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## Abstract

The adverse effect of natural organic matter (NOM) on the capacity of activated carbon to adsorb 2-methylisoborneol (MIB), a compound with an earthy/musty odor, is less severe for submicron-sized powdered activated carbon (SPAC) than for conventionally sized powdered activated carbon (PAC) (Matsui et al., 2012). In this study the NOM effect was confirmed, and the mechanism responsible for the effect was investigated by studies with another malodorous compound, geosmin. The mechanism was investigated with respect to the properties of NOM by simplified equivalent background compound (EBC) estimation and penetration index. Correlations between penetration index values and fractional areas of size-exclusion chromatogram indicated that higher NOM loading on SPAC were associated mainly with a fraction of NOM having a molecular weight (MW) > 2 kDa and a chromophoric moiety, which did not diffuse into the inner region of adsorbent particles and instead adsorbed only onto their external surfaces. Therefore SPAC, which has a larger specific surface area per unit mass of adsorbent, adsorbs such high-MW chromophoric NOM to a greater extent than does PAC. However, such NOM does not compete for adsorption sites with geosmin because geosmin adsorbs onto the interior surfaces of adsorbent particles. Contrariwise, NOM with a MW of <2 kDa and with a nonchromophoric moiety penetrates adsorbent particles and adsorbs onto interior surfaces. The estimated EBC concentration and its correlations with both size-exclusion chromatogram fractions and penetration index values indicated the characteristics of the NOM that competes with geosmin to be similar to those of MIB. Chromophoric NOM with a MW of <230 Da competes for adsorption sites with both geosmin and MIB. Beside the nonchromophoric, low-MW (<2 kDa) NOM, such chromophoric, very-low-MW NOM also penetrates adsorbent particles and adsorbs onto interior surfaces. The loading of such NOM is therefore independent of the size of the carbon particles (SPAC or PAC). The NOM effects on geosmin adsorption capacity were therefore found to be similar for SPAC and PAC, despite the fact that more NOM was loaded onto SPAC than PAC. The very-low-MW chromophoric NOM accounted for <2% of the entire NOM.

**Keywords:** super-fine; submicron; powdered activated carbon; natural organic matter; water treatment

## 1. Introduction

Geosmin is a metabolite produced by several classes of microbes, including cyanobacteria and actinomyces, and confers an unpleasant earthy/musty taste and odor to drinking water. Because geosmin has an exceptionally low detection threshold (4 to 10 ng/L) by human taste and smell [1, 2], the unpleasant taste and odor can be detected when geosmin is present even in low concentrations, and it can easily affect consumer acceptability. Because drinking water that is aesthetically unacceptable reduces consumer confidence in the water treatment and supply system, the treatment goal for water utilities is to provide drinking water that is not only safe but also acceptable in appearance, taste, and odor.

Adsorption by powdered activated carbon (PAC) is the most conventional treatment method for the removal of micro-pollutants such as geosmin, but the treatment is expensive because of the limited capacity of activated carbon to adsorb geosmin [3]. The presence of natural organic matter (NOM) in untreated water limits the adsorption capacity of activated carbon [4]. NOM is considered to be a target for removal by activated carbon adsorption, but at the same time its loading onto activated carbon reduces the number of adsorption sites available for other compounds, such as geosmin. Because the number of adsorption sites available for adsorptive removal is limited for a given amount of activated carbon, compounds compete for adsorption sites. Because this competition leaves only a few adsorption sites available for compounds present in low concentrations, reducing the concentration of geosmin below its extremely low detection threshold (<10 ng/L) requires large dosages of carbon relative to geosmin concentrations.

To improve adsorptive removal efficiency, our research group has proposed the use of submicron-sized super-fine powdered activated carbon (SPAC) [5]. The original concept behind the use of SPAC was to improve the uptake rate of the adsorbate. In fact, adsorptive uptake onto SPAC is very fast, and SPAC is far superior to PAC in removing geosmin and natural organic matter (NOM) in a given contact time [6-8]. Furthermore, the capacity of SPAC to adsorb NOM is higher than that of PAC [5, 9]. It has also been reported that the capacity of SPAC and PAC to adsorb 2-methylisoborneol (MIB, another earthy/musty taste and odor compound) decrease to the same extent as a result of NOM loading, although SPAC loads NOM more than PAC [10]. This means that the extra amount of NOM loading on SPAC compared with PAC does not result in an extra reduction of MIB adsorption capacity. The explanation is that the NOM that competes with MIB comprises a small portion of NOM (<2% in dissolved

organic carbon, DOC) [11]. It has been reported that the NOM that competes with MIB has a very low MW (<230 Da) and chromophoric properties, and that it adsorbs onto internal pores of activated carbon particles as does MIB, thereby reducing the capacity of activated carbon to adsorb MIB to a similar extent regardless of adsorbent size (SPAC or PAC). The same study has also suggested that the competing NOM has a MW similar to that of the target compound. However, these mechanisms, including the competition between a target compound and the NOM fraction with a similar molecular size, were derived from the results of adsorption experiments with one compound, MIB, in waters containing NOM. Generalization of the mechanisms therefore requires adsorption data for other compounds. Meanwhile, another previous study [9] has suggested that NOM with chromophoric properties is adsorbed onto the external surface of activated carbon particles and is hence adsorbed more on the small particles of SPAC than PAC. These results can be reconciled by hypothesizing that the NOM that adsorbs onto the external surface of activated carbon particles is a high-MW fraction of the chromophoric NOM.

The results of adsorption experiments with various NOMs experimentally verified this hypothesis in the present study. We further investigated the characteristics of the competing NOM and the competition mechanism, which had been reported for MIB, by using another micro-pollutant, geosmin.

## **2. Materials and methods**

### **2.1 Activated carbon**

Commercially available wood-based PAC (Taikou-W, Futamura Chemical Industries Co., Gifu, Japan) was prepared as a slurry in ultrapure water and pulverized to super-fine particles of submicron diameter with a wet bead mill (Metawater Co., Tokyo, Japan). In this paper, we refer to the PAC received directly from the supplier as PAC and the pulverized activated carbon prepared with the wet bead mill as SPAC. The PAC and SPAC were stored as slurries in ultrapure water at 4 °C and used after dilution. Particle size distributions of the activated carbons were determined with a laser-light scattering instrument (LA-700, Horiba, Ltd., Kyoto, Japan) following the addition of a dispersant (0.02 mL of 18% anionic surfactant solution per 200 mL SPAC/PAC sample suspension containing between 0.001 and 0.01% carbon) and a 4-min sonication with ultrasound. Median diameters are 13.5 and 0.86  $\mu\text{m}$  for PAC and SPAC,

respectively. BET surface areas were determined with an Autosorb-iQ gas adsorption analyzer (Quantachrome Instruments). BET surface areas are 1070 and 1130 g/m<sup>3</sup> for PAC and SPAC, respectively.

## **2.2 Water samples**

Water samples from Lake Kasumigaura (Ibarak, Japan) and Lake Hakucho (Hokkaido, Japan) were used as examples of natural waters containing NOM (Table 1S, supplementary information). After collection and transportation to the laboratory, these samples were filtered through 0.2- $\mu$ m pore size membrane filters (Hydrophilic PTFE type membrane filter; Toyo Roshi Kaisha, Ltd., Tokyo) and adjusted to a similar DOC concentration of ~1.5 mg-C/L by dilution with ultrapure water (Milli-Q Advantage, Millipore Co.) amended with salts to obtain a uniform ionic composition. SHA (Suwannee humic acid) waters were prepared by dissolving Suwannee River humic acid in ultrapure water (Milli-Q Advantage, Millipore Co.) containing inorganic ions added to make the ionic composition similar to that of the Kasumigaura and Hakucho NOM waters.

Stock solutions of geosmin were prepared by dissolving reagent geosmin (Wako Pure Chemical Industries, Ltd., Osaka, Japan) in ultrapure water. Solutions of geosmin in NOM water (NOMW) were prepared by diluting the stock solution of geosmin with the above-described NOMWs to produce geosmin concentrations of about 1  $\mu$ g/L (5.5 nmol/L). Single-solute solutions of geosmin were prepared by diluting the stock solution of geosmin with organic-free waters (OFWs), which we prepared with ultrapure water containing inorganic ions added to make the ionic composition similar to that of the NOMWs. All waters were filtered through a 0.2- $\mu$ m pore size membrane filter before use. Geosmin concentrations were analyzed using a Purge and Trap Concentrator Coupled to a GC-MS (GCMS-QP2010 Plus; Shimadzu Corp., Kyoto, Japan; Aqua PT 5000 J, GL Sciences Inc., Tokyo, Japan).

DOC concentrations, measured in sample filtrates with a total organic carbon analyzer (Model 810; Sievers Instruments, Inc., Boulder, CO, USA), served as parameters for bulk NOM quantification. UV absorbance at 260 nm (UV<sub>260</sub>) was measured with a spectrophotometer (Model UV-240, Shimadzu Corp., Kyoto, Japan) and served as an indicator of chromophoric NOM. The MW distributions of the NOMs were determined by using high performance size exclusion chromatography [HPSEC, HP1100 (Agilent Technologies, Inc., CA, USA); packed column GL-P252 (Hitachi, Ltd.); eluent: 0.02 M Na<sub>2</sub>HPO<sub>4</sub> + 0.02 M KH<sub>2</sub>PO<sub>4</sub>]. Polystyrene

sulfonate (weight-average MW 1920, 5180, and 6130 Da) and salicylic acid (138 Da) were used for calibration. The UV<sub>260</sub> and DOC (Model 810 Turbo; GE Analytical Instruments) of the column effluent were measured continuously.

### **2.3 Batch adsorption tests**

Immediately after addition of a specified amount of SPAC/PAC, the 150-mL vials containing geosmin and/or NOM were shaken and then transferred to a shaker that shook them for one week at a constant temperature of 20 °C. Preliminary experiments confirmed that in one week geosmin adsorption had reached equilibrium and that NOM adsorption equilibrium was almost reached. Control tests were also conducted by using multiple bottles that did not contain carbon to confirm that concentration changes during the long-term mixing were negligible. After the water samples were filtered through a 0.2-μm membrane filter (DISMIC-25HP; Toyo Roshi Kaisha, Ltd., Tokyo), adsorbate (geosmin and NOM) concentrations in the water phase were measured.

## **3. Results and discussion**

### **3.1 The effect of carbon particle size on geosmin adsorption in the presence of NOM**

We conducted geosmin adsorption experiments by using the three NOMWs and the OFW. The capacities of both SPAC and PAC to adsorb geosmin were smaller in all NOMWs than in OFW (Fig. 1S). Ratios of capacities to adsorb geosmin in NOMW versus OFW at the equilibrium liquid-phase concentration of 100 ng/L are summarized in Fig. 1A. All experiments were conducted at the same initial NOM concentration, but the effects of NOM on geosmin removal were dependent on the type of NOM. The NOM in Kasumigaura water reduced geosmin adsorption to the greatest extent: less than 15% of adsorption capacity remained. However, the amount of DOC in Kasumigaura water that was adsorbed onto carbon was not high compared to the amount of DOC adsorbed from other waters (Fig. 1B). Therefore, the large reduction in geosmin adsorption from Kasumigaura water could not be attributed to the loading of entire NOM. For each of the NOMWs, the ratios of the capacities of SPAC and PAC to adsorb geosmin in NOMW versus OFW water were similar for SPAC and PAC (Fig. 1A), although SPAC loaded NOM more than PAC (Panel B). This means that the increased amount of NOM

loading associated with carbon particle size reduction (from PAC to SPAC) did not result in a further decrease in capacity to adsorb geosmin. Adsorption competition between NOM and geosmin did not become more severe even when NOM loading increased as a result of carbon particle size reduction (from PAC to SPAC).

### 3.2 Mechanism of NOM competition

The results in Subsection 3.1 indicate that not all of the NOM competes with geosmin for adsorption sites. Rather, only a portion of NOM seems to be competing with geosmin. Graham et al. [12] estimated the concentration of competing NOM by applying the equivalent background compound (EBC) method and assuming the MW of competing NOM to be 2500 Da: they concluded that the NOM competing with geosmin and MIB was 0.45% of the DOC concentration. The values of EBC parameters, including the initial competing-NOM concentration, are generally determined by a best fit model fit to an experimental isotherm, but the resulting solution for the EBC parameter values is not necessarily unique. In the present study, the amount of competing-NOM loading was estimated by a simplified EBC method, which can avoid the uniqueness problem. When competing NOM is represented by a single hypothetical compound (EBC), the system of micro-pollutant (i.e., geosmin in the present study) in NOMW is modeled as a bi-adsorbate system. The adsorption is described by a Freundlich+IAST (ideal adsorbed solution theory) model.

$$C_G = \frac{q_G}{q_G + q_E} \left( \frac{n_G q_G + n_E q_E}{n_G K_G} \right)^{n_G} \quad (1)$$

where,  $C_G$  is the liquid-phase concentration of geosmin (nmol/L),  $q_G$  is the solid-phase concentration of geosmin (nmol/mg),  $q_E$  is the solid-phase concentration of competing NOM (nmol/mg),  $n_G$  and  $K_G$  are the single-solute Freundlich isotherm exponent and constant, respectively, for geosmin [dimensionless and (nmol/L)/(nmol/mg)<sup>1/n</sup>, respectively], and  $n_E$  is the single-solute Freundlich isotherm exponent for EBC (competing NOM) (dimensionless).

With the two assumptions that i) the solid-phase concentration of the competing NOM is much greater than the solid-phase concentration of the target compound and ii) the Freundlich exponents of the two adsorbates are not very different, an equation for solid-phase concentration of the competing NOM can be derived [11]:

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$$q_E^* \equiv q_E n_E^{\frac{n_G}{n_G-1}} = (n_G K_G)^{\frac{n_G}{n_G-1}} \left( \frac{C_G}{q_G} \right)^{\frac{1}{n_G-1}} \quad (2)$$

220

221 where,  $q_E^*$  is the pseudo solid-phase concentration of competing NOM (nmol/mg).

222

223 At high carbon doses in batch adsorption, the mass balances are approximated to;

$$C_{G,0} \cong C_C q_M \quad (3)$$

$$C_{E,0} \cong C_C q_E \quad (4)$$

224

225 where,  $C_{G,0}$  is the initial geosmin concentration (nmol/L);  $C_{E,0}$  is the initial concentration of  
226 competing NOM (nmol/L).

227 When carbon doses are high, the isotherm for a micropollutant in natural water can be described  
228 by a pseudo-single solute isotherm equation with the same Freundlich exponent as that obtained  
229 for the single-solute micropollutant system [13, 14]. Therefore,

$$q_G = K_G^* C_G^{\frac{1}{n_G}} \quad (5)$$

230

231 where,  $K_G^*$  is the Freundlich constant describing the geosmin adsorption isotherm obtained in  
232 NOMW [(nmol/L)/(nmol/mg)<sup>1/n</sup>].

233 By substituting equations (3) into (5), equation (2) becomes;

234

$$C_{E,0}^* \equiv C_{E,0} n_E^{\frac{n_G}{n_G-1}} = C_{G,0} \left( n_G \frac{K_G}{K_G^*} \right)^{\frac{n_G}{n_G-1}} \quad (6)$$

235

236 where  $C_{E,0}^*$  is the initial pseudo liquid-phase concentration of competing NOM (nmol/L).

237 The value of  $n_E$ , the EBC Freundlich exponent, was unknown. However, the values of  
238  $q_E^*$  and  $C_{E,0}^*$  defined by Eq. (1) and Eq. (2), respectively, can be used to compare  
239 competing-NOM loadings on the carbon particles and to compare initial competing-NOM  
240 concentrations if the  $n_E$  values are not very different [11, 15].

241 The fact that values of  $q_E^*$  were similar for SPAC and PAC for all tested waters (Fig.  
242 2A) clearly indicates that SPAC and PAC adsorbed competing NOM to similar extents at a  
243 given carbon dose. However, SPAC adsorbed NOM to a greater extent at a given carbon dose  
244 than PAC did, as shown in Fig. 1B. These results suggest that SPAC adsorbed non-competing

NOM (NOM that is not competing with geosmin) to a greater extent than PAC did, but that SPAC and PAC adsorbed competing NOM to similar extents. Accordingly, the magnitudes of the effects of NOM on geosmin adsorption were almost the same for SPAC and PAC. The initial concentrations of the NOM that competes with geosmin ( $C_{E,0}^*$ ) were similar for SPAC and PAC (Fig. 2B).

For MIB adsorption in NOMWs, the values of  $C_{E,0}^*$  are highly correlated with the values of the penetration index, which is defined by the slope of plots of the logarithms of the median adsorbent diameters vs. the logarithms of the solid-phase NOM concentrations, and by which the extent of penetration of NOM into carbon particles can be quantitatively evaluated [11, 17]. For geosmin in the present study, the correlation obtained was fairly good, as shown in Fig. 3. The positive slope of the correlation plot indicates that the NOM consisted of a high percentage of competing-NOM molecules with a tendency to be highly penetrative. This suggests that the competing NOM penetrated and adsorbed onto interior surfaces of the carbon particles. If so, the extent of competing-NOM loading on SPAC and PAC would be similar. This conclusion is consistent with the results in Fig. 2 and related discussion, in which pseudo solid-phase concentrations, namely, competing-NOM loadings ( $q_E^*$ ) on SPAC and PAC, were not different.

### ***3.3 Characteristics of NOMs that penetrate and do not penetrate activated carbon***

In the previous study of Ando et al. [9], adsorption isotherms on SPAC and PAC were compared for NOM from different sources. These investigators reported that for high-SUVA (specific UV absorbance) NOM the ratio of SPAC to PAC adsorption capacities was high, suggesting that such NOM did not penetrate the carbon particle and preferentially adsorbed near the outer surface of the carbon particle. Instead of this ratio, in the present study we used the reciprocal value of the penetration index, the non-penetration index, to more precisely quantify the degree of limited penetration of NOM from the outer surface to the inner region of carbon particles. We evaluated NOM characteristics by using the data of HPSEC with UV<sub>260</sub> and DOC detection. We also used NOM adsorption and HPSEC data from previous studies [9, 11]. The fact that SUVA values were significantly correlated with non-penetration index values ( $R^2 = 0.71$ ,  $P < 0.0001$ , Fig. 4A) reflects the tendency of the adsorption capacity to be higher for SPAC than for PAC when the NOM consists mostly of chromophoric NOM. The correlation was much lower but nevertheless significant ( $R^2 = 0.28$ ,  $P = 0.028$ ) between the weight-average MW of the DOC and non-penetration index (Fig. 4B), whereas the correlation was higher and very significant

between the weight-average MW of UV<sub>260</sub> and non-penetration index ( $R^2 = 0.75$ ,  $P < 0.0001$ , Fig. 4C). These results suggest that MW also plays an important role in the degree of penetration. We then hypothesized that a high-MW fraction of the NOM could penetrate the carbon particle to a lesser extent than a low-MW fraction and would hence preferentially adsorb near the outer surface of activated carbon particles. We calculated the percentages of high-MW NOM fractions in the DOC by integrating partial areas of DOC chromatograms for MWs exceeding certain cutoff levels. We used the product of the SUVA value and the partial area of the UV<sub>260</sub> chromatograms for MWs exceeding certain cutoff levels as a metric of the chromophoric high-MW fraction. Figure 5 shows the relationships between the percentages of various high-MW NOM fractions and the non-penetration index values. The correlation was highly significant ( $R^2 > 0.7$ ,  $P < 0.0001$ ) for DOC with MWs of  $>2$  kDa (Fig. 5C) and chromophoric NOM with MWs of  $>0.5$ ,  $>1$ ,  $>2$ , and  $>3$  kDa (Fig. 5F–I). Overall, correlations were higher for chromophoric NOM fractions than for DOC fractions (Fig. 6), but a high correlation ( $R^2 > 0.75$ ) was commonly seen for MWs of  $>2$  kDa for both DOC and chromophoric NOM. It is therefore possible that chromophoric high-MW (MW  $> 2$  kDa) NOM is associated with low penetration into carbon particles. To explore the contrasting characteristics of NOM with high penetrative ability, we plotted low-MW NOM fractional areas, against penetration index values (Fig. 7). A fairly high and significant correlation ( $R^2 = 0.69$ ,  $P < 0.0001$ ) was evident for NOM fractions that consisted of DOC with MWs of  $<2$  kDa (Fig. 7C), but the correlation with chromophoric NOM with MWs of  $<2$  kDa was low and not significant ( $P = 0.35$ , Fig. 7H). Therefore nonchromophoric low-MW NOM could probably diffuse into the inner region of carbon particles and adsorb there.

To further confirm these estimates, we divided NOM into four fractions and conducted multiple regression analyses with non-penetration or penetration index values as the dependent variable and the percentages of three NOM fractions out of the total of four fractions as the explanatory (independent) variables. We used a MW of 2 kDa as a cutoff level for the NOM fractionation, on the basis of the results mentioned above in this subsection. The four NOM fractions were a) chromophoric NOM with MWs of  $<2$  kDa, b) chromophoric NOM with MWs of  $>2$  kDa, c) nonchromophoric NOM with MWs of  $<2$  kDa, and d) nonchromophoric NOM with MWs of  $>2$  kDa (see Table 1). The percentages of the four fractions were calculated from the DOC and UV chromatograms on the basis of the assumption that the SUVA of chromophoric NOM was  $6.1 \text{ m}^{-1} \text{ L/mg-C}$  [11, 16]. When the non-penetration index was the dependent variable, the explanatory variables were fractions a, b, and d, fraction c being the most likely to not include non-penetrating NOM. Results are shown in Table 1. Fraction b was

associated with a highly significant ( $P = 2.2 \times 10^{-5}$ ) positive regression coefficient. Fraction d was also associated with a significant ( $P = 0.028$ ) positive regression coefficient. It is therefore possible that the NOM that does not penetrate carbon particles and instead adsorbs onto the outer surface of the particles is composed mainly of chromophoric NOM with MWs of >2 kDa. Nonchromophoric NOM with MWs of >2 kDa could also be non-penetrating NOM. When the penetration index was the dependent variable, the explanatory variables were the three fractions a, c, and d, fraction b being the most likely to not include penetrating NOM. The fact that fraction c was associated with a positive and highly significant ( $P = 2.8 \times 10^{-5}$ ) regression coefficient indicates that the penetrating NOM was composed mainly of nonchromophoric NOM with MWs of <2 kDa.

### 3.4 Characteristics of NOMs that compete and do not compete with geosmin

The previous study (Matsui et al., 2012) revealed that MIB competes with very-low-MW (MW < 230 Da) chromophoric NOM. We assumed the NOM that competes with geosmin to be similar to that of MIB because the MW of geosmin (182 Da) is similar to that of MIB (168 Da). We plotted the  $UV_{260}$  absorbance of very-low-MW NOM, which we obtained from the fraction of the area of the  $UV_{260}$  chromatogram with MW of <230 Da, against the initial concentration of the NOM that competes with geosmin (Fig. 9). The slope of the linear relationship is the ratio of  $UV_{260}$  to  $C_{E,0}^*$ . The ratio is theoretically given by

$$\frac{UV_{260}}{C_{E,0}^*} = \frac{SUVA \times \text{Carbon content} \times MW}{n_E \frac{n_M}{n_M - 1}} \quad (3)$$

If the NOM that competes with geosmin is a chromophoric NOM, as is the case with MIB, its MW can be estimated by using Eq. (3). The estimated MW was 175 Da if we assumed the SUVA value and carbon content of the chromophoric NOM in Eq. (3) to be  $6.12 \text{ cm}^{-1} \cdot \text{L/mg}$  and 52%, respectively (International Humic Substances Society, 2012; Matsui et al., 2012). The estimated MW of 175 Da corroborated the cutoff MW value of 230 Da. When the cutoff MW values were changed, the estimated MWs changed accordingly, as shown in Table 2. The cutoff MW and the estimated MW were in agreement only when the cutoff MW was 230 Da. When DOC concentrations were used instead of  $UV_{260}$  absorbances and the DOC MW fractions were plotted against  $C_{E,0}^*$ , none of the plots produced agreement between the cutoff and estimated

MWs (Table 2). The estimated MW (175 Da) of competing NOM is very close to the MW of geosmin (182 Da). Moreover the  $R^2$  value is also high. The result therefore confirms that the competing NOM has a molecular size similar to that of the targeted micro-pollutant, a conclusion suggested from the MIB experiments (Matsui et al., 2012). If the MW of the competing NOM is 175 Da, the concentration of competing NOM in the NOM waters accounts for <2% of the total DOC concentration.

Subsection 3.4 has revealed that the competing NOM consists of very-low-MW (<230 Da) chromophoric NOM, whereas Subsection 3.2 revealed the competing NOM to be a penetrating-NOM. Therefore, the very-low-MW (< 230 Da) chromophoric NOM appears to be a penetrating NOM, though penetrating NOM is composed mainly of low-MW nonchromophoric NOM (Subsection 3.3). The low-MW nonchromophoric NOM would probably not compete with geosmin, although it diffuses into the inner region and adsorb to internal adsorption sites. Such NOM, because of its molecular size, would not mostly have access to pores where geosmin adsorbs. We also suspect that the adsorption affinity of such NOMs to activated carbon is weak and hence that they would not compete effectively with a strong adsorbate such as geosmin.

#### 4. Conclusions

NOM with a high-MW (>2 kDa) and with a chromophoric moiety adsorbs onto the external surface of activated carbon particles. Therefore, when NOM consists mostly of such NOM, SPAC adsorbs NOM to a greater extent than does PAC. Contrariwise, low-MW (<2 kDa) nonchromophoric NOM can adsorb to internal adsorption sites in carbon particles. Therefore, SPAC and PAC adsorb low-MW NOM to a similar extent.

NOM that competes with geosmin for adsorption is a very-low-MW (<230 Da) chromophoric NOM, as is the NOM that competes with another micro-pollutant, MIB. The NOM fraction that competes with a target compound for adsorption has a molecular weight similar to that of the target compound. We estimate that the competing NOM accounts for <2 % of the total DOC.

- The competing NOM can also adsorb onto internal adsorption sites in carbon particles. Although there is higher NOM loading onto SPAC than PAC, the NOM effect on

micro-pollutant adsorption capacity is no more severe for SPAC than for PAC, because SPAC and PAC adsorb the competing NOM, which accounts for only a small fraction of the entire NOM, to a similar extent.

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## Appendix. Supplementary Information

Table 1S and Fig. 1S are available in the online version at #####.

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Table 1. Regression analyses for NOM that penetrates and does not penetrate activated carbon

| Designation                                        |       | Fraction a       | Fraction b           | Fraction c           | Fraction d |
|----------------------------------------------------|-------|------------------|----------------------|----------------------|------------|
| Dependent variable =<br>un-penetration index value | $R^2$ | Chromophoric NOM |                      | Nonchromophoric NOM  |            |
|                                                    |       | MW < 2kDa        | MW > 2 kDa           | MW < 2 kDa           | MW > 2 kDa |
|                                                    |       | Fraction a       | Fraction b           | Fraction c           | Fraction d |
| Coefficient                                        | 0.83  | 0.0014           | 0.0057               |                      | 0.0038     |
| P-value                                            |       | 0.60             | $2.2 \times 10^{-5}$ |                      | 0.028      |
| Dependent variable =<br>penetration index value    | $R^2$ | Chromophoric NOM |                      | Nonchromophoric NOM  |            |
|                                                    |       | MW < 2kDa        | MW > 2 kDa           | MW < 2kDa            | MW > 2 kDa |
|                                                    |       | Fraction a       | Fraction b           | Fraction c           | Fraction d |
| Coefficient                                        | 0.77  | 0.077            |                      | 0.085                | -0.01      |
| P-value                                            |       | 0.82             |                      | $2.8 \times 10^{-5}$ | 0.56       |

Table 2. MW estimated from the slope of the plot of the concentration of the low-MW fraction and competing-NOM concentration, and the coefficients of determination ( $R^2$ ) of the plots. Coefficients of determination were equated to  $1 - \text{SSreg}/\text{SS}_{\text{tot}}$ , where SSreg is the sum of squares of the residuals around the regression line with an intercept of 0, and SS<sub>tot</sub> is the sum of squares of the residuals around a horizontal line representing the mean absorbance value of the data shown [18].

|                   | Cutoff MW (Da)                   | <1000 | <500 | <300 | <250  | < <b>230</b> | <200 |
|-------------------|----------------------------------|-------|------|------|-------|--------------|------|
| UV <sub>260</sub> | Estimated MW from the slope (Da) | 2130  | 1150 | 433  | 263   | <b>175</b>   | 13   |
|                   | $R^2$                            | 0.68  | 0.92 | 0.73 | 0.57  | <b>0.82</b>  | 0.29 |
| DOC               | Estimated MW from the slope (Da) | 5280  | 3480 | 2700 | 2030  | 1600         | 1060 |
|                   | $R^2$                            | 0.88  | 0.76 | -0.2 | -0.41 | -4.6         | -4.2 |

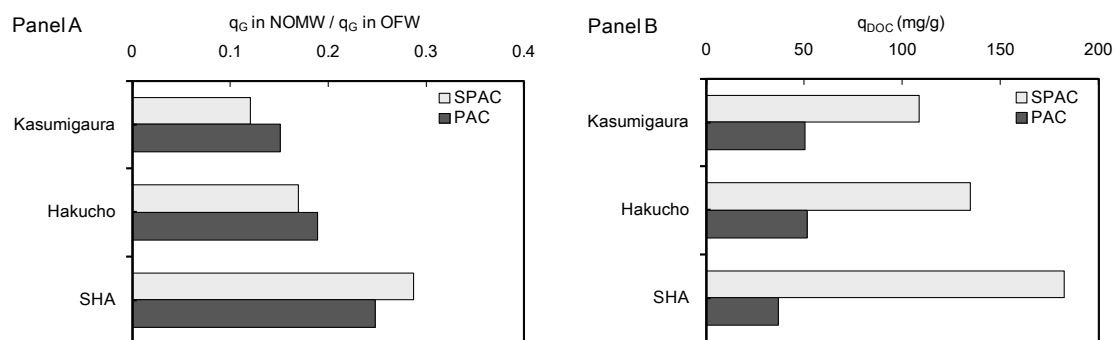


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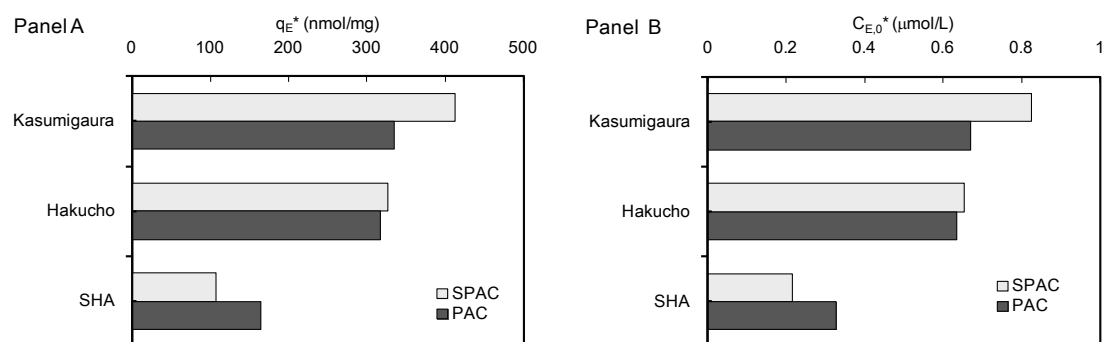


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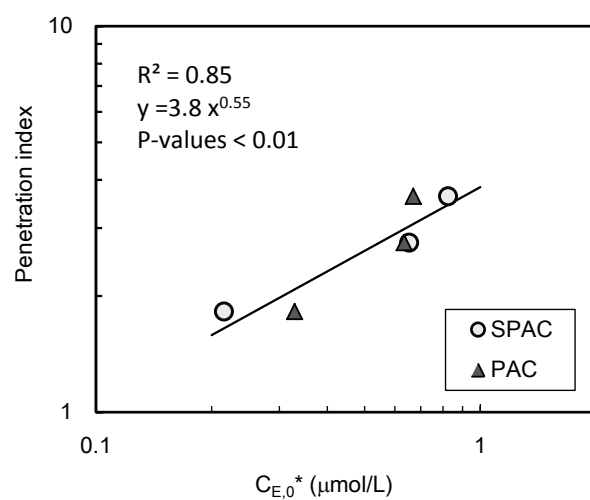


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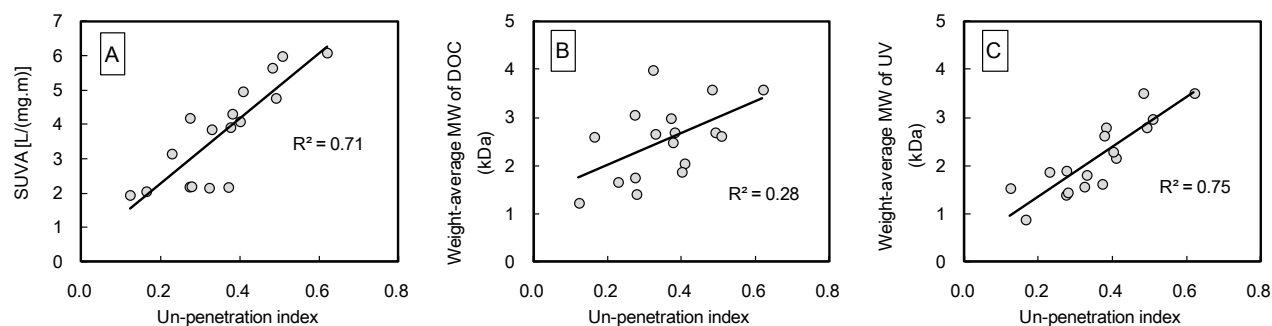


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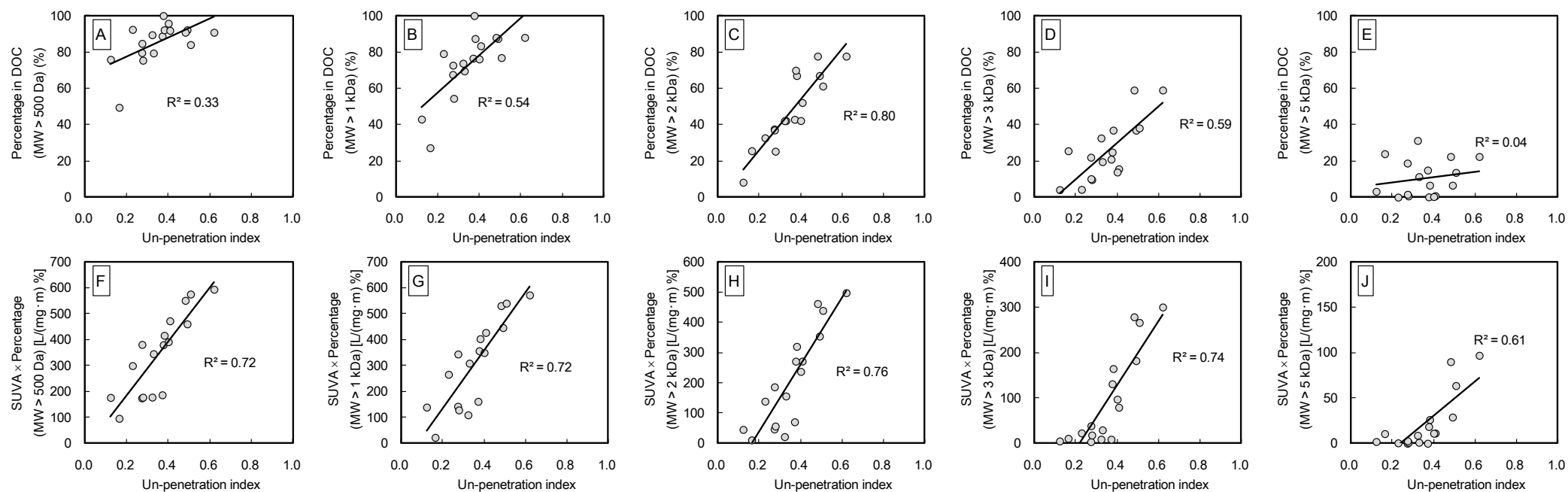


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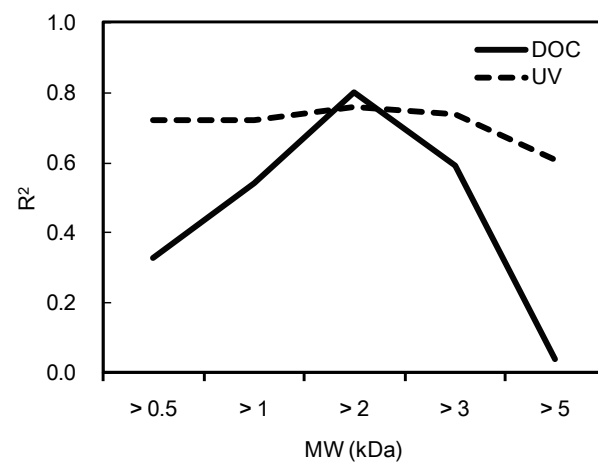


Fig. 6 — Change of  $R^2$  for un-penetration index against MW cutoff level.

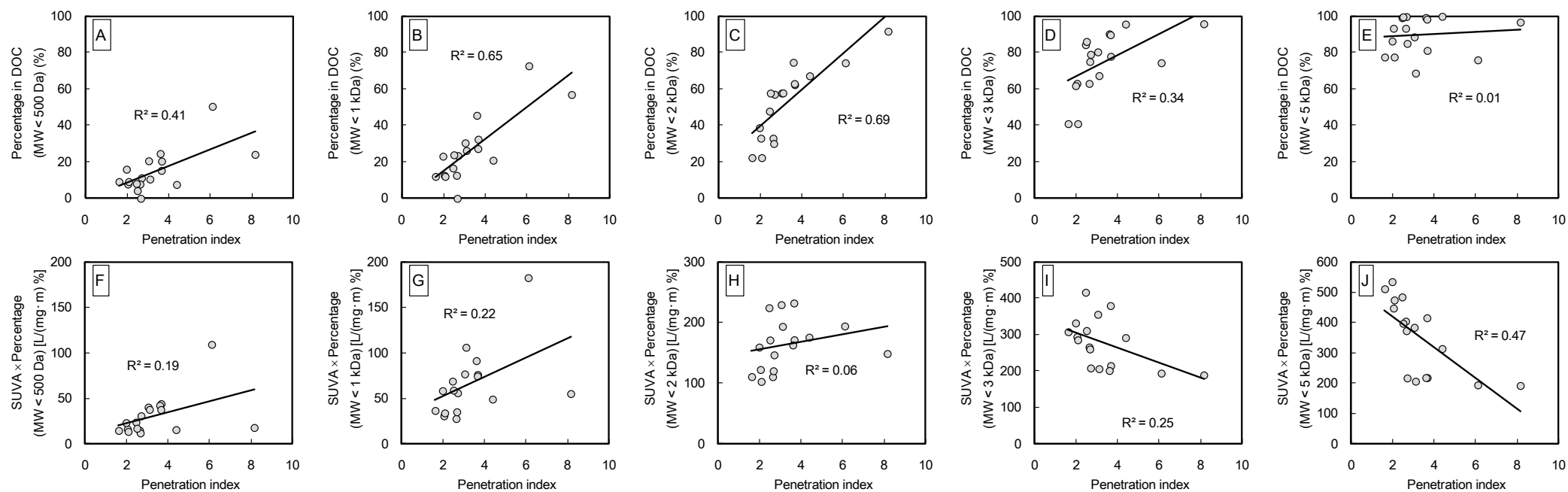


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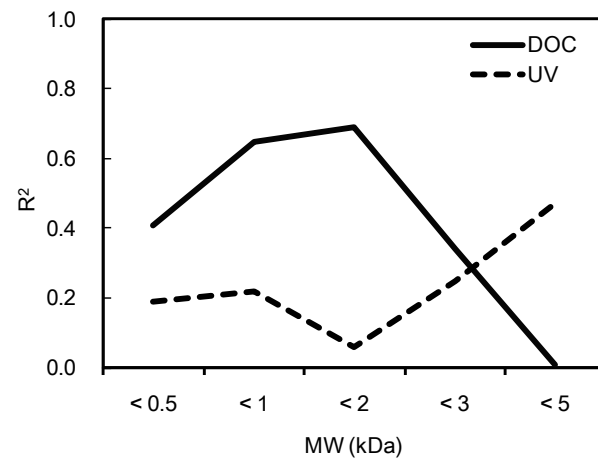


Fig. 8 — Change of  $R^2$  for penetration index against MW cutoff level.

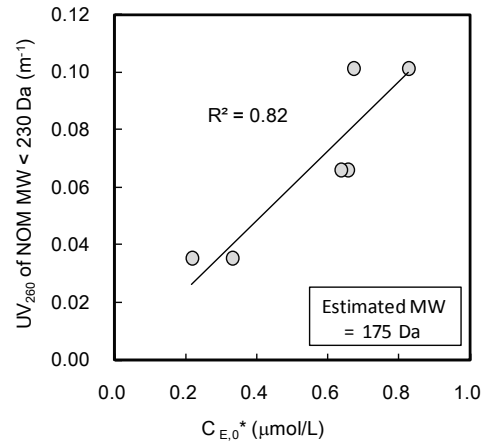


Fig. 9 — Relationship between the UV<sub>260</sub> absorbance of NOM with a MW of <230 Da and the competing-NOM concentration (C<sub>E,0</sub><sup>\*</sup>). UV<sub>260</sub> absorbance values were obtained from size-exclusion chromatograms. C<sub>E,0</sub><sup>\*</sup> values were estimated from geosmin isotherms by using Eq. (2). Coefficients of determination (R<sup>2</sup>) were determined from 1 – SSreg/SS<sub>tot</sub>, where SSreg is the sum of squares of the residuals around the regression line with an intercept of 0, and SS<sub>tot</sub> is the sum of squares of the residuals around a horizontal line representing the mean absorbance value of the data shown [18].



**Supplementary Data**  
**(Separation and Purification Technology)**

Natural organic matter that penetrates or does not penetrate activated carbon and  
competes or does not compete with geosmin

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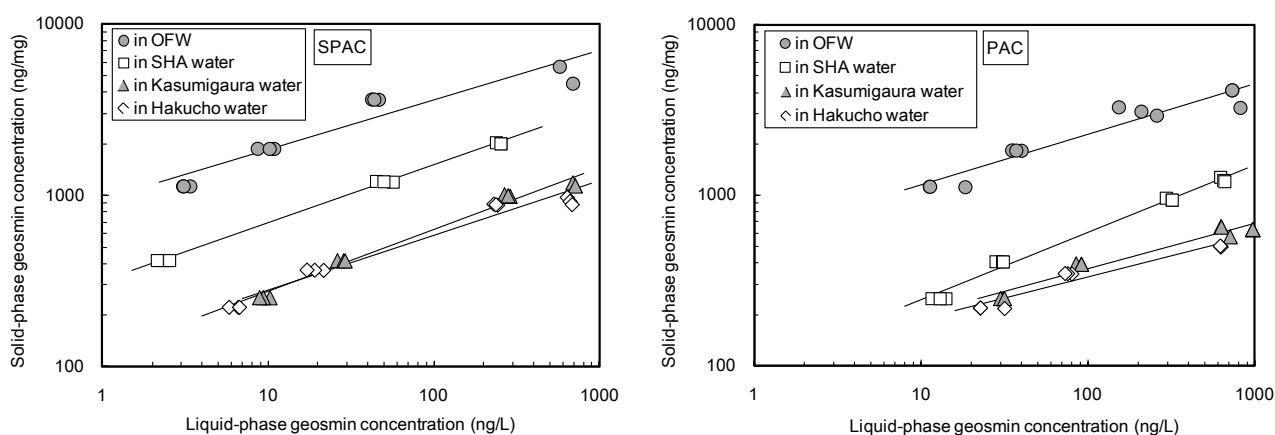
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**Table 1S — Characteristics of test solutions (DOC, UV<sub>260</sub>, and geosmin are the values measured for blank bottles in adsorption tests. Ionic concentrations represent target concentrations).**

| Sample water | DOC  | Weight-average MW of DOC | Number-average MW of DOC | UV <sub>260</sub> | Geosmin | Na <sup>+</sup> | K <sup>+</sup> | Ca <sup>2+</sup> | Mg <sup>2+</sup> | Cl <sup>-</sup> | SO <sub>4</sub> <sup>2-</sup> | HCO <sub>3</sub> <sup>-</sup> | NO <sub>3</sub> <sup>-</sup> | Conductivity | Sources                                                              | Sampling date     |
|--------------|------|--------------------------|--------------------------|-------------------|---------|-----------------|----------------|------------------|------------------|-----------------|-------------------------------|-------------------------------|------------------------------|--------------|----------------------------------------------------------------------|-------------------|
|              | mg/L | Da                       | Da                       | cm <sup>-1</sup>  | ng/L    | mM              | mM             | mM               | mM               | mM              | mM                            | mM                            | mM                           | μS/cm        |                                                                      |                   |
| Kasumigaura  | 1.38 | 3,060                    | 770                      | 0.030             | 0.88    | 0.83            | 0.08           | 0.44             | 0.2              | 0.86            | 0.12                          | 0.5                           | 0.11                         | 92           | Lake Kasumigaura, Ibarak, Japan                                      | 24 August 2010    |
| Hakucho      | 1.24 | 2,660                    | 710                      | 0.048             | 0.88    | 0.83            | 0.08           | 0.44             | 0.2              | 0.86            | 0.12                          | 0.5                           | 0.11                         | 92           | Lake Hakucho, Hokkaido, Japan                                        | 25 September 2010 |
| SHA          | 1.61 | 3,580                    | 1,280                    | 0.091             | 1.34    | 0.83            | 0.08           | 0.44             | 0.2              | 0.86            | 0.12                          | 0.5                           | 0.11                         | 92           | Suwannee River humic acid<br>(International Humic Substance Society) |                   |
| OFW          | 0.0  | —                        | —                        | 0.000             | 0.99    | 0.83            | 0.08           | 0.44             | 0.2              | 0.86            | 0.12                          | 0.5                           | 0.11                         | 92           |                                                                      |                   |



**Fig. 1S — Geosmin adsorption isotherms on SPAC and PAC (each line is a Freundlich model fit).**