



Title	Effects of Pre, Post, and Simultaneous Loading of Natural Organic Matter on 2-Methylisoborneol Adsorption on Superfine Powdered Activated Carbon : Reversibility and External Pore-blocking
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## **Highlights**

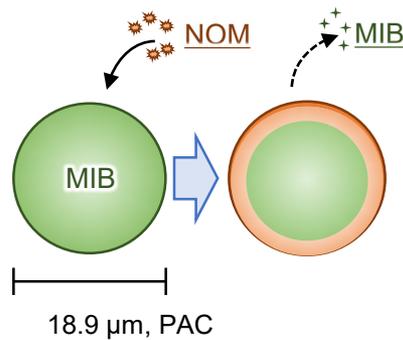
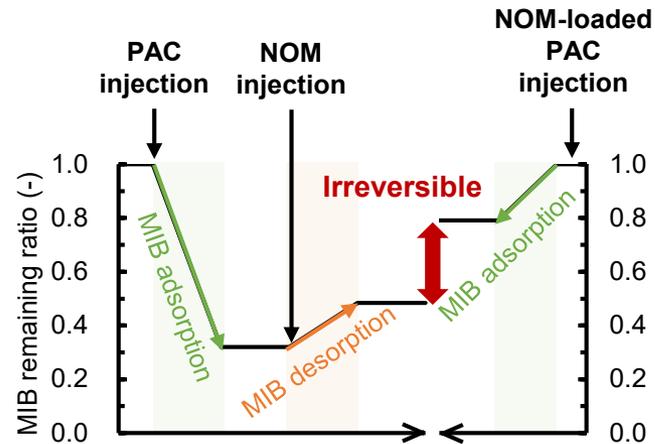
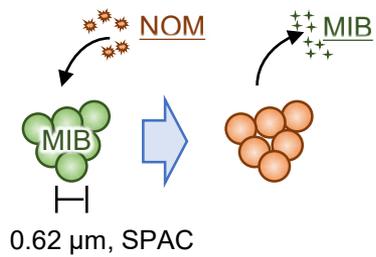
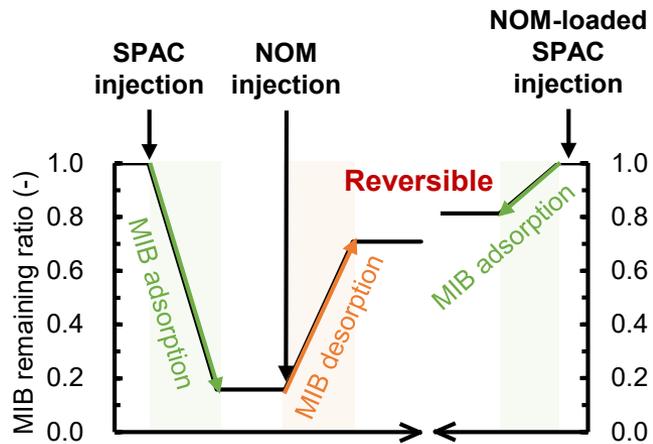
MIB adsorbed on SPAC was desorbed by NOM up to the adsorption equilibrium

MIB adsorbed on conventionally sized PAC was partially desorbed

MIB adsorption on SPAC was more reversible than on PAC

Irreversible adsorption was caused by pore blockage on the PAC particle surface

We observed external adsorption on a PAC particle by using  $^{15}\text{N}$ -labeled EfOM



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**Effects of Pre, Post, and Simultaneous Loading of Natural Organic  
Matter on 2-Methylisoborneol Adsorption on Superfine Powdered  
Activated Carbon: Reversibility and External Pore-blocking**

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18 **ABSTRACT**

19 Three different natural organic matter (NOM)-loading methods were compared for the adsorptive  
20 removal of 2-methylisoborneol (MIB) by superfine powdered activated carbon (SPAC) and  
21 conventionally-sized powdered activated carbon (PAC). The three NOM-loading methods were: NOM  
22 adsorption followed by MIB (MIB adsorption on NOM-preloaded carbon), MIB adsorption followed  
23 by NOM (MIB adsorption on NOM post-loaded carbon), and simultaneous NOM and MIB loading  
24 (MIB adsorption on NOM-simultaneously loaded carbon). MIB removals were similar for the smaller-  
25 sized carbon (SPAC) at higher AC dosages and at lower initial NOM concentrations. The similar MIB  
26 removals indicate direct site competition between MIB and NOM with MIB adsorption reversibility  
27 (complete desorption of MIB by NOM). At lower AC doses, especially for PACs, and at higher initial  
28 NOM concentrations, the adsorption of MIBs depended on the sequence of MIB or NOM adsorption.  
29 MIB removal was lowest for the NOM-preloaded carbon, followed by NOM-simultaneously loaded  
30 carbon. The highest MIB removal was achieved by post-loading of NOM, indicating that the  
31 adsorption is irreversible. MIB adsorption on SPAC was more reversible than on PAC, although the  
32 pore size distributions of the two carbons were similar. The high degree of adsorption irreversibility  
33 for PAC compared with SPAC indicated that pore blocking occurs due to NOM loading at the PAC  
34 particle surface. Images of the external adsorption were obtained using isotope mapping and <sup>15</sup>N-  
35 labeled effluent organic matter.

36

37 **KEYWORDS**

38 PAC; particle size; sub-micrometer; competitive adsorption; humic substance; taste and odor

39

## 40 **1. Introduction**

41 The ubiquity, abundance, and diversity of natural organic matter (NOM) in water sources is important  
42 for evaluating activated carbon (AC) adsorption for treating micropollutants. Micropollutant  
43 adsorption capacity decreases upon NOM loading compared to the initial capacity. The NOM effect  
44 on micropollutant adsorption originates from the direct competition for adsorption sites or by pore  
45 blockage (Summers et al. 2011). Direct competition occurs when competing compounds are of the  
46 same size, can access and compete for the same sites. Direct competition is the dominant mechanism  
47 of the NOM effect when the NOM loading level is below a certain threshold (Ding et al. 2006, Kilduff  
48 et al. 1998). Therefore, for the simultaneous removal of micropollutants and NOM in batch adsorption  
49 systems where the NOM loading is low, NOM marginally affects the internal diffusion of  
50 micropollutants in an AC particle, although NOM severely affects the adsorptive capacity of  
51 micropollutants (Cook et al. 2001, Huang et al. 1996, Matsui et al. 2003). Micropollutant adsorption  
52 capacity models in the presence of NOM have been developed to predict micropollutant removal, but  
53 are based on the direct competition mechanism, and reversible adsorption-desorption is implicitly  
54 assumed (Knappe et al. 1998, Najm et al. 1990, Zoschke et al. 2011). Experimental tests of  
55 simultaneous adsorption of target compounds and NOM have been reported, and previously developed  
56 models have been successfully verified. However, it remains unclear whether the NOM effect is truly  
57 reversible and whether the sequence of NOM/micropollutant loading affects adsorptive removal.  
58 Adsorption test of target compounds using adsorbent preloaded with NOM has not been applied in  
59 many of the landmark studies (Kilduff et al. 1998, Kilduff and Wigton 1999).

60 Studies using NOM-preloaded AC mostly aimed to elucidate pore blocking mechanisms by  
61 determination of adsorption/desorption and irreversibility (Karanfil et al. 2006, Pelekani and Snoeyink  
62 1999, Pelekani and Snoeyink 2000, To et al. 2008). Preloaded NOM does not desorb to a measurable  
63 extent (Kilduff and Wigton 1999, Summers and Roberts 1988), but this does not necessarily indicate  
64 that micropollutants fail to displace pre-adsorbed NOM because of the inability to detect the extremely

65 low NOM concentrations desorbed. In contrast, a preloaded micropollutant (a pesticide, atrazine) was  
66 displaced by NOM, while preloading with NOM showed adsorption capacity reduction compared with  
67 the simultaneous adsorption of NOM and atrazine (Pelekani and Snoeyink 1999). The authors  
68 attributed this phenomenon to direct site adsorption competition in secondary micropores that can be  
69 accessed by both atrazine and NOM. Competitive adsorption between atrazine and model compounds  
70 also showed that preloaded atrazine can be displaced from secondary micropores to a larger extent  
71 than from primary micropores by model compounds (Pelekani and Snoeyink 2000, 2001). The authors  
72 also showed the adsorption reversibility of atrazine. However, atrazine adsorption capacities are not  
73 equivalent between the three types of ACs: NOM-preloaded AC, AC with preloaded atrazine followed  
74 by displacement by NOM, and AC simultaneously loaded by NOM and atrazine, and complete  
75 reversibility was not observed. On the primarily microporous AC, the uptake of atrazine in the presence  
76 of NOM (simultaneous adsorption) was comparable to the NOM-preloaded capacity. In addition,  
77 preloaded atrazine was not displaced by the subsequently adsorbed NOM. These results were attributed  
78 to pore blockage wherein NOM molecules block access to, but do not penetrate into, the primary  
79 micropores. When the AC preloaded with atrazine was dosed into NOM water, the amount of atrazine  
80 displaced by NOM increased with decreasing AC dosage, which increased NOM loading (Li et al.  
81 2002). Very recently, Aschermann et al. (2018) reported that micropollutant desorption by NOM is  
82 dependent on the pore sizes. Macroporous AC shows a higher degree of desorption than microporous  
83 AC because pore blockage effects are minor (Aschermann et al. 2019).

84 However, apart from these studies, investigations of the pore blockage mechanisms have focused on  
85 partial pore blocking and pore constriction wherein adsorption kinetics decrease through internal  
86 diffusion (Ding et al. 2006, Ding et al. 2008, Li et al. 2003a, Li et al. 2003b, To et al. 2008) rather than  
87 complete pore blocking which lowers adsorption reversibility. The extent of displacement reversibility  
88 remains unclear, namely whether the micropollutant remained on the AC after displacement by NOM  
89 is larger than or the same as that obtained on the NOM-preloaded AC.

90 The effect of adsorbent particle size in the sub-micrometer range on micropollutant removal has been  
91 recently investigated (Cai et al. 2013, Delgado et al. 2012, Ellerie et al. 2013, Huang et al. 2009, Matsui  
92 et al. 2004, Wang et al. 2011). Superfine powdered activated carbon (SPAC) adsorbs NOM more  
93 effectively and is loaded highly with NOM compared to conventionally-sized powdered activated  
94 carbon (PAC) at a given AC dosage (Ando et al. 2010). However, the higher NOM loading on SPAC  
95 relative to PAC does not result in a decrease in the adsorption capacity for a micropollutant beyond  
96 that obtained for PAC. This phenomenon can be explained by the localization of NOM loading in an  
97 AC particle. Different effects of NOM between SPAC and PAC are expected on micropollutant uptake-  
98 displacement.

99 Herein, SPAC and PAC were used as adsorbents and 2-methylisoborneol (MIB), a major organic  
100 micropollutant responsible for undesirable taste and odor at much less than  $\mu\text{g/L}$  levels for many water  
101 utilities, was used as the target molecule. To investigate the reversibility of MIB adsorption-desorption  
102 in the presence of NOM, MIB adsorption tests were performed under three conditions: adsorption of  
103 NOM followed by MIB (NOM preloading), simultaneous MIB and NOM adsorption (NOM  
104 simultaneous-loading), and adsorption of MIB followed by NOM (NOM post-loading).

105

## 106 **2. Materials and Methods**

### 107 *2.1. Activated carbon*

108 Commercially available wood-based PAC (Taikou-W, Futamura Chemical Industries Co., Gifu, Japan)  
109 was obtained, prepared as a slurry in ultrapure water (Milli-Q Advantage, Millipore Co.), and milled  
110 to superfine particles using a wet bead mill (LMZ015, Ashizawa Finetech, Chiba, Japan). Herein, the  
111 as-received PAC is referred to as PAC, and the milled activated carbons as SPAC. The ACs were stored  
112 as slurries in ultrapure water at 4 °C and used after dilution and vacuum treatment. The AC particle  
113 size distributions were determined using a laser-light-scattering instrument (Microtrac MT3300EXII,

114 Nikkiso Co., Tokyo, Japan) after dispersant addition (Triton X-100, Kanto Chemical Co., Tokyo,  
115 Japan; final concentration, 0.08 vol%) and subsequent ultrasonic dispersion. The median diameters of  
116 PAC and SPAC were 18.9 and 0.62  $\mu\text{m}$ , respectively, unless otherwise stated. The pore size  
117 distributions were determined using the nitrogen gas adsorption-desorption method (Autosorb-iQ,  
118 Quantachrome Instruments, Kanagawa, Japan).

119

## 120 2.2. *Water samples*

121 Water containing natural organic matter (NOM) was prepared by dissolving Suwannee River humic  
122 acid (SHA) and fulvic acid (SFA; International Humic Substance Society) in ultrapure water containing  
123 inorganic ions. The ion compositions of the prepared samples were the same as that used in a previous  
124 study (Ando et al. 2010). Besides these NOM water samples, natural water samples containing NOM  
125 were collected from the Chibaberi River (Hokkaido, Japan). The water was filtered through a 0.2  $\mu\text{m}$   
126 PTFE membrane (DISMIC-25HP; Toyo Roshi Kaisha, Ltd., Tokyo) to remove any undissolved NOM.  
127 The dissolved organic carbon (DOC) concentration and absorbance at 260 nm (UV260) were used as  
128 parameters for bulk NOM quantification (TOC: Model 810; Sievers 900, Ionics Instrument Business  
129 Grp., Boulder Co.; UV260: UV-1800, Shimadzu Co., Kyoto, Japan).

130

131 Stock solutions of MIB were prepared by dissolving reagent pure MIB (Wako Pure Chemical  
132 Industries, Osaka, Japan) in ultrapure water and filtering the resulting solution through a 0.2  $\mu\text{m}$  PTFE  
133 membrane filter. Single solute solutions of MIB were prepared by diluting the MIB stock solution with  
134 NOM-free water, which were prepared with ultrapure water containing inorganic ions added to make  
135 the ionic composition equal to those of the SFA and SHA water samples. Solutions of MIB in NOM-  
136 containing water were prepared by diluting MIB with the SFA, SHA, and Chibaberi waters. MIB  
137 concentrations were adjusted to 1000 ng/L unless otherwise stated. MIB concentrations were analyzed

138 using a Purge and Trap Concentrator (OI Analytical/Xylem Inc., TX, USA) coupled to a GC-MS (789  
139 GC + 5975 MSD, Agilent Technologies Japan, Tokyo) using <sup>2</sup>H-labeled geosmin (Hayashi Pure  
140 Chemical Ind., Ltd., Osaka, Japan) as an internal standard.

141

### 142 2.3. *Batch adsorption tests*

143 Equilibrium removals of MIB in the presence/absence of NOM were examined by five tests as follows:

144 1) *NOM simultaneous-loading tests*. Aliquots (150 mL) from 1 or 3 L solutions containing both MIB  
145 (1000 ng/L) and NOM (0.9 to 7 mg-C/L) were transferred to vials. A specified amount of SPAC/PAC  
146 was added, and the vials were immediately shaken by hand vigorously and transferred to a shaker for  
147 two weeks of mixing at a constant temperature of 20 °C.

148 2) *NOM post-loading test*. After adding a specified amount of SPAC/PAC to vials containing 140 mL  
149 of MIB solution, the samples were vigorously shaken by hand and transferred to a shaker for one week  
150 of shaking at a constant temperature of 20 °C. Afterward, a small amount of high concentration NOM  
151 (SFA or SHA) solution (10 mL, 12 to 90 mg-C/L) was added to the vial to bring the initial DOC  
152 concentration to the same level as those used in the NOM simultaneous-loading test. After vigorous  
153 shaking by hand, the vials were returned to the shaker for one week of mixing. The NOM post-loading  
154 test of the Chibaberi water samples was conducted by adding SPAC/PAC to vials containing a MIB  
155 solution of 2000 ng/L. After shaking the vials for one week, Chibaberi water (DOC: 3.4 mg-C/L) was  
156 added at 1:1 vol/vol ratio for final MIB and DOC concentrations of 1000 ng/L and 1.7 mg/L,  
157 respectively. After vigorous shaking by hand, the vials were returned to the shaker for mixing for one  
158 week.

159 3) *NOM preloading test*. The procedure of the NOM preloading test was the opposite of the NOM  
160 post-loading test. After adding a specified amount of SPAC/PAC to vials containing 140 mL of the

161 NOM solution and shaking the vials for one week, a small amount of high concentration MIB solution  
162 (10 mL, 15 µg/L) was added to the vial containing the NOM-preloaded AC to bring an initial MIB  
163 concentration of approximately 1000 ng/L. The vials were subsequently shaken for two weeks.

164 4) *Single MIB test*. MIB removal in the absence of NOM was examined using the same procedure as  
165 for the NOM simultaneous-loading tests except that the solution did not contain NOM.

166 5) *Preloading-pulverization test*. After a specified amount of PAC was added to a bottle containing a  
167 1.5-mg/L NOM solution (5 L), the bottle was shaken and transferred to a shaker for one week of mixing  
168 for adsorption. After shaking, the PAC was recovered and pulverized by the following procedure. The  
169 bottle was kept at rest for 3 days for the PAC particles to settle to the bottom. The top 4.5 L of the  
170 water (supernatant) was discarded. The remaining water containing NOM-loaded PAC particles was  
171 centrifuged at 1000 rpm (133 g) for 60 min, and the upper part was carefully discarded to reduce the  
172 volume containing PAC particles to 10 mL. The water containing the PAC particles was transferred to  
173 a mortar and placed under vacuum for 3 h to evaporate most of the remaining water. Afterward, the  
174 wet PAC particle sludge was obtained, which was then pounded by a pestle for 10 min for fracturing.  
175 The particle sizes of the PACs before and after fracturing were determined using a laser light-scattering  
176 instrument. A portion of the sludge containing the fractured PAC was added to a vial containing 140  
177 mL of water (MIB concentration of 1000 ng/L, same ionic composition as the NOM water) at a  
178 concentration of 1.5 mg/L. The PAC sludge before fracturing was added to a vial to prepare a control  
179 sample. The vials were shaken for two weeks.

180 According to a previous report (Matsui et al. 2013), MIB adsorption equilibrium can be reached within  
181 one week, and NOM adsorption nearly reached equilibrium. However, internal diffusion of the  
182 desorbed compound by displacement in an AC particle may slow (To et al. 2008). Therefore, it was  
183 previously confirmed in long-term shaking tests that after two weeks of MIB contact, adsorption  
184 equilibrium could be reached. In the long-term shaking tests, MIB removal ratios were unchanged

185 between two and three weeks of MIB contact time (see Fig. 1S in the Supplementary Information).  
186 Therefore, an AC-water contact time of  $\geq$  two weeks was used. Control tests were also conducted using  
187 multiple bottles that did not contain AC to confirm that concentration changes during long-term mixing  
188 were negligible without the adsorbent. After the water samples were filtered through a 0.2  $\mu\text{m}$  PTFE  
189 membrane filter, the MIB and NOM concentrations in the water phase were measured.

190

### 191 2.5. *Isotope microscopy of the internal adsorption profile*

192  $^2\text{H}$ -labeled MIB was obtained from Wako Pure Chemical Industries, and  $^{15}\text{N}$ -labeled EfOM (effluent  
193 organic matter) was produced via the following procedure. Activated sludge sampled from a  
194 wastewater treatment plant (Soseigawa, Sapporo, Japan) was injected into M9 minimal medium  
195 containing  $^{15}\text{N}$ -labeled  $\text{NH}_4\text{Cl}$  and natural  $\text{NH}_4\text{Cl}$  at a 1:1 ratio, and subsequently cultured by adding  
196 glucose every day. After culturing for 16 days, the water was filtered through a 0.45  $\mu\text{m}$  pore size  
197 mixed cellulose ester (MCE) membrane to remove the activated sludge and then filtered through  
198 ultrafiltration membranes with a nominal MW cutoff of 10 kD (regenerated cellulose membrane,  
199 PLGC04310, Millipore). Most of the ammonia remained in the water was removed by air stripping at  
200 pH 12. After returning pH to 7, the water was filtered through ultrafiltration membranes with nominal  
201 MW cutoff of 1 kDa (regenerated cellulose membrane, PLAC04310, Millipore) in order to separate  
202 EfOM from ammonia. The membrane retentate containing EfOM was obtained. The  $^{15}\text{N}/^{14}\text{N}$  ratio of  
203 the EfOM was 0.018, markedly higher than the natural  $^{15}\text{N}/^{14}\text{N}$  ratio of 0.0030.

204 PAC particles that adsorbed  $^2\text{H}$ -labeled MIB and  $^{15}\text{N}$ -labeled EfOM were obtained using the adsorption  
205 procedures described in Section 2.3. Only the conventionally-sized PAC was used for isotope  
206 microscopy analysis because the image resolution was not sufficient to visualize adsorption profiles in  
207 the SPAC particles. After adsorption, the waters were filtered through a 0.2- $\mu\text{m}$  alumina membrane  
208 (Spectrum Chemical Mfg. Corp., USA) covered with a 100-nm thick gold layer produced by gold

209 evaporation, and PAC particles were collected on the membrane. Gold evaporation was conducted to  
210 improve conductivity and prevent the membrane from becoming charged during the isotope  
211 microscopy measurements. After the particles on the membrane were imaged using a low vacuum  
212 scanning electron microscope (LV-SEM; JSM-6360LA, JEOL), the intensities of  $^2\text{H}$ ,  $^1\text{H}$ ,  $^{15}\text{N}$ , and  $^{14}\text{N}$   
213 on the AC particles were observed as a two-dimensional map using an isotope microscope system  
214 (Hokkaido University, Sapporo, Japan). Details of the observation procedure are described elsewhere  
215 (Matsui et al. 2014). The  $^2\text{H}/^1\text{H}$  ratios were calculated on the spots that had sufficient  $^1\text{H}$  detection  
216 signal intensities in the maps to estimate the intraparticle MIB distributions, while  $^{15}\text{N}/^{14}\text{N}$  ratios were  
217 calculated on the spots with sufficient  $^{14}\text{N}$  signal intensities to estimate the intraparticle EfOM  
218 distributions.

219

### 220 **3. Results and Discussion**

#### 221 *3.1. Comparison of MIB removal*

222 Proportions of MIB remaining ( $C/C_0$ ) are plotted against AC dosages in Figs. 1–3. The proportions of  
223 MIB remaining were higher in the presence of NOM compared to those without NOM (single  
224 adsorbate system). Of all three tests in the presence of NOM, the proportion of MIB remaining was  
225 the highest on the NOM-preloaded AC and lowest on the NOM-post-loaded AC. However, the  
226 difference in the proportions of MIB remaining in the three tests was small at high AC dosages of  $>10$   
227 mg/L. A small difference was also observed at low AC dosages for SPAC when the initial NOM  
228 concentration was low (left panel of Fig. 1 and upper left panels of Figs. 2 and 3).

229 When ACs were added to the NOM-free MIB water and shaken for two weeks to equilibrate, MIB  
230 concentrations corresponding to the proportion of remaining were obtained, as shown in the diamond  
231 plots in Figs. 1–3. When water samples where MIB had previously been equilibrated were spiked with  
232 NOM and shaken for another week, the MIB concentrations increased and became higher than that

233 before spiking NOM (the diamond plots moved to the circle plots in Figs. 1–3). This indicated that the  
234 preloaded MIB was desorbed back to the water phase by the displacement with NOM. Therefore, the  
235 fact that the proportion of MIB removal by post-loaded AC was the same as that by NOM-preloaded  
236 AC can be interpreted as the complete reversibility of MIB adsorption. Furthermore, since adsorption  
237 reversibility is not expected when pore blocking occurs, it is presumed that the NOM effect was caused  
238 by direct site competition (Matsui et al. 2012, Newcombe et al. 1997).

239 Similar proportions of MIB removals for the NOM-preloaded AC, NOM-post-loaded AC and NOM-  
240 simultaneously loaded AC indicate that the displacement of preloaded MIB occurred until the  
241 equilibrium of the competitive MIB and NOM adsorption was reached. However, it could not tell  
242 whether or not the preloaded NOM was desorbed. DOC removals were not significantly different  
243 between the three ACs (Fig. 2S in the Supplementary Information). Because the initial MIB  
244 concentration was  $\sim 6$  nmol/L ( $\sim 1$   $\mu\text{g/L}$ ), the concentration of the NOM that could be displaced with  
245 MIB would be estimated to be comparable to that concentration. However, the total NOM  
246 concentration in the experiments was  $>0.8$  mg-C/L ( $> 1.5$   $\mu\text{mol/L}$ ). The NOM that could be displaced  
247 with MIB was negligible compared to the total NOM, so if NOM displacement occurred, it would be  
248 difficult to detect.

249

### 250 3.2. Adsorption irreversibility: the pore blockage effect

251 Differences in MIB removals between the three sample types can be attributed to the irreversible  
252 adsorption (incomplete desorption) with direct site competition or pore blockage by NOM molecules.  
253 Irreversible adsorption occurs when MIB molecules are tightly adsorbed in small micropores with  
254 significant overlap with the pore wall potentials (Pelekani and Snoeyink 2000). However, almost  
255 complete reversibility was observed for SPAC, unlike PAC, at the same AC dosages, although the pore  
256 size distributions were not different between the two ACs (see Fig. 3S in the Supplementary

257 Information) as Ando et al. (2010) noted. Therefore, irreversible adsorption with direct site competition  
258 cannot explain the incomplete desorption. As a remaining plausible mechanism, pore blockage was  
259 proposed for the incomplete desorption of MIB. Pelekani and Snoeyink (1999) observed no desorption  
260 of preloaded micropollutant (atrazine) on AC fibers containing primarily micropores and attributed  
261 this phenomenon to a pore blockage mechanism wherein NOM molecules block access to, but do not  
262 penetrate into, the primary micropores. Aschermann et al. (2018) also report that NOM adsorption  
263 prevents the desorption of organic micropollutant from granular activated carbon (GAC). However, it  
264 remained unanswered: whether internal or external pore blockage occurs. Internal pore blockage  
265 occurs at the entrance of a micropore inside an AC particle, whereas external pore blockage occurs at  
266 the outer interface area. If the pore blockage occurred internally, both SPAC and PAC would have  
267 exhibited a similar pore blockage effect leading to similar irreversibility as the pore size distributions  
268 are similar for both ACs. As a plausible mechanism, therefore, external pore blockage was proposed  
269 for the irreversibility of MIB adsorption on AC.

270

### 271 3.3. *Effect of activated carbon particle size and NOM concentration*

272 Herein, the magnitude of irreversible adsorption was quantitatively evaluated using an index,  
273  $\Delta_{pre-post}$ , defined by the difference in MIB removal obtained by NOM-preloaded and NOM-post-  
274 loaded ACs as follows:

$$275 \quad \Delta_{pre-post} = R_{pre} - R_{post}$$

276 Where  $\Delta_{pre-post}$  is a pore blockage index (dimensionless),  $R_{pre}$  is the proportion of MIB remaining  
277 ( $C/C_0$ ) of the NOM-preloaded AC adsorption (dimensionless), and  $R_{post}$  is the proportion of MIB  
278 remaining ( $C/C_0$ ) of the NOM-post-loaded AC adsorption (dimensionless).

279 The values of  $\Delta_{pre-post}$  were calculated and shown in Fig. 4. The  $\Delta_{pre-post}$  values were higher at

280 higher initial NOM concentrations (7 mg-C/L for SFA and 6 mg-C/L for SHA) and lower AC dosages  
281 (0.9 mg-C/L for SFA and 1.6 mg/L for SHA). This is reasonable because these experimental conditions  
282 should yield higher NOM loading per AC, resulting in a larger pore blockage effect. The NOM MWs  
283 used herein descend in the following order: SHA, SFA, and Chibaberi in terms of peak MW (Fig. 4S).  
284 When comparing the  $\Delta_{Pre-Post}$  values at similar AC dosages in Fig.4, however, no such ordering trend  
285 was observed for their values between Chibaberi, SFA, and SHA. Therefore, the magnitudes of  
286 irreversible adsorption of MIB does not appear to be related to NOM MW. Actually, this result was  
287 somewhat unexpected, because it is widely accepted that pore blockage hindering intraparticle  
288 transport of micropollutant molecules in an AC particle is more effectively achieved by higher MW  
289 NOM (Pelekani and Snoeyink 2001). However, our result is in accordance with a very recent finding  
290 of Aschermann et al. (2019). They prepared two NOM fractions of low and high molecular weights  
291 and found that the impacts of the two fractions on organic micropollutant desorption were similar  
292 though pore blockage and micropollutant displacement occurred on both fractions. With reference to  
293 their paper, therefore, we feel our result is a possible outcome.

294

295 Overall, the  $\Delta_{Pre-Post}$  values were lower for SPAC than PAC. SPAC with a smaller particle size  
296 showed higher MIB adsorption reversibility compared to the PAC samples. This is in agreement with  
297 the previous paper of Thacker et al. (1983), which stated that the quantity of adsorbate that can desorb  
298 from the GAC bed in response to decreased influent concentration increased with decreasing GAC  
299 particle size. It should be noted, however, that the particle sizes tested in the previous study are very  
300 different to those used herein. The higher reversibility for SPAC than PAC indicates that SPAC did not  
301 experience significant pore blockage effects, unlike PAC. This result is interesting because SPAC has  
302 been reported to exhibit higher NOM removal than PAC (Ando et al. 2010). NOM removals were  
303 actually higher for SPAC than for PAC (Fig. 2S in the Supplementary Information), and NOM loadings  
304 were higher on SPAC than on PAC. On the one hand, the high NOM loading on SPAC is explained by  
305 the Shell Adsorption in which NOM is adsorbed mainly in the vicinity of the outer surface of AC

306 particles (Ando et al. 2010, Ando et al. 2011). At a given AC dose, NOM is probably loaded to a lesser  
307 extent on the outer surface area of SPAC particles compared to PAC particles because the total outer  
308 particle surface area is much larger, and then external pore blocking probably occurs at a lower degree  
309 for SPAC.

310

#### 311 3.4. *NOM and MIB adsorption profiles on the activated carbon particles*

312 External pore blockages where NOM is loaded near the outer surface of AC particles, thereby blocking  
313 the access of MIB molecules to the inner region was presented in the previous sections. Then, we tried  
314 to achieve direct observation of the adsorbate distribution in AC particles using an isotope microscope  
315 system and isotope-labeled adsorbates.  $^{15}\text{N}$ -labeled EfOM was prepared and used as a NOM substitute.  
316 The use of  $^{15}\text{N}$ -labeled NOM was ideal, but it was not available, and its laboratory preparation was  
317 impossible. However, we confirmed that the molecular weight distributions of the prepared  $^{15}\text{N}$ -labeled  
318 EfOM and the NOM are similar (Fig. 5S, SI). Figs. 5 and 6S (SI) show the isotope ( $^{15}\text{N}/^{14}\text{N}$  ratio) maps  
319 of the AC particles obtained after the upsides of the AC particles were removed using ion beam  
320 sputtering, exposing the particle interior (Matsui et al. 2014). The SEM pictures of the particles before  
321 isotope microscopy measurements are also provided. The observed isotope ratios of EfOM-loaded ACs  
322 ranged from 0.01 to 0.46, while the  $^{15}\text{N}/^{14}\text{N}$  ratio of an entire AC particle is predicted to be  $\sim 0.1$ ,  
323 according to the  $^{15}\text{N}/^{14}\text{N}$  ratio (0.018) of the EfOM, N/C ratio (0.10, w/w) of EfOM (Chen et al. 2009),  
324 and carbon mass balance after adsorption. Fair agreement was found between the prediction and  
325 calculation. The ratio of the non-loaded ACs was  $< 0.01$ .

326

327 For 9 AC particles of the 10 observed,  $^{15}\text{N}/^{14}\text{N}$  ratios were relatively high in the outer regions and in  
328 the region with large macropore(s) as both regions were in direct contact with water during the  
329 adsorption compared with the other regions which were not exposed to water. The  $^{15}\text{N}/^{14}\text{N}$  ratio was,

330 however, not always high over the entire outer region for each particle, likely because some outer  
331 regions were removed during ion beam sputtering, exposing the particle interior. The differences in the  
332  $^{15}\text{N}/^{14}\text{N}$  ratios between the regions in contact with and shielded from water were approximately a factor  
333 of  $\geq 2$ . Adsorption of NOM at the external region has been hypothesized implicitly or explicitly (Ando  
334 et al. 2010, Randtke and Snoeyink 1983), but this is the first evidence that EfOM (a type of NOM)  
335 mainly adsorbed near the outer surface area of AC particles and did not significantly diffuse inside the  
336 particle.

337

338 The  $^2\text{H}/^1\text{H}$ -ratios on ACs loaded with  $^2\text{H}$ -labeled MIB are presented in Fig. 7S (SI), where the high  
339 ratio indicates significant MIB adsorption. The  $^2\text{H}/^1\text{H}$ -ratios in the NOM-preloaded AC particles were  
340 always low, and those of the NOM-post-loaded AC and NOM-free AC varied (the reason for the  
341 variation was not clearly known, but it might be due to the evaporation of MIB during the observation).  
342 Low  $^2\text{H}/^1\text{H}$ -ratios were observed in the NOM-preloaded ACs (Fig. 8S, SI) in all studied regions.  
343 Overall, NOM-preloaded AC particles showed significantly lower  $^2\text{H}/^1\text{H}$ -ratios than the NOM-post-  
344 loaded and NOM-free AC particles. These data support the external pore-blockage mechanism, which  
345 would cause irreversible adsorption on PAC.

346

### 347 *3.5. Changes in MIB removal by pulverization of NOM-preloaded activated carbon*

348 If pore blockage occurs at the external interface area of PAC particles, the pulverization of the PAC  
349 particles would break the blocking layer and enhance MIB adsorption because the inside of the PAC  
350 particles, which were not available for adsorption due to external pore blockage, became available.  
351 Then, the preloading-pulverization test was conducted to prove this. The results of MIB removal in the  
352 test are shown in Fig. 6. While the proportion of MIB remaining after contact with the preloaded-PAC  
353 was approximately 80%, that observed for the pulverized preloaded-PAC was 60%. Pulverization of

354 the preloaded-PAC particles actually enhanced MIB adsorption. Before concluding that the breakage  
355 of external blocking layer was the main cause of the enhanced MIB removal, the possibilities of other  
356 interpretations for the result were ruled out. One possibility (Interpretation A) is the occurrence of the  
357 Shell Adsorption on MIB (Matsui et al. 2015). It has been reported that particle size reduction can  
358 increase the adsorption capacity for hydrophobic compounds (including MIB) for some types of virgin  
359 AC (not-preloaded AC) because adsorption mainly occurs at the external region of the AC particles.  
360 For the tested PAC, particle size reduction without NOM-preloading did not increase the adsorption  
361 capacity or MIB removal (Fig. 9S, SI). Thus, Interpretation A was denied. The other possibility  
362 (Interpretation B), is the desorption of pore-blocking NOM by pulverization. However, Interpretation  
363 B is not plausible because pulverization did not change the DOC. The DOC of the pulverized preloaded  
364 PAC suspension was similar to that of the non-pulverized preloaded PAC (Fig. 10S, SI). Finally, the  
365 MIB removal enhancement by pulverization of the preloaded PAC supported the external pore-  
366 blocking mechanism as described previously.

367

## 368 **CONCLUSIONS**

369 The major conclusions of this study can be summarized as follows:

370 1) With small AC particle diameters (SPAC) and low NOM concentrations (0.9 and 1.6 mg-C/L), MIB  
371 removals were similar between the NOM-preloaded, NOM-simultaneously loaded and NOM-post-  
372 loaded ACs, and MIB adsorption was reversible for the MIB/NOM loading sequence. Similar results  
373 were obtained at high AC dosages ( $> 10$  mg/L) for PAC as well as SPAC. The reversibility of MIB  
374 adsorption indicated direct site competition between MIB and NOM. Almost complete desorption of  
375 MIB by NOM occurred until competitive adsorption equilibrium was reached.

376 2) At high NOM concentration or low PAC dosages, MIB removal was higher for NOM-post-loaded  
377 AC compared to NOM-preloaded AC, and MIB adsorption was irreversible. The degree of

378 irreversibility was high on PAC compared to SPAC, although the two ACs were almost the same on  
379 pore size distribution. The lower degree of reversibility on PAC indicated external pore blockage via  
380 NOM adsorption at the outer interface area of PAC particles. External pore blockage by NOM on PAC  
381 was due to the smaller external particle surface area of PAC compared to SPAC, which would result in  
382 high NOM loading on the pores close to the outer interface area of AC particles.

383 3) EfOM as a substitute for NOM was labeled with  $^{15}\text{N}$  and used for the adsorption experiments. The  
384 distribution of  $^{15}\text{N}$  as a marker of EfOM inside the AC particles was directly observed using an isotope  
385 mapping system. Direct evidence was obtained for the high loading of EfOM at the external region of  
386 the PAC particles.

387

## 388 **ACKNOWLEDGEMENTS**

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393

394

## 395 **Appendix. Supplementary Information**

396 Figs. 1S-9S are available in the online version at #####.

397

## 398 **REFERENCES**

399 Ando, N., Matsui, Y., Kurotobi, R., Nakano, Y., Matsushita, T. and Ohno, K. (2010) Comparison of natural organic matter  
400 adsorption capacities of super-powdered activated carbon and powdered activated Carbon. *Water Research* 44(14), 4127-  
401 4136.

402 Ando, N., Matsui, Y., Matsushita, T. and Ohno, K. (2011) Direct observation of solid-phase adsorbate concentration profile  
403 in powdered activated carbon particle to elucidate mechanism of high adsorption capacity on super-powdered activated  
404 carbon. *Water Research* 45(2), 761-767.

405 Aschermann, G., Neubert, L., Zietzschmann, F. and Jekel, M. (2019) Impact of different DOM size fractions on the  
406 desorption of organic micropollutants from activated carbon. *Water Research* 161, 161-170.

407 Aschermann, G., Zietzschmann, F. and Jekel, M. (2018) Influence of dissolved organic matter and activated carbon pore  
408 characteristics on organic micropollutant desorption. *Water Research* 133, 123-131.

409 Cai, Z., Wee, C. and Benjamin, M.M. (2013) Fouling mechanisms in low-pressure membrane filtration in the presence of  
410 an adsorbent cake layer. *Journal of Membrane Science* 433(0), 32-38.

411 Chen, B., Nam, S.-N., Westerhoff, P.K., Krasner, S.W. and Amy, G. (2009) Fate of effluent organic matter and DBP  
412 precursors in an effluent-dominated river: A case study of wastewater impact on downstream water quality. *Water Research*  
413 43(6), 1755-1765.

414 Cook, D., Newcombe, G. and Sztajn bok, P. (2001) The application of powdered activated carbon for mib and geosmin  
415 removal: predicting pac doses in four raw waters. *Water Research* 35(5), 1325-1333.

416 Delgado, L.F., Charles, P., Glucina, K. and Morlay, C. (2012) The removal of endocrine disrupting compounds,  
417 pharmaceutically activated compounds and cyanobacterial toxins during drinking water preparation using activated  
418 carbon—A review. *Science of the Total Environment* 435–436(0), 509-525.

419 Ding, L., Mariñas, B.J., Schideman, L.C., Snoeyink, V.L. and Li, Q. (2006) Competitive Effects of Natural Organic Matter:  
420 Parametrization and Verification of the Three-Component Adsorption Model COMPSORB. *Environmental Science &  
421 Technology* 40(1), 350-356.

422 Ding, L., Snoeyink, V.L., Mariñas, B.J., Yue, Z. and Economy, J. (2008) Effects of Powdered Activated Carbon Pore Size  
423 Distribution on the Competitive Adsorption of Aqueous Atrazine and Natural Organic Matter. *Environmental Science &  
424 Technology* 42(4), 1227-1231.

425 Ellerie, J.R., Apul, O.G., Karanfil, T. and Ladner, D.A. (2013) Comparing graphene, carbon nanotubes, and superfine  
426 powdered activated carbon as adsorptive coating materials for microfiltration membranes. *Journal of Hazardous Materials*  
427 261(0), 91-98.

428 Huang, C., VanBenschoten, J.E. and Jensen, J.N. (1996) Adsorption kinetics of MIB and geosmin. *Journal American Water  
429 Works Association* 88(4), 116-128.

430 Huang, H., Schwab, K. and Jacangelo, J.G. (2009) Pretreatment for low pressure membranes in water treatment: a review.  
431 *Environmental Science & Technology* 43(9), 3011-3019.

432 Karanfil, T., Dastgheib, S.A. and Mauldin, D. (2006) Exploring Molecular Sieve Capabilities of Activated Carbon Fibers  
433 to Reduce the Impact of NOM Preloading on Trichloroethylene Adsorption. *Environmental Science & Technology* 40(4),  
434 1321-1327.

435 Kilduff, J.E., Karanfil, T. and Weber, W.J. (1998) TCE adsorption by GAC preloaded with humic substances. *Journal  
436 American Water Works Association* 90(5), 76-89.

437 Kilduff, J.E. and Wigton, A. (1999) Sorption of TCE by Humic-Preloaded Activated Carbon: Incorporating Size-Exclusion  
438 and Pore Blockage Phenomena in a Competitive Adsorption Model. *Environmental Science & Technology* 33(2), 250-256.

439 Knappe, D.R.U., Matsui, Y., Snoeyink, V.L., Roche, P., Prados, M.J. and Bourbigot, M.-M. (1998) Predicting the Capacity  
440 of Powdered Activated Carbon for Trace Organic Compounds in Natural Waters. *Environmental Science & Technology*  
441 32(11), 1694-1698.

442 Li, Q., Mariñas, B.J., Snoeyink, V.L. and Campos, C. (2003a) Three-Component Competitive Adsorption Model for Flow-  
443 Through PAC Systems. 1. Model Development and Verification with a PAC/Membrane System. *Environmental Science &  
444 Technology* 37(13), 2997-3004.

445 Li, Q., Snoeyink, V.L., Campos, C. and Mariñas, B.J. (2002) Displacement Effect of NOM on Atrazine Adsorption by  
446 PACs with Different Pore Size Distributions. *Environmental Science & Technology* 36(7), 1510-1515.

447 Li, Q., Snoeyink, V.L., Mariñas, B.J. and Campos, C. (2003b) Elucidating competitive adsorption mechanisms of atrazine  
448 and NOM using model compounds. *Water Research* 37(4), 773-784.

449 Matsui, Y., Fukuda, Y., Inoue, T. and Matsushita, T. (2003) Effect of natural organic matter on powdered activated carbon  
450 adsorption of trace contaminants: characteristics and mechanism of competitive adsorption. *Water Research* 37(18), 4413-  
451 4424.

452 Matsui, Y., Fukuda, Y., Murase, R., Aoki, N., Mima, S., Inoue, T. and Matsushita, T. (2004) Micro-ground powdered  
453 activated carbon for effective removal of natural organic matter during water treatment. *Water Science & Technology:  
454 Water Supply* 4(4), 155-163.

455 Matsui, Y., Nakao, S., Sakamoto, A., Taniguchi, T., Pan, L., Matsushita, T. and Shirasaki, N. (2015) Adsorption capacities  
456 of activated carbons for geosmin and 2-methylisoborneol vary with activated carbon particle size: Effects of adsorbent and  
457 adsorbate characteristics. *Water Research* 85, 95-102.

458 Matsui, Y., Nakao, S., Taniguchi, T. and Matsushita, T. (2013) Geosmin and 2-methylisoborneol removal using superfine  
459 powdered activated carbon: Shell adsorption and branched-pore kinetic model analysis and optimal particle size. *Water*

460 Research 47(8), 2873-2880.  
461 Matsui, Y., Sakamoto, A., Nakao, S., Taniguchi, T., Matsushita, T., Shirasaki, N., Sakamoto, N. and Yurimoto, H. (2014)  
462 Isotope Microscopy Visualization of the Adsorption Profile of 2-Methylisoborneol and Geosmin in Powdered Activated  
463 Carbon. *Environmental Science & Technology* 48(18), 10897-10903.  
464 Matsui, Y., Yoshida, T., Nakao, S., Knappe, D.R.U. and Matsushita, T. (2012) Characteristics of competitive adsorption  
465 between 2-methylisoborneol and natural organic matter on superfine and conventionally sized powdered activated carbons.  
466 *Water Research* 46(15), 4741-4749.  
467 Najm, I.N., Snoeyink, V.L., Suidan, M.T., Lee, C.H. and Richard, Y. (1990) Effect of particle-size and background natural  
468 organics on the adsorption efficiency of PAC. *Journal American Water Works Association* 82(1), 65-72.  
469 Newcombe, G., Drikas, M. and Hayes, R. (1997) Influence of characterised natural organic material on activated carbon  
470 adsorption: II. Effect on pore volume distribution and adsorption of 2-methylisoborneol. *Water Research* 31(5), 1065-1073.  
471 Pelekani, C. and Snoeyink, V.L. (1999) Competitive adsorption in natural water: role of activated carbon pore size. *Water*  
472 *Research* 33(5), 1209-1219.  
473 Pelekani, C. and Snoeyink, V.L. (2000) Competitive adsorption between atrazine and methylene blue on activated carbon:  
474 the importance of pore size distribution. *Carbon* 38(10), 1423-1436.  
475 Pelekani, C. and Snoeyink, V.L. (2001) A kinetic and equilibrium study of competitive adsorption between atrazine and  
476 Congo red dye on activated carbon: the importance of pore size distribution. *Carbon* 39(1), 25-37.  
477 Randtke, S.J. and Snoeyink, V.L. (1983) EVALUATING GAC ADSORPTIVE CAPACITY. *Journal American Water Works*  
478 *Association* 75(8), 406-413.  
479 Summers, R.S., Knappe, D.R.U. and Snoeyink, V.L. (2011) *Water quality and treatment: a handbook of community water*  
480 *supplies*. Edzwald, J.K. and American Water Works Association (eds), McGraw-Hill.  
481 Summers, R.S. and Roberts, P.V. (1988) Activated carbon adsorption of humic substances: I. Heterodisperse mixtures and  
482 desorption. *Journal of Colloid and Interface Science* 122(2), 367-381.  
483 Thacker, W.E., Snoeyink, V.L. and Crittenden, J.C. (1983) Desorption of compounds during operation of GAC adsorption  
484 systems. *Journal of American Water Works Association* 75(3), 144-149.  
485 To, P.C., Mariñas, B.J., Snoeyink, V.L. and Ng, W.J. (2008) Effect of Pore-Blocking Background Compounds on the  
486 Kinetics of Trace Organic Contaminant Desorption from Activated Carbon. *Environmental Science & Technology* 42(13),  
487 4825-4830.  
488 Wang, Y., Rao, G.Y. and Hu, J.Y. (2011) Adsorption of EDCs/PPCPs from drinking water by submicron-sized powdered  
489 activated carbon. *Water Science and Technology-Water Supply* 11(6), 711-718.  
490 Zoschke, K., Engel, C., Börnick, H. and Worch, E. (2011) Adsorption of geosmin and 2-methylisoborneol onto powdered  
491 activated carbon at non-equilibrium conditions: Influence of NOM and process modelling. *Water Research* 45(15), 4544-  
492 4550.  
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494

495 List of figures

496

497 Figure 1. Removal of MIB from the Chibaberi water samples as a function of AC dosage. The plots are  
498 experimental data and the lines are those obtained by fitting with Eqs. (1) or (3) provided in the SI.

499

500

501 Figure 2. Removal of MIB from the SFA water samples as a function of AC dosage. The plots are  
502 experimental data and the lines are those obtained by fitting with Eqs. (1) or (3) provided in the SI.  
503 The upper and lower panels correspond to SFA concentrations of 0.9 and 7 mg-C/L, respectively.

504

505

506 Figure 3. Removal of MIB from the SHA water samples as a function of AC dosage. The plots are  
507 experimental data and the lines are those obtained by fitting with Eqs. (1) or (3) provided in the SI.  
508 The upper and lower panels correspond to SHA concentrations of 1.6 and 6 mg-C/L, respectively.

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511 Figure 4. The  $\Delta_{pre-post}$  values (difference in MIB removal obtained using NOM-preloaded and  
512 NOM-post-loaded carbons) used to evaluate effect of the pore blockage (irreversible adsorption of  
513 MIB). The upper left, upper right, and lower panels correspond to the Chibaberi, SFA, and SHA  
514 water samples, respectively. Cc indicates the AC dosage.

515

516

517 Figure 5. Left panels: LV-SEM images of AC particles loaded with <sup>15</sup>N-labeled EfOM before isotope  
518 microscopy measurements. Right panels: Isotopic maps (<sup>15</sup>N/<sup>14</sup>N ratio) of the AC particles (non-  
519 target particles were identified after referring to the LV-SEM image and is depicted in white). Panels  
520 A and B: EfOM-loaded carbons. Panel C: EfOM-free AC. White dotted lines indicate the particle  
521 periphery. The LV-SEM images and isotopic maps of the other AC particles are provided in Fig. 5S  
522 (SI).

523

524

525 Figure 6. Comparison of MIB removal obtained using pulverized and non-pulverized NOM-  
526 preloaded AC particles with median diameters of 5.8 and 18.8  $\mu\text{m}$ , respectively (Chibaberi water, 1.5  
527 mg/L DOC, 1 mg/L AC dosage).

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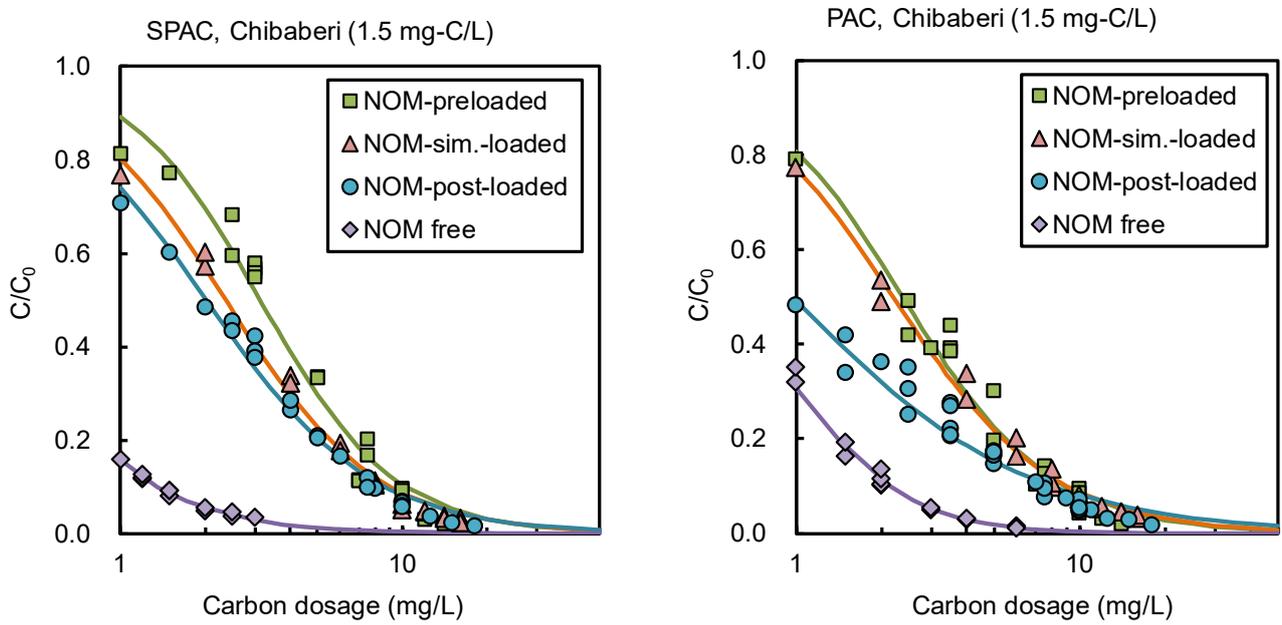


Figure1. Removal of MIB from the Chibaberi water samples as a function of AC dosage. The plots are experimental data and the lines are those obtained by fitting with Eqs. (1) or (3) provided in the SI.

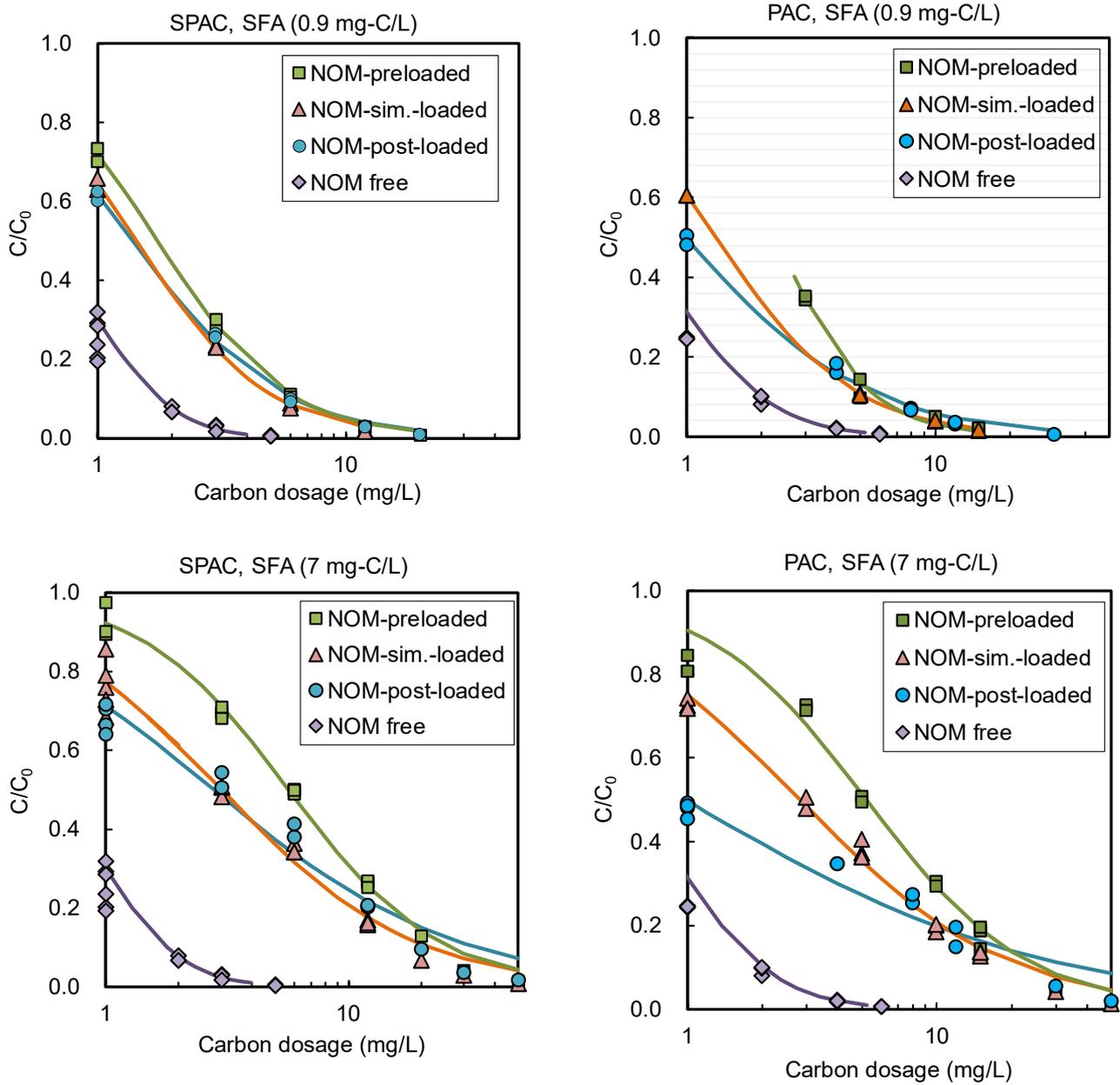


Figure 2. Removal of MIB from the SFA water samples as a function of AC dosage. The plots are experimental data and the lines are those obtained by fitting with Eqs. (1) or (3) provided in the SI. The upper and lower panels correspond to SFA concentrations of 0.9 and 7 mg-C/L, respectively.

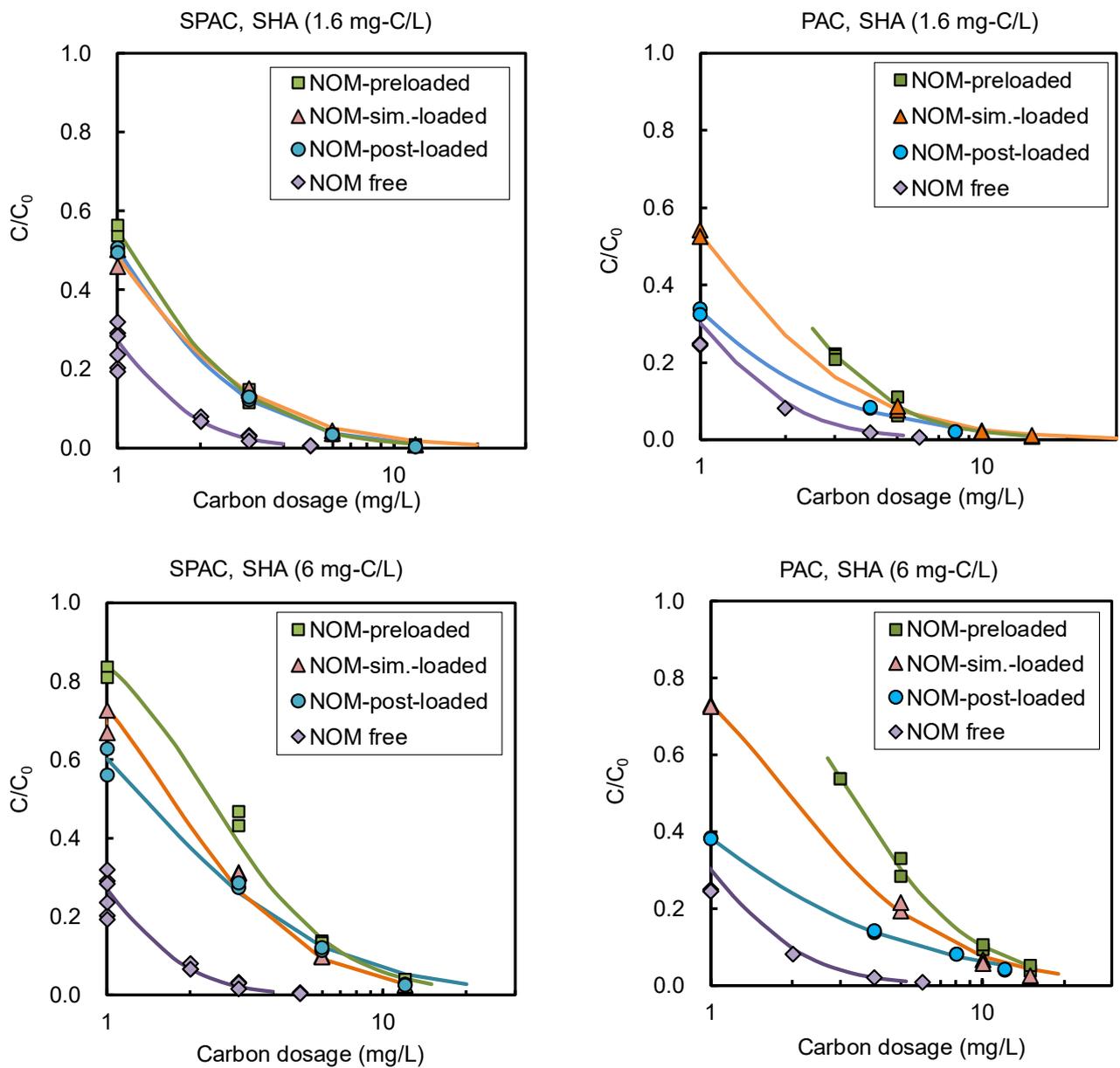


Figure 3. Removal of MIB from the SHA water samples as a function of AC dosage. The plots are experimental data and the lines are those obtained by fitting with Eqs. (1) or (3) provided in the SI. The upper and lower panels correspond to SHA concentrations of 1.6 and 6 mg-C/L, respectively.

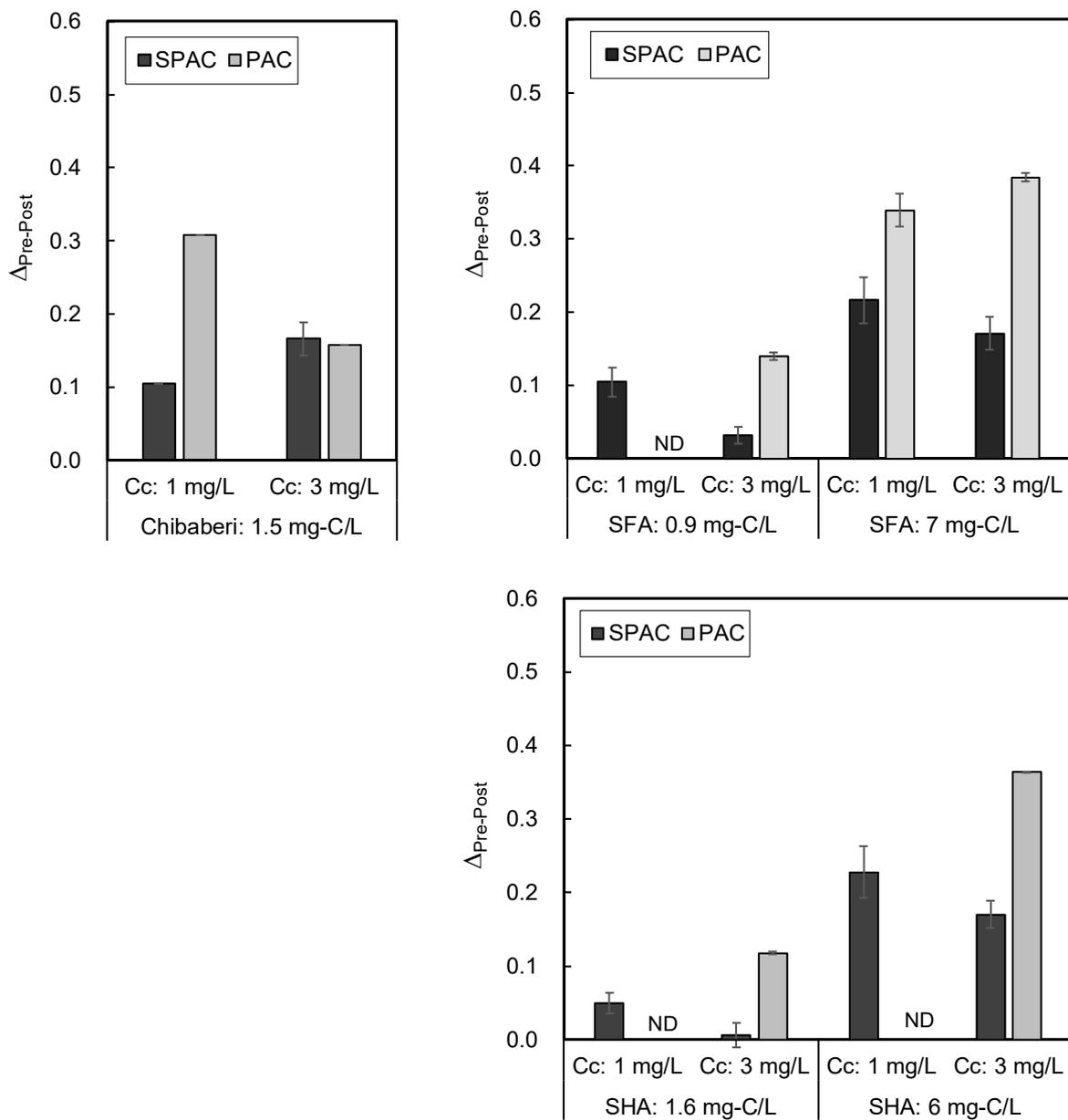


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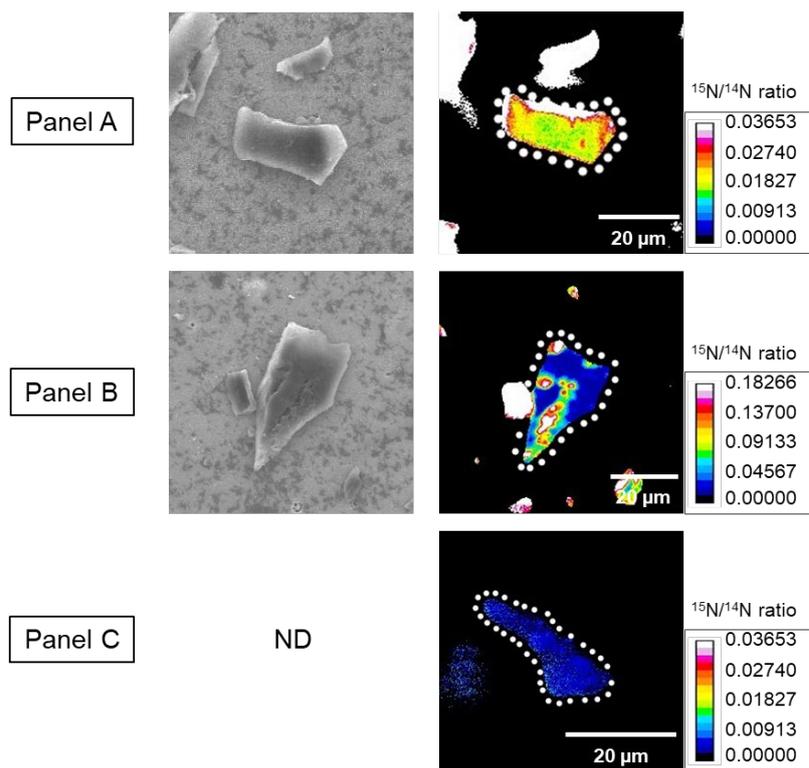


Figure 5. Left panels: LV-SEM images of AC particles loaded with  $^{15}\text{N}$ -labeled EfOM before isotope microscopy measurements. Right panels: Isotopic maps ( $^{15}\text{N}/^{14}\text{N}$  ratio) of the AC particles (non-target particles were identified after referring to the LV-SEM image and is depicted in white). Panels A and B: EfOM-loaded carbons. Panel C: EfOM-free AC. White dotted lines indicate the particle periphery. The LV-SEM images and isotopic maps of the other AC particles are provided in Fig. 5S (SI).

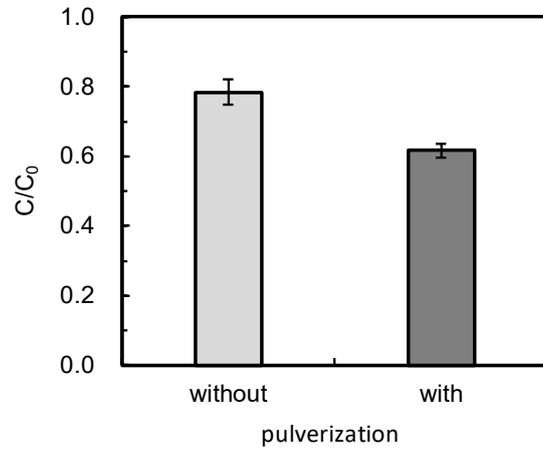


Figure 6. Comparison of MIB removal obtained using pulverized and non-pulverized NOM-preloaded AC particles with median diameters of 5.8 and 18.8  $\mu\text{m}$ , respectively (Chibaberi water, 1.5 mg/L DOC, 1 mg/L AC dosage).

## Supplementary Information

### **Effects of Pre, Post, and Simultaneous Loading of Natural Organic Matter on 2-Methylisoborneol Adsorption on Superfine Powdered Activated Carbon: Reversibility and External Pore-blocking**

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## Data analysis

Micropollutant isotherms obtained by batch adsorption tests in the presence of NOM vary with the initial micropollutant concentration (Knappe et al. 1998). However, the proportion of micropollutant remaining ( $C/C_0$ , where  $C$  is the concentration and subscript zero indicates the initial concentration) after AC adsorption in the presence of NOM is a function of AC dosage and independent of the initial micropollutant concentration. In the MIB adsorption tests, the initial concentrations were adjusted to 1000 ng/L, but there was variation from 800 to 1290 ng/L. To prevent any complications from the varied initial concentration, the experimental adsorption data were expressed in the plot of  $C/C_0$  vs. AC dosage instead of isotherm plots. The curve of  $C/C_0$  as a function of AC dosage can be described mathematically using the two parameter equation (Qi et al. 2007, Zoschke et al. 2011).

$$\frac{C}{C_0} = \frac{1}{AC_c^{1/n} + 1} \quad (1)$$

where  $C$  is concentration of the removal-target micropollutant (ng/L);  $C_c$  is the AC dosage (mg/L); the subscript 0 (zero) indicates the initial concentration of the removal-target micropollutant; and  $A$  and  $n$  are model parameters.

This equation was derived from ideal adsorption solution theory (IAST) simplification with the following assumptions: 1) the adsorbed amount of competing NOM is greater than the competing NOM remaining in the solution and 2) the competing NOM dominates surface loading in the AC pores over that of the micropollutant. Qi et al. (2007) discussed how these assumptions affect the estimation of  $C/C_0$  values and showed that the estimations were within reasonable errors (15%).

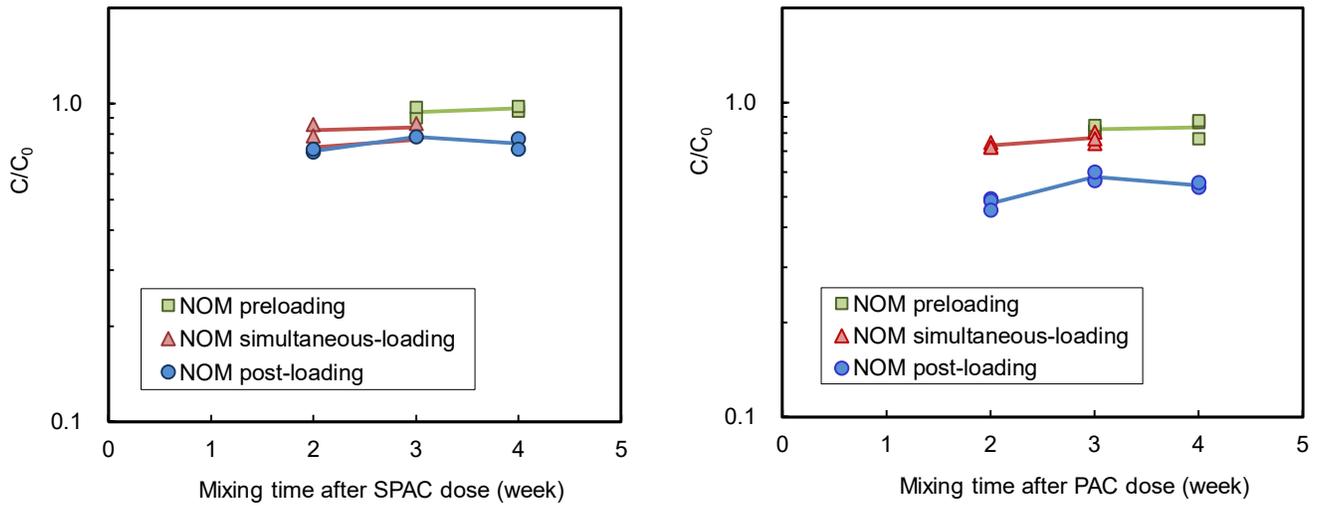
Eq. (1) was fitted to the experimental data under the minimum error criteria and the model parameters were optimized.

$$\sum \left( \frac{C}{C_{0_{\text{observation}}}} - \frac{C}{C_{0_{\text{calculation}}}} \right)^2 \quad (2)$$

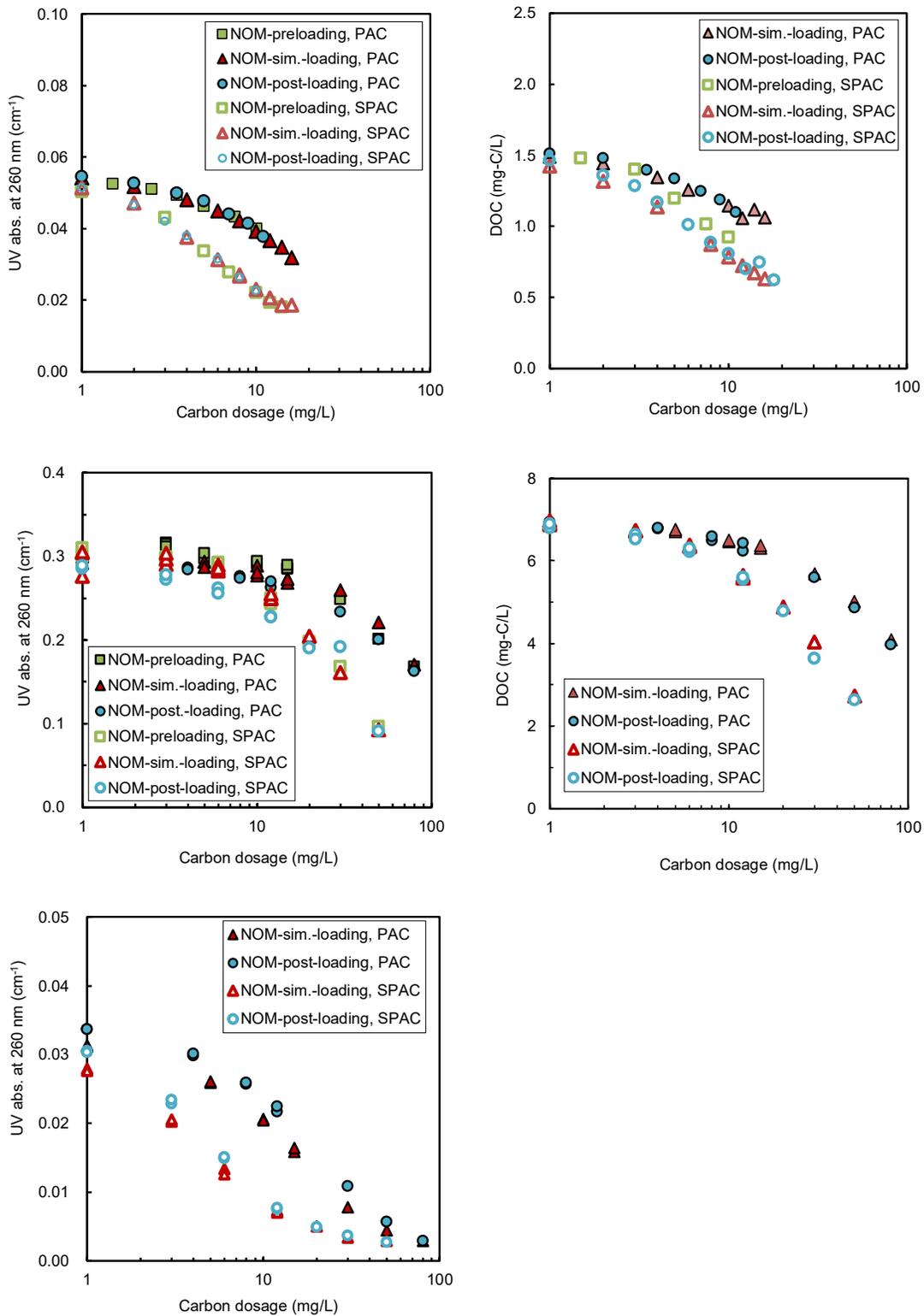
The curve of  $C/C_0$  as a function of AC dosage in single solute system (MIB in organic-free water) was fitted to the following equation, which was derived from the Freundlich isotherm and the mass balance equation in the batch adsorption system.

$$\frac{C}{C_0} + \frac{k_F C_c}{C_0^{1-\frac{1}{n_F}}} \left( \frac{C}{C_0} \right)^{\frac{1}{n_F}} - 1 = 0 \quad (3)$$

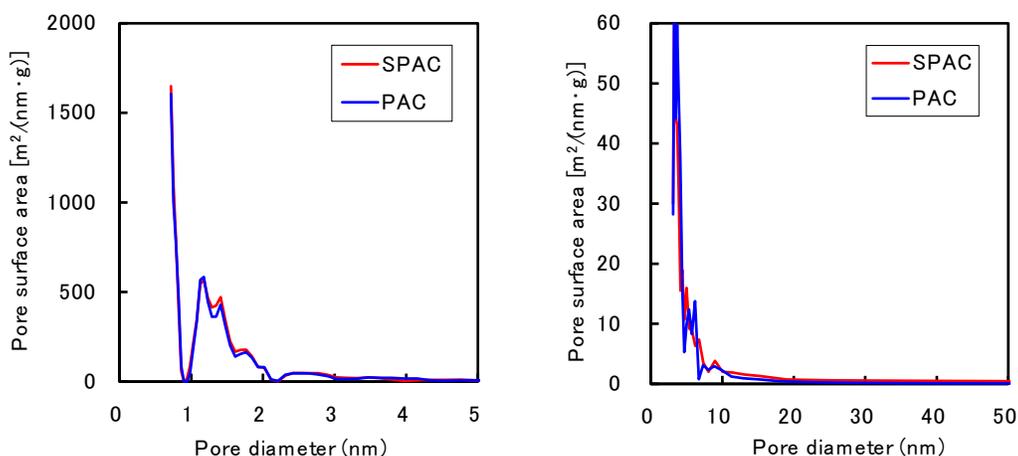
where  $k_F$  and  $n_F$  are the Freundlich constant and exponent, respectively.



**Figure 1S.** Change in the MIB concentration during mixing. The left panel shows the SPAC results and the right panel is the PAC results.  $C/C_0$  indicates the proportion of MIB remaining. SFA (6 mg-C/L) was used as the NOM. AC dosages were 1 mg/L. In the NOM preloading test, MIB was added to the NOM-AC solution, which had been shaken for one week. The MIB-NOM-AC mixture was shaken for 3 weeks. The MIB concentrations in the water phase were measured after 2 weeks (total mixing time: 3 weeks) and after 3 weeks (total mixing time: 4 weeks). In the NOM simultaneous-loading tests, the MIB concentrations in the water phase were measured after both 2 and 3 weeks. In the NOM post-loading test, NOM was added to a MIB-AC solution that had been shaken for one week at 6 mg-C/L. The NOM-MIB-AC solution was shaken for 3 weeks, and the MIB concentrations in the water phase were measured after 1 week (total mixing time: 2 weeks), 2 weeks (total mixing time: 3 weeks), and 3 weeks (total mixing time: 4 weeks).

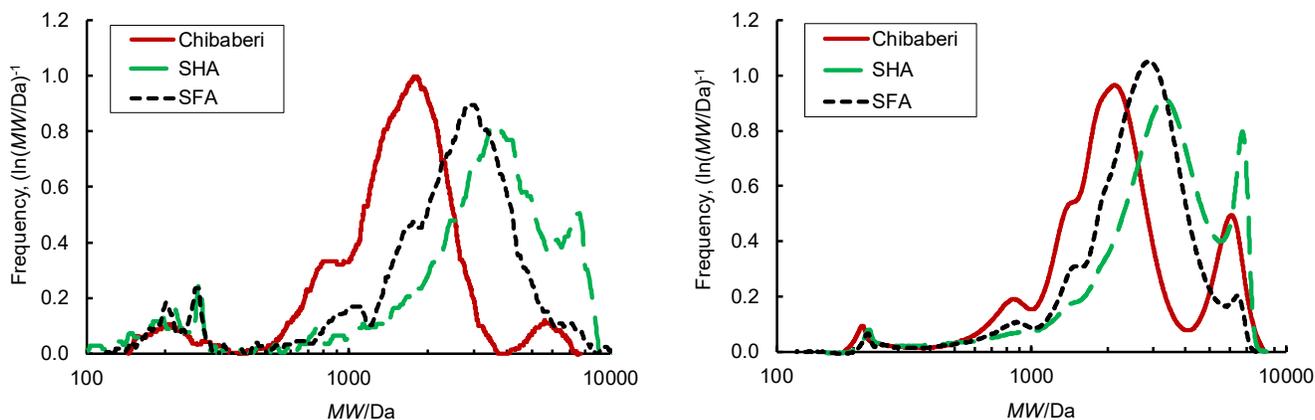


**Figure 2S.** Changes in the NOM concentration in terms of UV absorbance (left panels) and DOC (right panel) as a function of AC dosage. The upper panel shows the results of Chibaberi water (initial DOC of 1.5 mg-C/L). The middle and lower panels show the SFA water (7 and 0.9 mg/L, respectively) results.



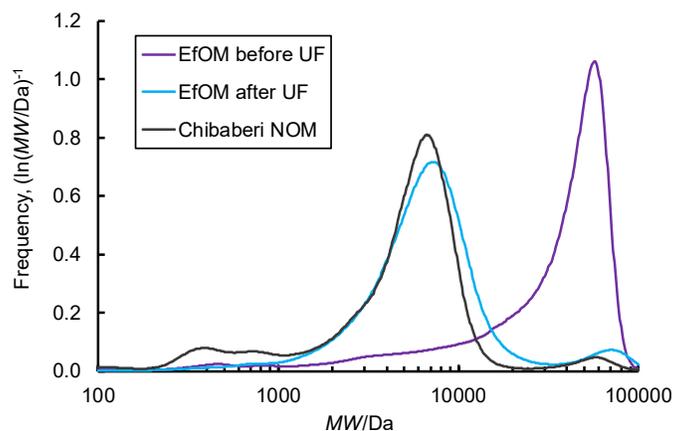
**Figure 3S.** Micropore (left panel) and mesopore (right panel) size distributions of SPAC and PAC.

The pore size distributions were determined using the nitrogen gas adsorption-desorption method (Autosorb-iQ, Quantachrome Instruments, Kanagawa, Japan). Isotherm data for nitrogen gas desorption at 77.4 K were analyzed using the Barrett-Joyner-Halenda (BJH) method for the mesopore region (pore diameter 2–20 nm) and with the density functional theory (DFT) for the micropore region (pore diameter 0.7–2 nm) (ASiQwin, ver.3.01, Quantachrome Instruments).

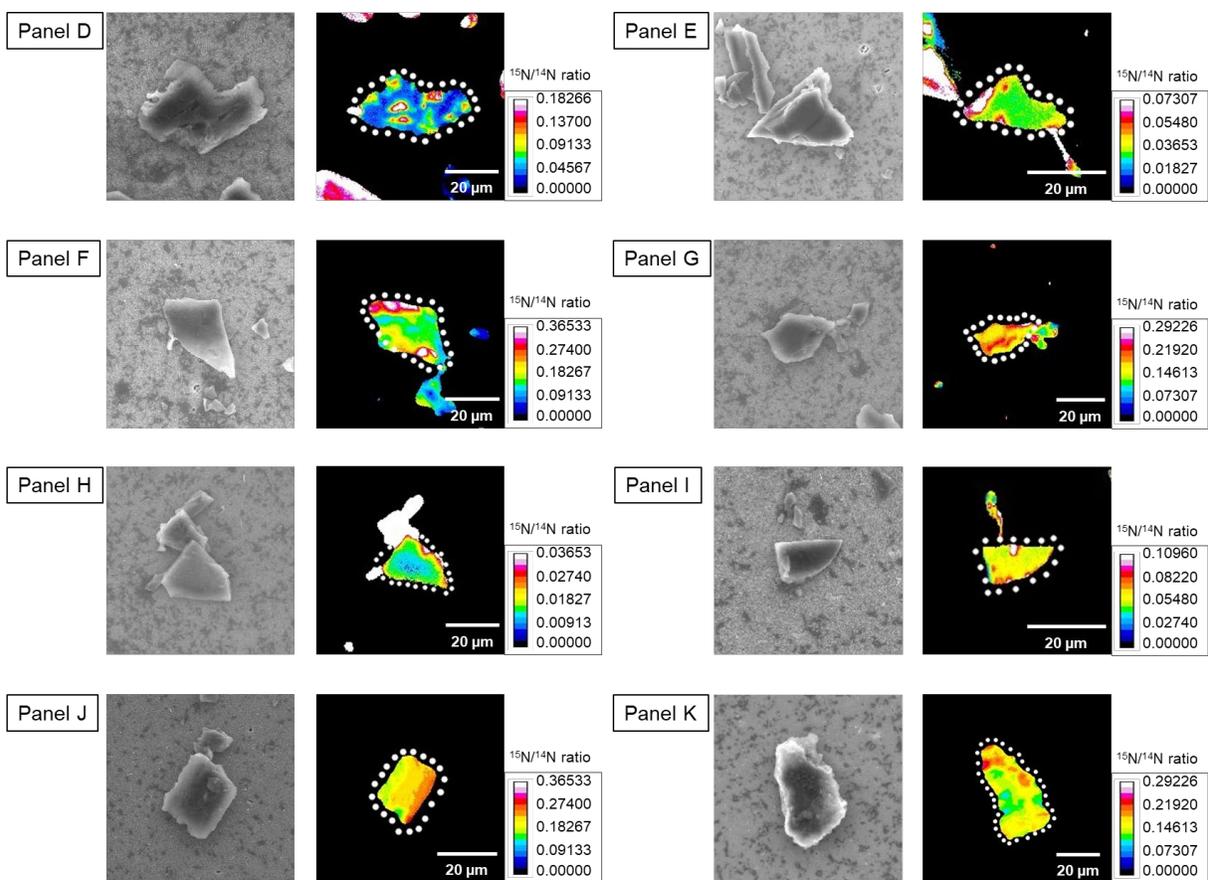


**Figure 4S.** Molecular weight distributions of Chibaberi, SHA, and SFA water NOM in terms of DOC (left panel) and UV absorbance at 260 nm (right panel).

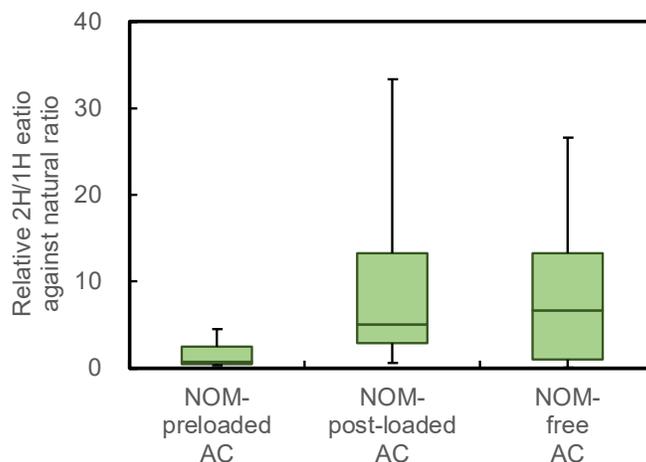
The NOM MW distributions were determined using high performance size exclusion chromatography (HP1100 Agilent Technologies, Inc., CA, USA) with a packed column of GL-P252 (Hitachi, Ltd., Japan). Eluent was 0.02 M  $\text{Na}_2\text{HPO}_4$  + 0.02 M  $\text{KH}_2\text{PO}_4$ . Polystyrene sulfonate (weight-average MWs of 1920, 5180, and 6130 Da) and salicylic acid (138 Da) were used for calibration (Zhou et al. 2000). The UV260 absorbance and DOC (Model 810 Turbo; GE Analytical Instruments, Boulder Co.) of the HPSEC column effluent were continuously measured.



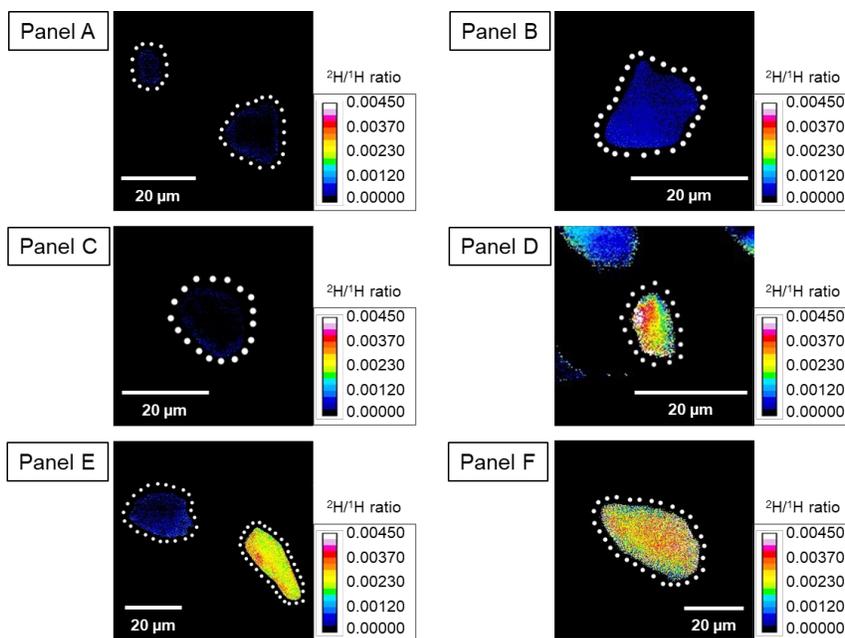
**Figure 5S.** Comparison of molecular weight distributions between EfOM and Chibaberi NOM. The NOM MW distributions were determined using high performance size exclusion chromatography (HP1100 Agilent Technologies, Inc., CA, USA) with a packed column of TSK HW50S (Tosoh Corp., Japan). To measure the macromolecular components in raw EfOM, a different packed column was used than the one shown in Figure 4. Therefore, the absolute value of molecular weight is different from that of Figure 4S. Eluent was 0.00845 M  $\text{Na}_2\text{HPO}_4$  + 0.018 M  $\text{KH}_2\text{PO}_4$ . Polystyrene sulfonates (weight-average MWs of 3610, 6520, and 29100 Da) were used for calibration. DOC (Model 810 Turbo; GE Analytical Instruments, Boulder Co.) of the HPSEC column effluent were continuously measured.



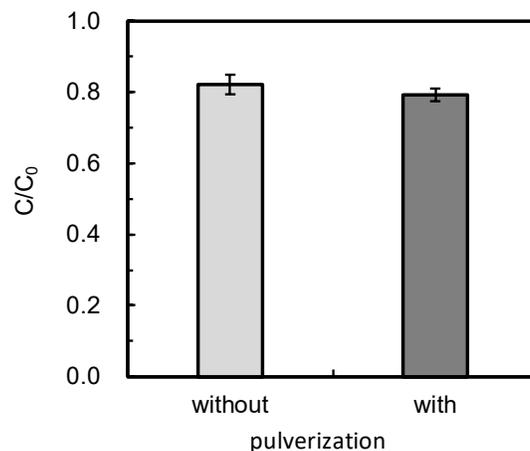
**Figure 6S.** Left panels: LV-SEM images of AC particles loaded with  $^{15}\text{N}$ -labeled EfOM before isotope microscopy measurements. Right panels: Isotopic maps ( $^{15}\text{N}/^{14}\text{N}$  ratio) of the obtained AC particles (background identified after referring to the LV-SEM image and is depicted in black/white). Panel D to K: EfOM-loaded carbons. White dotted lines indicate the particle periphery. Except Panel J,  $^{15}\text{N}/^{14}\text{N}$  ratios were high in the outer regions of the particle, which was in direct contact with water, and in regions with very large pores.



**Figure 7S.** Average  $^2\text{H}/^1\text{H}$  ratios in the AC particles loaded with  $^2\text{H}$ -labeled MIB. The boxplots present 13, 12 and 9 sample statistics of NOM-preloaded, NOM post-loaded and NOM-free ACs, respectively - the minimum, the lower quartile, the median, the upper quartile and the maximum.

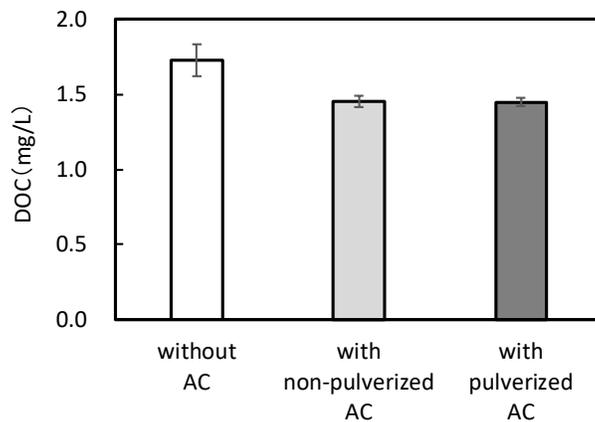


**Figure 8S.** Isotopic maps ( $^2\text{H}/^1\text{H}$  ratio) of the AC particles loaded with  $^2\text{H}$ -labeled MIB. Panels A and B: NOM-preloaded AC. Panels C and D: NOM-post-loaded AC. Panels E and F: NOM-free AC. White dotted lines indicate the particle periphery. Chibaberi water with 1.4 mg/L DOC was used as NOM water and the AC dosage was 1 mg/L.



**Figure 9S.** Comparison of the MIB removal obtained using pulverized and non-pulverized AC particles with median diameters of 6.7 and 21  $\mu\text{m}$ , respectively (Chibaberi water with 1.4 mg/L DOC, AC dosage of 1 mg/L).

Experimental procedure: after a specified amount of PAC was added to a bottle containing a NOM-free solution (5 L, the ionic composition was same as the NOM water), the PAC was recovered and pulverized using the same procedure as the preloading-pulverization test. A portion of the PAC sludge containing the pulverized or non-pulverized PAC was added to a vial containing 140 mL of NOM solution (Chibaberi water) at 1.5 mg/L DOC, and shaken for one week. Subsequently, a small amount of high concentration MIB solution (10 mL, 15  $\mu\text{g/L}$ ) was added to the vial containing the NOM-preloaded PAC so that the initial MIB concentration was approximately 1000 ng/L. The vials were then shaken for two weeks and the MIB concentration in the water phase was determined.



**Figure 10S.** DOC concentrations in the water with/without contact with pulverized/non-pulverized PAC.

Experimental procedure: Chibaberi water was used as the NOM solution. The NOM-loaded PAC sludge particles were obtained in the preloading-pulverization test and pounded in a mortar. After the NOM-loaded PAC particles were pulverized for 10 min using a mortar and pestle, ultrapure water (Milli-Q Advantage) was added. After thorough mixing for approximately 5 min, the water was passed through a membrane filter and the DOC concentration was determined. A control sample was prepared using the same procedure except that the PAC was not pulverized. Another control sample was prepared by the following procedure: a 10-mL NOM solution without the NOM-loaded PAC particles was obtained by filtering a portion of the 5-L water after the one-week adsorption in the preloading-pulverization test. The water was transferred to a mortar (10 mL) and placed under vacuum for 3 h for evaporation. Then, 10 mL of ultrapure water was added to the mortar, mixed, and the DOC concentration was determined.

## References

- Knappe, D.R.U., Matsui, Y., Snoeyink, V.L., Roche, P., Prados, M.J. and Bourbigot, M.-M. (1998) Predicting the Capacity of Powdered Activated Carbon for Trace Organic Compounds in Natural Waters. *Environmental Science & Technology* 32(11), 1694-1698.
- Qi, S., Schideman, L., Marinas, B.J., Snoeyink, V.L. and Campos, C. (2007) Simplification of the IAST for activated carbon adsorption of trace organic compounds from natural water. *Water Research* 41(2), 440-448.
- Zhou, Q., Cabaniss, S.E. and Maurice, P.A. (2000) Considerations in the use of high-pressure size exclusion chromatography (HPSEC) for determining molecular weights of aquatic humic substances. *Water Research* 34(14), 3505-3514.
- Zoschke, K., Engel, C., Börnick, H. and Worch, E. (2011) Adsorption of geosmin and 2-methylisoborneol onto powdered activated carbon at non-equilibrium conditions: Influence of NOM and process modelling. *Water Research* 45(15), 4544-4550.