunjo342 [blue], Yamabuki121 [yellow]; Nakagawa Gofun Enogu Co., Ltd., Kyoto, Japan).

When lightness only was used to identify carbon particles, the particle count for the suspension containing SPAC and pigments was larger than that for the suspension containing SPAC only because some of the pigment particles were erroneously counted as carbon particles. When the HSL (hue, saturation, lightness) color model was used (see Figure 4S), the counts of the suspension containing SPAC and pigment were similar to those containing SPAC, indicating that the majority of false positives were eliminated. Note that this analysis using the HSL color model still required visual examination. In the present study, however, this more advanced analysis using the HSL color model was not required because the particles in the photomicrographs were mostly black particles interspersed with a few gray particles so colored particles were hardly observed. Therefore, the detection of carbon particles according to lightness alone could be enough for analysis.

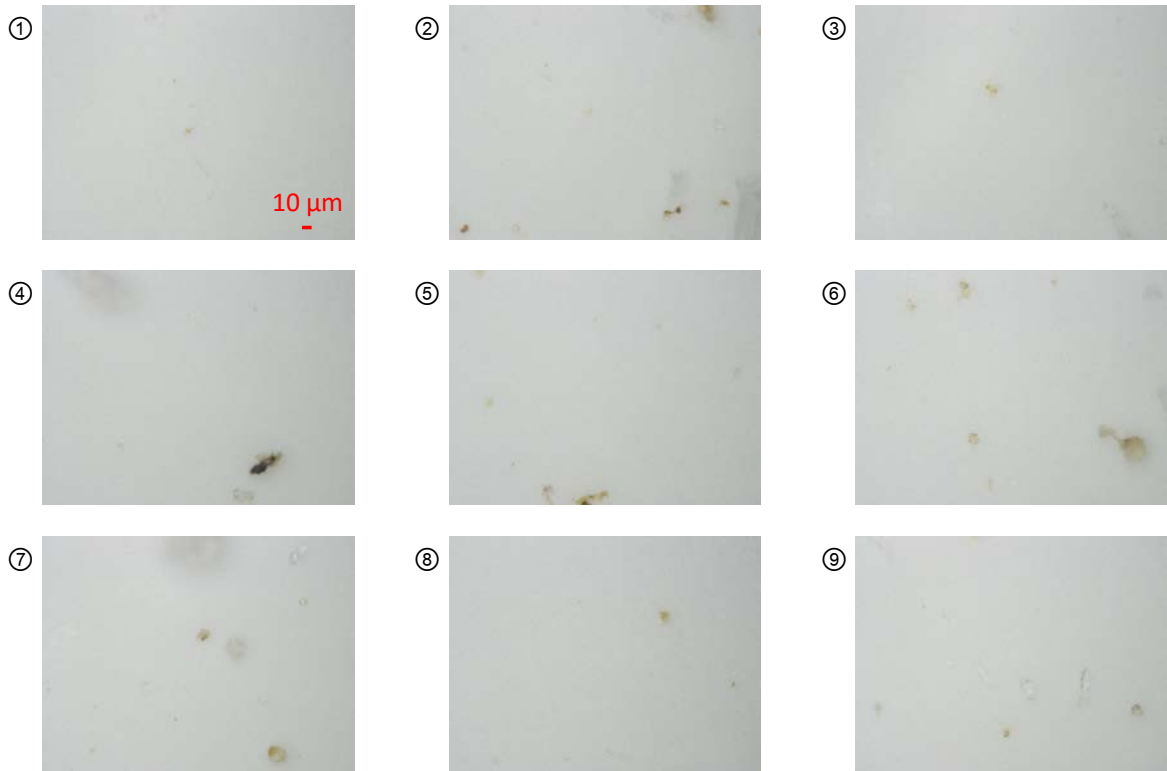


Figure 6S. Photomicrographs of nine observation zones on a filter that was passed a diluted river water (Turbidity and DOC of the river water were 5.7 NTU and 0.9 mg/L, respectively). The river water was diluted 100 times with by Milli-Q water). The concentration of black particles in the river water was  $5.1 \times 10^3$  particles/mL, that was far small compared to the concentration of carbon particles. For example,  $3.9 \times 10^7$  carbon particles/mL exist in SPAC<sub>S2</sub> suspension of 7.5-mg/L.

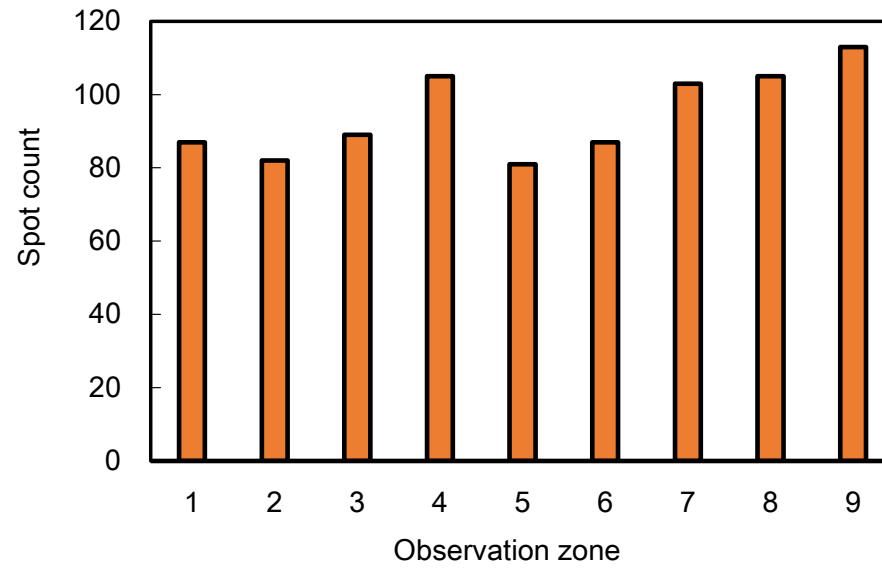


Figure 7S. Particle counts for the nine observation zones in a filter. An aliquot (100 mL) of standard suspension containing 1- $\mu\text{g/L}$  SPAC<sub>S1</sub> was filtered through a membrane filter. The observation zone numbers correspond with those presented in Figure 3S.

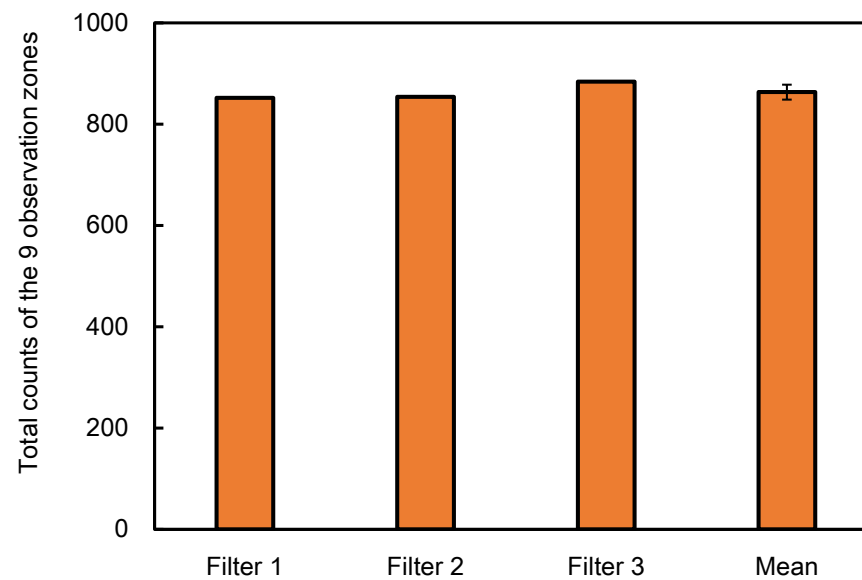


Figure 8S. Total particle counts for the nine observation zones in three filters and their mean value. An aliquot (100 mL) of standard suspension containing 1- $\mu\text{g/L}$  SPAC<sub>S1</sub> was filtered through each filter. The error bar represents the standard deviation.

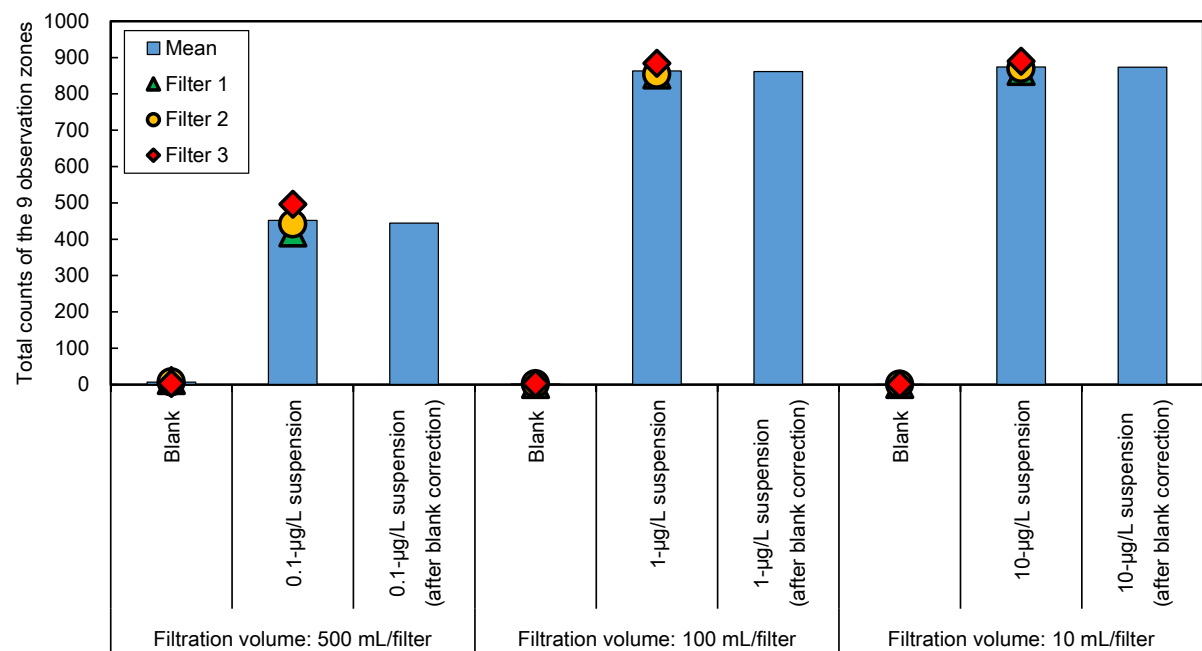


Figure 9S. Total particle counts for filters through which SPAC<sub>S1</sub> standard suspensions and blank water were passed.

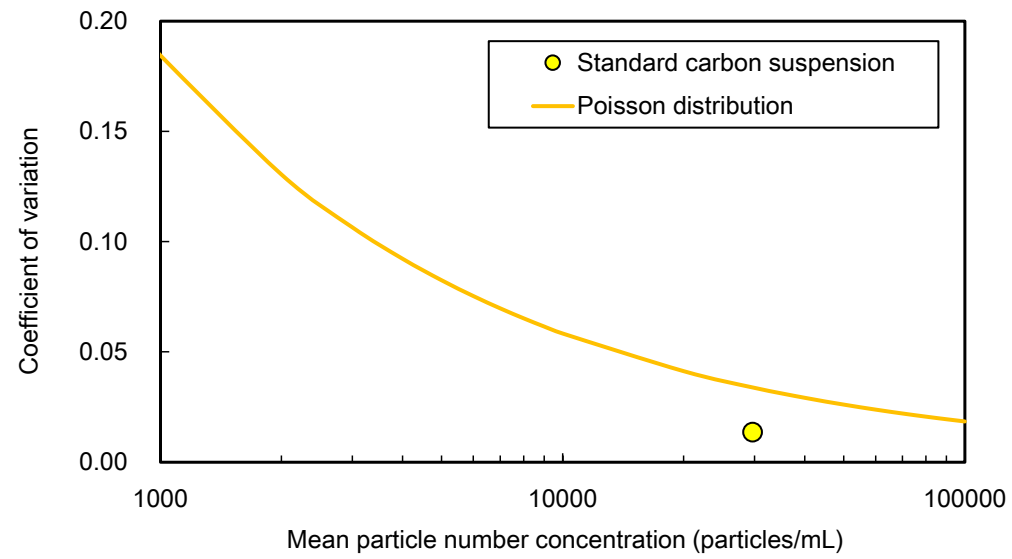
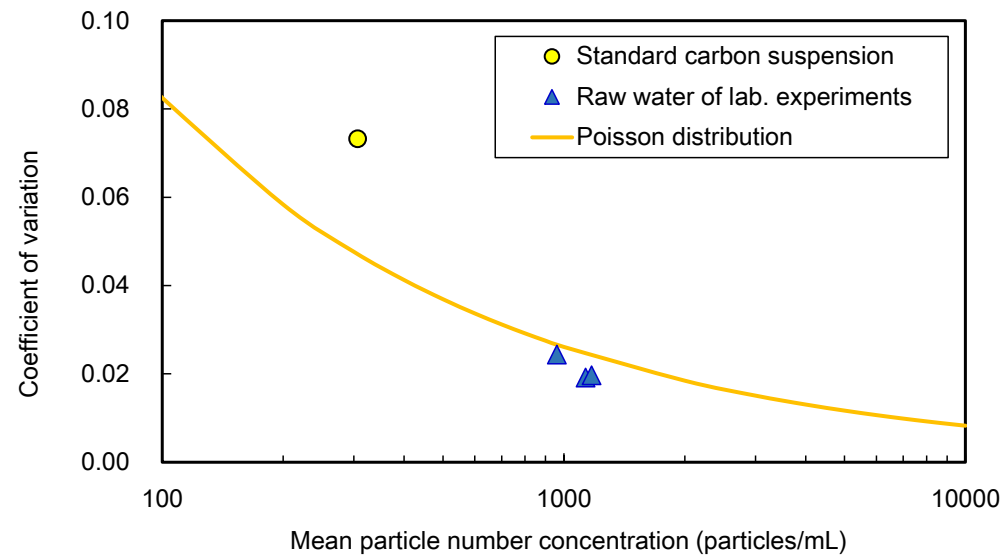


Figure 10S. Particle number concentration mean versus coefficient of variation. Filtration volume, 500 mL and 10 mL/filter for the upper and lower panel, respectively. The lines were calculated by using equation (4), which was derived from the Poisson distribution.



500  $\mu\text{m}$

Figure 11S. Photograph of the sintered glass in the filter holder.



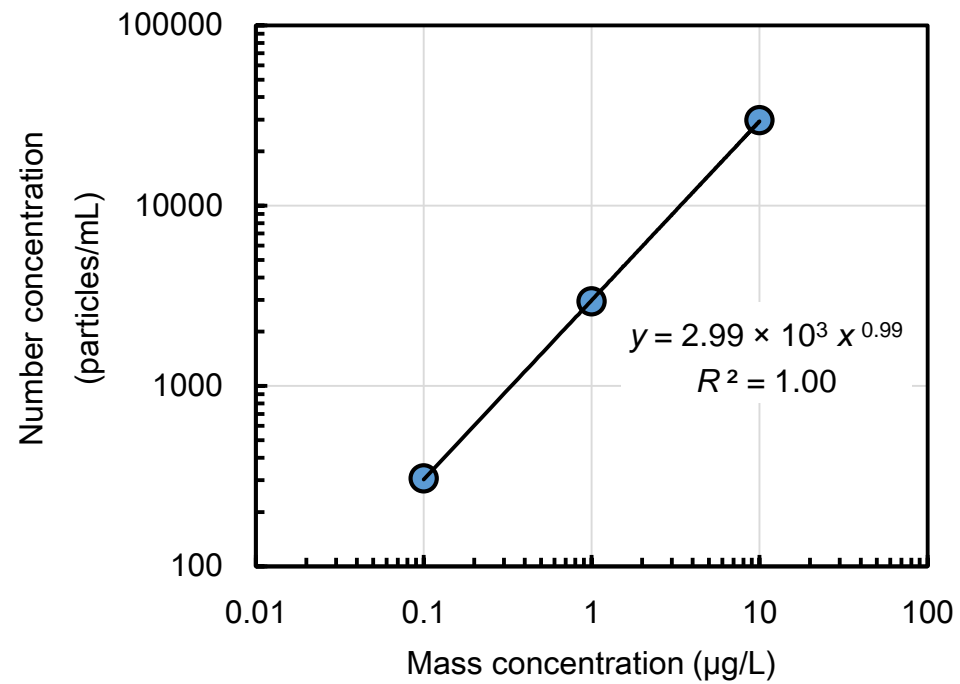


Figure 12S. Number concentration, as obtained by membrane-filtration and microscopic image analysis, versus mass concentration for the three SPAC<sub>S1</sub> standard suspensions. Error bars are hidden in the plot.

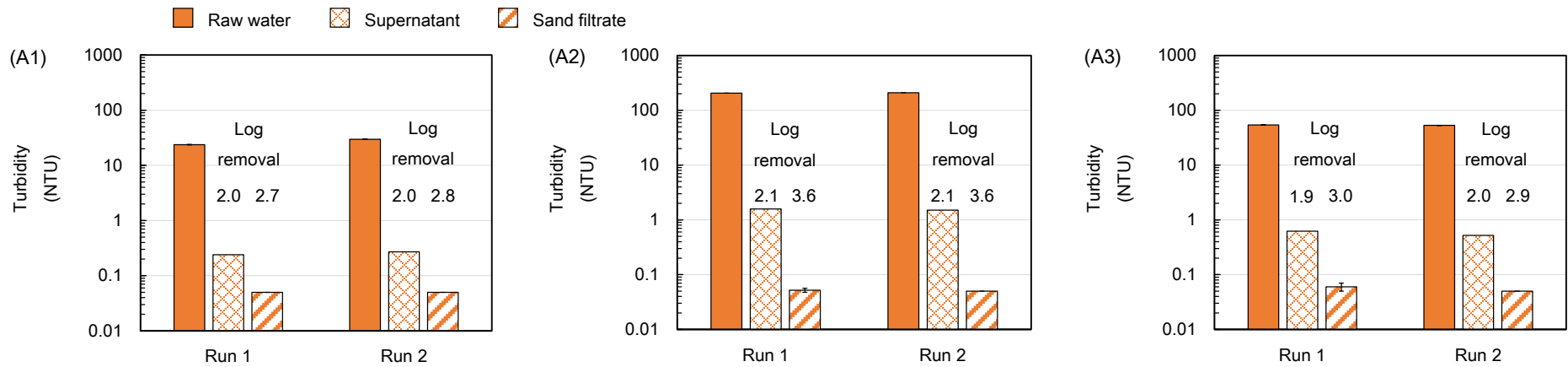


Figure 13S. Change of turbidity by coagulation-flocculation, sedimentation, and rapid sand filtration. Panels A1, 30-mg/L PAC; panels A2, 30-mg/L SPAC<sub>S2</sub>; panels A3, 7.5-mg/L SPAC<sub>S2</sub>. Experiments were conducted twice for each experimental condition (Run 1 and Run 2). Error bars indicate standard deviations.

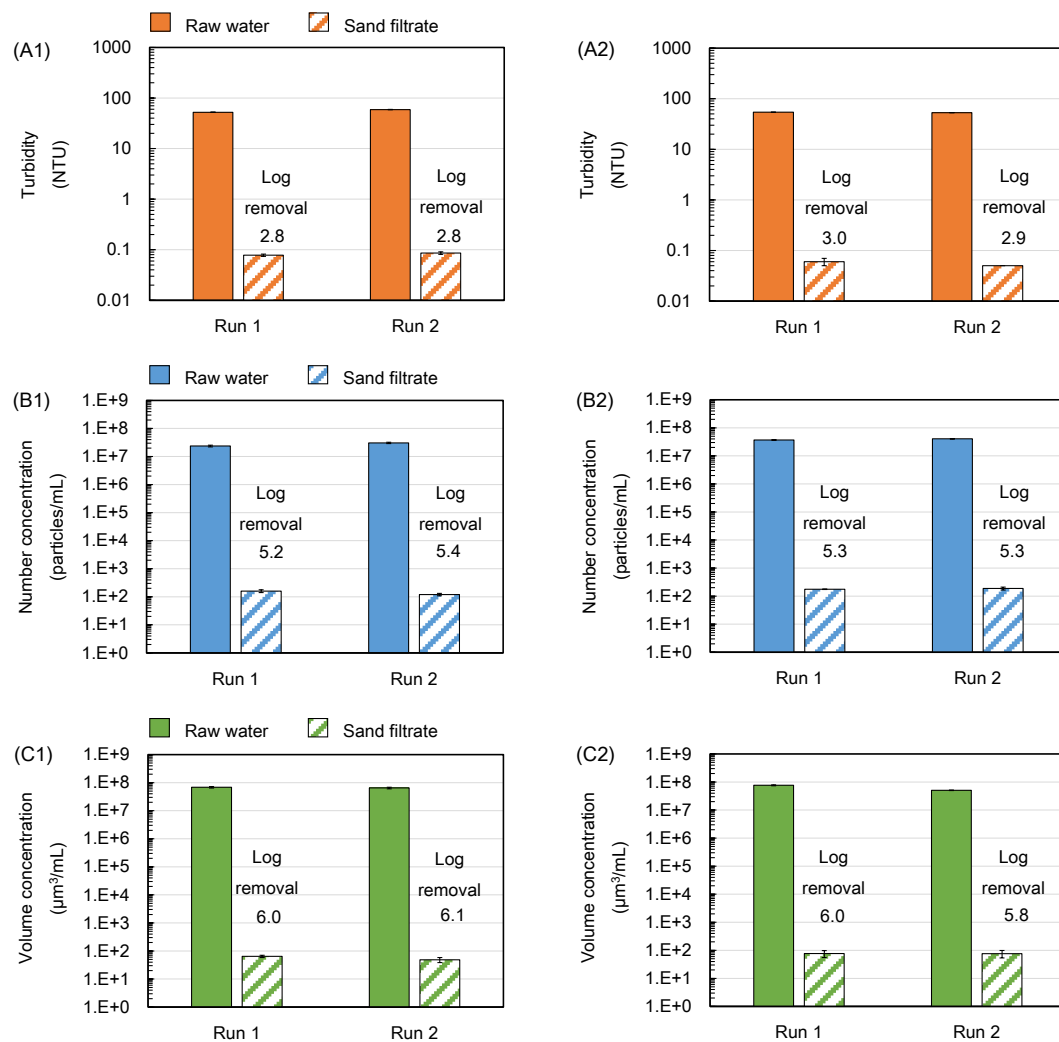


Figure 14S. Reduction of carbon particles by the CSF treatment. Panels A1–C1, river water (turbidity 5.7 NTU and DOC 0.9 mg/L) supplemented with SPAC<sub>S2</sub> at 7.5 mg/L; panels A2–C2, filtered tap water (turbidity < 0.07 NTU and DOC 0.5 mg/L) supplemented with SPAC<sub>S2</sub> at 7.5 mg/L. Experiments were conducted twice for each experimental condition (Run 1 and Run 2). Error bars indicate standard deviations of measurement for each experiment.

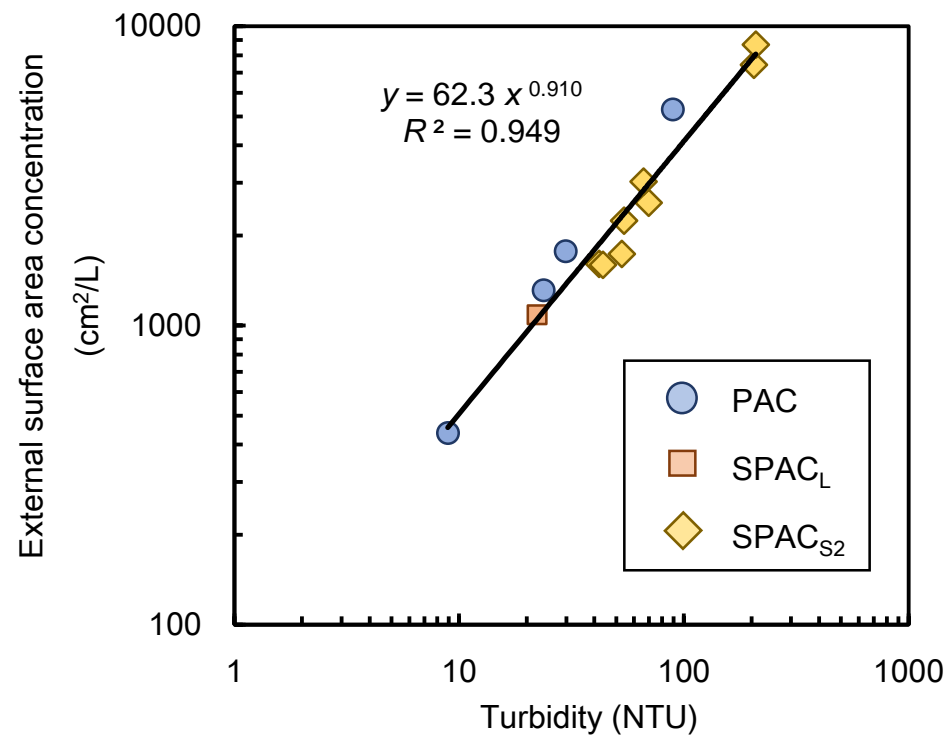


Figure 15S. External surface area concentration, as obtained by membrane-filtration and microscopic image analysis, versus turbidity. Standard suspensions of PAC (10, 30, and 80 mg/L), SPAC<sub>L</sub> (10 mg/L), and SPAC<sub>S2</sub> (6.0, 7.5, 10, and 30 mg/L).