GAC adsorption has been identified by the Safe Drinking Water Act amendments of 1986 as the best available technology for removing synthetic organic contaminants (SOCs) from drinking water supplies.\(^1\)

GAC is particularly suited for treating water because it effectively removes a wide range of organic compounds and can protect water supplies from such transient occurrences as occasional spills and seasonal loadings of toxic or potentially carcinogenic compounds. However, naturally occurring, macromolecular dissolved organic matter makes a difference—lower-molecular-weight substances reduce TCE adsorption.

James E. Kilduff, Tanju Karanfil, and Walter J. Weber Jr.
(DOM) can greatly reduce the efficiency and complicate the design of activated carbon adsorbers that remove SOCs. DOM components can move rapidly through fixed-bed adsorbers used in treatment applications, fouling the carbon before the pollutant passes through. Because of their prevalence and relative stability, humic substances are thought to be the DOM components that most reduce SOC adsorption.

The effects of background DOM on adsorption processes and process modeling have been extensively investigated. A number of studies have shown that the fouling or “preloading” phenomenon can greatly reduce both the equilibrium capacity of GAC for SOCs and the rate of SOC adsorption, most likely as a result of increased resistance to diffusion within particles. Some researchers, however, have observed no effect of DOM on equilibrium adsorption.

Various approaches have been developed to incorporate the effects of DOM into modeling strategies, including (1) determining equilibrium and rate parameters for the homogeneous surface diffusion model by treating DOM as a system-specific but uncharacterized background component, (2) incorporating an expression for a time-variable isotherm capacity or rate parameters into the pore-surface diffusion model, and (3) employing such physical models as the rapid small-scale column test to predict adsorber breakthrough.

Although preloading phenomena are becoming better understood, few systematic studies have sought to identify the mechanisms of DOM preloading or the factors that contribute to changes in adsorbent characteristics resulting from preloaded organic matter. In a study of preloading effects on activated carbon exposed to DOM in Huron River water, it was concluded that at early preloading times, reductions in GAC capacity for trichloroethylene (TCE) were primarily a result of direct competition with the DOM for adsorption sites. However, at extended preloading times, it was found that pore blockage may be the mechanism that reduces capacity the most. To date, no study has addressed how the molecular weight of DOM affects preloading. Molecular weight has been shown to influence the adsorption of humic and fulvic acids composing DOM. This research

![Graph showing TCE adsorption data and Langmuir-Freundlich isotherm model fit](image)
investigated the effects of the molecular weights of preloaded humic and fulvic acids on the subsequent adsorption of TCE by activated carbon.

Approach

The effect of molecular weight was investigated by preloading the carbon with different humic fractions prepared by ultrafiltration (UF). Mixtures of these fractions were used to investigate interactions among humic fractions and the effects of initial molecular-weight distribution. The effects of preloading complex mixtures of humic substances were investigated using an adsorptive fractionation technique in which different adsorbent dosages ($D_{o}$ mg GAC/L) were equilibrated with a range of initial humic concentrations. In these experiments, although the initial molecular-weight distribution was constant, the adsorbed-molecular-weight distribution varied. Molecular-weight distributions of UF fractions and whole humic solutions were measured using high-performance size-exclusion chromatography.

Methods and materials

Sorbates. Humic and fulvic acids extracted from a Laurentian soil* were received as a dry powder. Humic materials were dissolved in deionized, distilled, and filtered water,† adjusted to pH 10 (using sodium hydroxide [NaOH]), and stirred for a minimum of one hour. The solution pH was then adjusted to about 7.0 (using hydrochloric acid [HCl]), diluted to a desired stock concentration, and sequentially filtered through a 10-µm polyethylene filter, a 1-µm glass fiber filter, and a 0.45-µm polysulfone filter.‡ Stock solutions were kept in dark refrigerated storage until use. The solution pH was checked prior to adsorption experiments and adjusted to 7.0 ± 0.1 with HCl or NaOH as necessary.

Stock solutions of reagent-grade (pesticide-free) TCE§ were prepared in methanol. Working solutions were prepared by spiking background water with stock solution to achieve the desired initial concentration of solute. Stock concentrations and spike volumes were designed to maintain methanol concentrations sufficiently low (below 10–3 mole fraction) to preclude any cosolvent effect on TCE adsorption.21,22

The inorganic matrix for all solutions consisted of 10–3-molar (M) phosphate§ to buffer pH, 0.0015-M sodium azide** to control biological activity, and sodium chloride to achieve an ionic strength of 0.01M. All chemicals were reagent grade. Experiments were conducted at room temperature (23 ± 3°C) at pH 7.0 ± 0.2; pH was adjusted by either HCl or NaOH as required.

Activated carbon. Carbon obtained from the manufacturer†† was crushed and mechanically sieved to a uniform particle size (mean diameter of 165 µm) using US standard sieves. Carbon was washed, sonicated to remove fines,23 oven-dried at 105°C to constant weight, and stored in a desiccator until use. The same particle size (165 µm) was used for both preloading and TCE isotherm experiments.

Humic fractionation. Because humic substances occur naturally as mixtures of compounds with a distribution of molecular weights,20 two fractionation techniques were employed to characterize adsorbed-molecular-weight distributions. A UF system was used to fractionate the mixture into distinct molecular-weight fractions, using an approach described previously.24 The UF system‡‡ incorporated hydrophilic, neutral, cellulosic-type spiral-wound membranes having nominal molecular-weight cutoffs of 100K, 30K, 10K, and 3K. The average molecular weight of each fraction was determined by size exclusion chromatography, calibrated with polystyrene sulfonate (PSS) standards, as described in detail elsewhere.20 Each successive fraction possessed a significantly lower polydispersity than the original solution.

The second approach was based on an adsorptive fractionation phenomenon in which the preferential adsorption of low-molecular-weight fractions from

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solution fractionates humic and fulvic acid mixtures according to molecular weight. Thus, the molecular-weight distribution of adsorbed macromolecules was controlled by preloading the carbon under different combinations of initial humic substance concentration and adsorbent dose.

**Humic substance preloading.** Most of the preloading was conducted in 1-L amber-colored glass bottles mixed on a rotary tumbler for an operational equilibration period of 30 days. After the equilibration period reactors were sampled with glass syringes, and the solution was filtered through 0.45-µm polysulfone filter. Macromolecule concentrations were quantified by total organic carbon (TOC) analysis and UV spectrophotometry. Activated carbon was recovered from preloaded reactors by vacuum filtration on a 0.2-µm filter and washed. Washing or mechanically scouring this particular GAC did not in any way mitigate the effects of preloading. The carbon was dried under vacuum at room temperature for 14 days, after which the moisture content was below measurable levels. Samples were stored in a desiccator under vacuum.

In a second method, some carbon was preloaded directly in the 250-mL bottles used for the TCE isotherm experiments. First, the adsorbent was contacted with a humic acid solution for a desired period ranging from zero to 30 days. After the preloading period, TCE was spiked into the reactor and allowed to equilibrate for an additional two weeks. Preloading isotherms for dichloroethene were compared using these two techniques for preparing preloaded carbon; the isotherms were identical regardless of whether the carbon was used wet or vacuum-dried.

**Adsorption isotherms.** Isotherm experiments were conducted using the CMBR method. Carbon was equilibrated with TCE solutions in 250-mL amber-colored glass bottles sealed with screw caps and PTFE-lined silicone septa. Reactors were filled completely and sealed with no headspace. The reactors were kept well mixed by tumbling end-over-end on a rotary tumbler for two weeks. Preliminary rate studies indicated that this time was sufficient to reach equilibrium based on constant liquid-phase TCE concentrations. This equilibrium state should be considered operational because it is likely that true equilibrium was not achieved. Because macromolecule diffusion and surface rearrangement is slow and because preloading causes a decrease in TCE intra-particle diffusion rates, TCE transport may proceed for extended periods without causing measurable changes in solution phase concentrations.

After the equilibration period, carbon was settled, reactors were sampled with glass pipettes, and one, two, or three GAC samples were collected for analysis. The solution was filtered through a 0.2-µm filter, and the TCE concentration was determined by gas chromatography.

---

*Fredrik's Research Products, Amsterdam, the Netherlands
†MQ-water, Millipore Inc., Bedford, Mass.
‡Gelman Sciences, Ann Arbor, Mich.
§Mallinckrodt Specialty Chemical, Paris, Ky.
**Fluka AG, Fuchs, Switzerland
††Calgon F400, Calgon Carbon Corp., Pittsburgh, Pa.
‡‡Model CH2RPS, Amicon, Danvers, Mass.
§§Supor, Gelman Sciences, Ann Arbor, Mich.
***TOC 500, Shimadzu Corp., Columbia, Md.
†††Varian Optical, Victoria, Australia

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samples were extracted into hexane for quantification by gas chromatography using electron capture detection.*

The gas chromatograph was calibrated using external standards prepared in aqueous solution and extracted into hexane using the same procedure as for isotherm samples. Precision for TCE analysis, including the extraction step, was 3 percent or better. Potential losses resulting from volatilization, sorption onto reactor components, or bacterial activity were assessed with control reactors that did not contain adsorbent. Because losses in these experiments were consistently less than 5 percent, no corrections were made for them.

Modeling adsorption equilibria. Isotherm data were collected over a wide range of concentration and displayed some curvature on log-log coordinates, suggesting the need for a three-parameter isotherm model to accurately describe the data. Several such models were fit to representative experimental data using a nonlinear least-squares regression analysis.26 Based on a residual sum-of-squares criterion for goodness-of-fit, the three-parameter Langmuir–Freundlich (LF) model was chosen:

\[ q_e = \frac{Q^0 (bC_e)^n}{1 + (bC_e)^n} \]  

(1)

in which \( q_e \) is the amount adsorbed at equilibrium (normalized to adsorbent mass); \( C_e \) is the equilibrium solution phase concentration; and \( Q^0, b, \) and \( n \) are empirically determined parameters. The LF model is based on a symmetric, quasi-Gaussian site energy distribution, and its parameters can be shown to relate to properties of this distribution.27,28 In this context, \( Q^0 \) represents maximum adsorption capacity, \( b \) represents an average site energy, and \( n \) represents the heterogeneity of site energies.

In many adsorption studies reported in the literature, the classical Freundlich isotherm equation is used to model adsorption data throughout ranges of concentration of interest in engineering applications:

\[ q_e = K_F C_e^n \]  

(2)

in which \( K_F \) is a unit-capacity parameter, equal to the amount adsorbed at a value of \( C_e \) equal to unity (in whatever concentration units chosen), and \( n \) is a dimensionless parameter related to the site-energy distribution.27,28 The Freundlich equation represents the low concentration limit of the LF isotherm equation; that is, for \( bC_e << 1 \):

\[ q_e = Q^0 b^n C_e^n = K_F C_e^n \]  

(3)

The Freundlich unit capacity parameter, \( K_F \), incorporates parameters representing maximum capacity, average site energy, and site-energy heterogeneity. It was possible to accurately fit data in which \( C_e < 100 \) µg/L with the Freundlich model. An advantage of the Freundlich model in this regard is that its two parameters can be estimated with greater statistical significance than the three parameters of the LF.

Site-energy distributions. Approximate site-energy distributions were calculated from isotherm

---

**TABLE 1** Humic acid preloading with ultrafiltration-size fractions

<table>
<thead>
<tr>
<th>Preloading Conditions</th>
<th>Langmuir-Freundlich Isotherm Parameter Values and Statistics</th>
<th>Freundlich Isotherm Parameter Values and Statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preloading Fraction</td>
<td>Parameter</td>
<td>Parameter</td>
</tr>
<tr>
<td></td>
<td>( Q^0 ) X 10^{-2} b X 10^n</td>
<td>( K_F )</td>
</tr>
<tr>
<td>No preloading</td>
<td>1.83</td>
<td>1.26</td>
</tr>
<tr>
<td>&lt;3K</td>
<td>1.70</td>
<td>0.76</td>
</tr>
<tr>
<td>3–10K</td>
<td>1.97</td>
<td>1.40</td>
</tr>
<tr>
<td>10–30K</td>
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<td>30–100K</td>
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</tr>
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<td>&gt;100K</td>
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<td>0.57</td>
</tr>
<tr>
<td>&gt;3K</td>
<td>0.59</td>
<td>0.57</td>
</tr>
</tbody>
</table>

*MW* — molecular weight determined by size-exclusion chromatography calibrated with polystyrene sulfonate standards (g/mol as PSS)

†Isotherm parameters correspond to uptake in units of µg/mg and concentration in units of µg/L.

‡CI — confidence interval

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data to relate observed changes (resulting from preloading) in experimentally measured isotherms to changes in the energetic characteristics of sorbate-sorbent interactions. Some effects of preloading may result because preloaded solutes block access to some micropores.\textsuperscript{13} Such changes may be reflected phenomenologically in the adsorption isotherm; the effects of these changes are therefore included implicitly in the site-energy distribution.

The condensation approximation\textsuperscript{29} was used to generate approximate site-energy distribution functions. The method results in a stable, analytical expression that does not require any prior assumptions about the shape of the distribution.\textsuperscript{30} As discussed in detail elsewhere,\textsuperscript{28} the method involves taking the first derivative of isotherm data. A smoothing function was applied to the experimental data before differentiating to eliminate variability that may cause spurious or negative peaks when derivatives are taken.\textsuperscript{30} Although any function could have been chosen to smooth the data, the LF model was chosen because it described the data accurately. Specifying a functional form for the isotherm is not required to apply the method, and the use of an isotherm function to fit the data does not make any prior assumption about the shape of the site-energy distribution. However, because the LF model was used as a smoothing function, the approximate site-energy distributions are functions written in terms of model parameters:\textsuperscript{28}

\[
F(E^*) = \frac{Q_0 (bC_s)^n}{R T} \exp \left( \frac{-nE^*}{RT} \right) \times \left( 1 + (bC_s)^n \exp \left( \frac{-nE^*}{RT} \right) \right)^{-2} \tag{4}
\]

in which $E^*$ represents the net adsorption energy, $C_s$ is the sorbate solubility, $R$ is the universal gas constant, $T$ is the absolute temperature, and the remaining terms are as previously defined. The net adsorption energy, which was computed using a Polanyi-type expression, accounts for the energy of solvent displacement. These values should be viewed as approximate and used for comparison purposes.

Results and discussion

The adsorption of TCE on nonpreloaded carbon was characterized to provide a basis for assessing changes in TCE isotherms resulting from preloading. TCE uptake shows a slight curvature (on log-log coordinates) that was described well by the LF model (Figure 1). Uptake by preloaded carbons exhibited similar curvature that was also described well by the LF model.

Isotherm model parameters are tabulated in Table 1. LF parameters were estimated by fitting the entire data set, and Freundlich parameters were estimated by fitting the low concentration data (<100 µg/L TCE). For comparison, the Freundlich unit capacity factors calculated from the three LF parameters ($K_F = Q_0 b^n$) are also reported; the agreement is generally excellent.

Preloading with UF-size fractions. The effects of macromolecule molecular weight on adsorbent preloading and the subsequent adsorption of TCE were investigated by preloading a commercial carbon\textsuperscript{†} with different UF fractions. These fractions are designated according to the nominal membrane molecular-weight cutoff values: <3 K, 3–10 K, 10–30 K, 30–100 K, and >100 K.

The actual cutoffs are nominal, because the molecular-weight cutoff is based on 90 percent rejection of globular proteins with structures different from those of HAs. Furthermore, the membrane pore sizes are not uniform. Therefore, molecules having a size near the average pore size will be present in more than one fraction. The fraction designated <3 K contained components that passed the 3-K membrane. The three fractions designated 3–10 K, 10–30 K, and 30–100 K contain components that passed the larger membrane and were retained on the smaller one. Components retained on the 100-K membrane are designated >100 K.

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Corresponding molecular weights are given in Table 1. Carbon was also preloaded with a mixture, designated >3-K, prepared by removing the

\*Model 5890, Hewlett Packard, Palo Alto, Calif.
\tF400, Calgon Corp., Pittsburgh, Pa.
<3-K fraction from the whole humic mixture. The preloading experiments were designed to compare the effects of different, relatively narrow molecular-weight ranges at similar TOC loading. An adsorbent dose of 0.556 g/L was used for all experiments, and the initial humic acid concentration was adjusted to yield similar adsorbed amounts. The initial concentrations for all but the smallest fraction were higher than typically found in natural systems.

Carbon preloaded with all fractions except the <3-K fraction, at loadings ranging from 14.6 to 18.1 mg TOC/g, adsorbed as much TCE as did nonpreloaded carbon. This conclusion is suggested by visual inspection of the TCE isotherms shown in Figure 2, and it is confirmed by the statistics for both the LF and Freundlich isotherm model parameters (Table 1). However, as indicated in both Table 1 and Figure 3, which shows the effects of preloading on the Freundlich unit capacity factor, \( K_F \), the carbon preloaded with 12.1 mg TOC/g of the <3-K fraction adsorbed a statistically significant lesser amount of TCE. A slight increase in the Freundlich \( n \) value was observed for all fractions except the <100-K fraction (Table 1), although the increase was not statistically significant. The results demonstrated two things: (1) although there was significant uptake of the higher-molecular-weight material, it did not compete effectively with TCE and (2) the low-molecular-weight components of the humic solution most effectively reduced adsorption of TCE. The carbon preloaded with the >3-K mixture, prepared by removing the <3-K fraction from the whole humic acid, adsorbed as much TCE as did nonpreloaded carbon, confirming this interpretation.

One explanation for the observed trend is that larger humic molecules cannot physically occupy carbon surfaces present in small pores. Support for such an explanation follows from a comparison of carbon pore dimensions with the sizes of humic molecules.

<table>
<thead>
<tr>
<th>Preloading Time</th>
<th>( C_0 ) mg TOC/L</th>
<th>( C_o/D_o ) g/g</th>
<th>( q_e ) mg/g</th>
<th>Parameter</th>
<th>Parameter Estimate*</th>
<th>95 Percent CI</th>
<th>95 Percent CI</th>
<th>( Q^b ) Parameter</th>
<th>Parameter Estimate*</th>
<th>95 Percent CI</th>
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<td>NA§</td>
<td>NA</td>
<td>Q</td>
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</table>

* Isotherm parameters correspond to uptake in units of µg/mg and concentration in units of µg/L.
† CI—confidence interval
‡ Equilibrium was not achieved in the samples preloaded for less than 30 days; thus the concentrations and adsorbed amounts do not represent operational equilibrium values.
§ NA—not analyzed
** Data for the 30-day sample with \( q_e = 12.1 \) mg TOC/g also appear in Table 1 as the <3-K fraction.
A large fraction of the total surface area of the activated carbon used in this study is contained in pores having radiuses less than about 10 Å. Although measurements of humic substance molecular weight and size depend in part on the analytical techniques used, and although the relationship between molecular weight and molecular size depends on solution ionic strength, pH, divalent metal ion concentration, and temperature, there is evidence that humic molecule sizes are of the same order of magnitude. Humic substances separated by ultracentrifugation were found to have radiuses of gyration of 15, 20, and 32 Å, which correspond to molecular weights of 2,600, 4,400, and 12,800, respectively.31 The radiuses of gyration of humic substances, estimated by small-angle X-ray scattering to be on the order of 5 to 33 Å, correspond to a molecular-weight range of 500 to >10,000 g/mol.32 Radiuses of gyration for aquatic fulvic substances ranged from 4.5 to 8.8 Å, which correspond to molecular weights ranging from about 500 to 1,000 g/mol.33 The <3-K fraction had a weight-averaged molecular weight of 1,400 g/mol as PSS, determined by size exclusion chromatography.20 This molecular weight compares to that of 2,700 for the 3–10-K fraction and about 4,000 to 22,000 for the larger fractions.

Thus, it is likely that larger humic fractions were prevented from occupying a large percentage of the carbon surface area and could not compete directly with TCE for adsorption sites. Based on evidence that preloaded humic molecules can physically block pores,13 it would be reasonable to expect that preloaded humic material might reduce TCE uptake by preventing access to carbon surfaces. However, this preloading mechanism did not appear to be operative for the high-molecular-weight humic materials.

The preceding analysis suggests that the effect of preloaded natural organic matter on TCE adsorption can be assessed by measurements of molecular weight. Previous studies13 also found marked preloading effects of Huron River water. The average molecular weight of organic matter in this water was about 1,000 g/mol as PSS, supporting the relationship between molecular weight and the effect of preloading in this case. Based on the demonstrated reactivity of the smaller-molecular-weight molecules, additional preloading experiments were performed with the <3 K fraction to further evaluate the effects of preloaded organic matter on TCE adsorption.

Preloading with the <3-K UF-size fraction. Four preloading experiments, including the experiment discussed in the previous section, used the <3-K fraction to investigate the effects of TOC loading and equilibration time. Experimental conditions are shown in Table 2. In two experiments, the <3-K fraction was preloaded for a full 30-day equilibration time. Carbon preloaded in these experiments reached an operational equilibrium condition (Cfinal/H11061 Ce).

Components of DOM can move rapidly through fixed-bed adsorbers used to treat drinking water, fouling the carbon before the pollutant passes through.
was exposed to TCE and humic acid simultaneously, and it equilibrated for two weeks. In a final experiment the carbon was preloaded for two weeks. TCE isotherms measured on carbon preloaded with the <3-K fraction are shown in Figure 4. The simultaneous adsorption isotherm is not shown because it is similar to the isotherm measured for the carbon preloaded for 14 days. A smaller reduction in TCE uptake for the simultaneous adsorption experiment was expected, although it has been documented that the presence of humic acid can reduce the extent of TCE adsorption when the two sorbates are adsorbed simultaneously. The interpretation of this result is made more difficult because the TOC loading in the simultaneous adsorption experiment could not be determined accurately because TCE and a small amount of methanol were present in the system. It is possible that the <3-K fraction contains relatively low-molecular-weight components that do not have to be preloaded to compete effectively with TCE.

TCE capacity was greatly reduced throughout the entire range of concentration as a result of humic acid preloading (Figure 4). However, because the relative reduction was greater at lower concentrations, the isotherm slope as plotted on log-log coordinates increased. LF and Freundlich isotherm model fits to the data are tabulated in Table 2. The LF parameter \( Q^0 \) decreased with increasing TOC loading, and the \( Q^0 \) of the 30-day preloaded sample decreased by a statistically significant amount. The heterogeneity parameter \( n \) for all Freundlich and LF isotherms increased, and the increase was statistically significant for all but the lowest level of preloading. The average site-energy parameter \( b \) appeared to increase somewhat at high levels of preloading, but the increase was not statistically significant, and no strong trend is evident. The Freundlich unit-capacity parameters computed from LF parameters and those estimated by fitting the Freundlich isotherm model to the low concentration data are in excellent agreement. The Freundlich \( K_F \) value decreased by a statistically significant amount at all preloading conditions. A plot of Freundlich isotherm parameters \( K_F \) and \( n \) as a function of humic acid preloading is shown in Figure 5. These results are consistent with the experimental results reported for TCE adsorption on carbon preloaded with Huron River water and synthetic polymaleic acid, and they provide insight into the mechanisms responsible for the observed changes in TCE uptake.

Increases in the isotherm heterogeneity parameter \( n \) reflected a decrease in the number of high-energy sites. This decrease in high-energy sites tended to make the surface less heterogeneous and to reduce uptake in the low-concentration region of the isotherm. The decrease in uptake was reflected in a decrease in the Freundlich \( K_F \) value. Site-energy distributions were computed to illustrate how changes in isotherm parameters reflect changes in the energetic character of the adsorbent surface (Figure 6). At lower preloading concentrations, almost all of the loss in capacity was the result of a reduction in the number of high-energy sites. As preloading concentrations increased, sites were lost throughout the entire range of site energies; however, the greatest relative reduction was still among high-energy sites. Although the marked loss of low-energy sites at high preloading concentrations suggests a pore blockage, the data are not conclusive in this regard.

The data reported in Table 2 are consistent with the findings of Carter et al, who developed empirical relationships to describe how adsorption isotherm (and rate) parameters changed with preloading time. Although this approach is useful for dynamic modeling, the effects of preloading should relate funda-
mentally to the mass (or molar) loading of the preloaded compound. The effects of mass (TOC) loading and preloading time are reconciled by recognizing that the rate of macromolecule adsorption can be slow. It may take months for macromolecules to attain true equilibrium, particularly for the particle sizes used in full-scale adsorbers. The data for the 14-day and 30-day experiments, each of which started with the same initial TOC concentration adsorbent dosage, illustrate that TOC loading can increase significantly during relatively long periods of time, causing further reductions in subsequent TCE adsorption.

Preloading of mixtures of UF fractions. Carbon was preloaded with mixtures of the <3-K and 10–30-K fractions to determine whether larger-molecular-weight components could interact with smaller, more reactive components and to investigate the effect of initial molecular-weight distribution. Experimental conditions are tabulated in Table 3. In this experiment, the mass of the <3-K fraction in solution (mg TOC) per unit mass of adsorbent was held approximately constant, and the initial TOC concentration of the preloading solution was increased by increasing the TOC contributed by the 10–30-K fraction. Therefore, increases in the amount adsorbed could only be due to the 10–30-K fraction, and such increases would correspond to a shift in the adsorbed-molecular-weight distribution to higher molecular weights.

On the basis of results previously presented, it was hypothesized that reductions in TCE uptake would be caused by preloading of the <3-K fraction. It was further hypothesized that the uptake of this fraction would remain constant because (1) the initial concentration of the <3-K fraction was held constant; (2) the <3-K molecules are adsorbed preferentially, as suggested by size-exclusion chromatography analysis of humic substance adsorption; and (3) larger and smaller fractions did not interact. Under these hypotheses, the effects of preloading should be independent of the initial molecular-weight distribution (i.e., the fraction of the initial TOC contributed by the 10–30-K fraction) as long as the mass of the <3-K fraction per unit mass of adsorbent remains constant. This hypothesis is supported by the TCE isotherm data (Table 3 and Figure 7). Statistically significant reductions in the Freundlich $K_F$ value were observed as long as the <3-K fraction was pre-

<table>
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*Preloading data for the <3-K and 10–30-K fractions alone are given in Table 1.
†Isotherm parameters correspond to uptake in units of µg/mg and concentration in units of µg/L.
‡CI—confidence interval

TABLE 4 Humic acid preloading—effect of sequential loading*

Humic substances are thought to be the DOM components that most reduce the adsorption of synthetic organic contaminants.
the second experiment, the order of equilibration was reversed. Experimental conditions for the sequential loading experiment and LF and Freundlich isotherm model fits to the data are given in Table 4.

When the <3-K fraction was loaded before the 10–30-K fraction, the $K_F$ value for TCE was greatly reduced. In contrast, no major change occurred when the order was reversed, even at a fairly high total loading of 23.4 mg TOC/g. Adsorption of the larger fraction effectively prevented subsequent adsorption of the <3-K fraction from competing with TCE. This implies that the <3-K fraction was unable to occupy the smaller pores that it could access in the absence of the 10–30-K fraction.

Neither fraction appeared to significantly displace the other. Consistent with the findings of Summers and Roberts, the lower-molecular-weight <3-K fraction may have a lower intrinsic affinity for the surface than the 10–30-K fraction and therefore could not displace this component. Although the 10–30-K fraction may have a higher intrinsic affinity for the surface, it probably could not reach surfaces on which the <3-K fraction was adsorbed, thereby making displacement impossible. The lack of displacement may also relate to steric hindrances of both the potential displacer and the adsorbed species.

These findings have implications for the operation of fixed-bed adsorbers. If natural organic matter is fractionated by molecular weight along the GAC bed, then smaller, more adsorbable components will be removed earlier in the bed. Larger components will penetrate deeper into the bed, loading the carbon ahead of the smaller components. This process will effectively limit the effects of preloading by smaller-molecular-weight components. For fractionation to occur along a GAC bed, organic matter with a polydisperse molecular-weight distribution would be required. However, some natural water (e.g., Huron River water) has relatively narrow molecular-weight distributions and may not exhibit fractionation phenomena.

Preloading by adsorptive fractionation. Experiments evaluated TCE uptake after carbon was preloaded with the whole humic mixture. Preloading experiments using UF fractions showed that smaller-molecular-weight components are responsible for reductions in TCE adsorption. On the basis of these results, Kilduff et al hypothesized that when a range of molecular weights are present in solution, greater reductions in TCE adsorption capacity would be observed when the adsorbed-molecular-weight distribution was shifted to smaller molecular weights. This hypothesis was tested by equilibrating carbon samples to achieve a range of $C_D/D_0$ ratios (from about 5 to 170 mg DOC/g), creating different adsorbed-molecular-weight distributions as a result of adsorptive fractionation. Adsorptive fractionation occurs because low-molecular-weight components are adsorbed preferentially from a mixture, as demonstrated previously. Large values of the $C_D/D_0$ ratio shift the adsorbed-molecular-weight distribution to smaller weights; small values of this ratio shift the adsorbed distribution toward that of the original solution.

A significant advantage of preloading by adsorptive fractionation is that preloaded molecules are adsorbed from the whole humic solution; therefore, any competition among components will be revealed. Preloading by adsorptive fractionation has one significant limitation, however. An increase in the $C_D/D_0$ ratio is accompanied by an increase in the mass of the small-molecular-weight fraction relative to the mass of adsorbent. Therefore, shifts in the adsorbed-molecular-weight distribution are accompanied by changes in the TOC loading.

The design of preloading conditions was based on humic and fulvic acid adsorption isotherms, and a summary of preloading conditions for both the humic and fulvic acid adsorption isotherms, 20 experiments evaluated TCE uptake after carbon was preloaded with the whole humic mixture. Preloading experiments using UF fractions showed that smaller-molecular-weight components are adsorbed preferentially from a mixture, as demonstrated previously. Large values of the $C_D/D_0$ ratio shift the adsorbed-molecular-weight distribution to smaller weights; small values of this ratio shift the adsorbed distribution toward that of the original solution.
The shift in the adsorbed-molecular-weight distribution to larger molecular weights at low $C/D_0$ ratios means that a large fraction of the initial solution was adsorbed, including nearly all of the low-molecular-weight fraction. The low-molecular-weight fraction was therefore present on the adsorbent surface at nearly all values of $C/D_0$ (although at different loadings), yet significant decreases in TCE capacity were noted only at high values of this parameter. Two explanations for this behavior are possible. It is possible that at low $C/D_0$ ratios, the surface loading or adsorption density was too low to affect TCE uptake. A second explanation is that the presence of larger-molecular-weight components reduced the ability of low-molecular-weight fractions to compete with TCE. The results of preloading experiments using mixtures of UF fractions suggests that the first explanation is more likely.

This conclusion is supported by the dependence of $K_F/K_{Fo}$ on the amount of humic material adsorbed (Figure 9). The greatest reductions in TCE capacity occurred at the highest humic loadings, which correspond to high $C/D_0$ ratios and a shift in the molecular-weight distribution of adsorbed humic substances to smaller molecular weights. At the higher humic loadings, most of the preloaded material was expected to be composed of low-molecular-weight components. This composition was expected because the percentage of DOC removed by adsorption was similar to the percentage of <3-K components composing the whole humic acid solution (smaller components were adsorbed preferentially). Thus, the effects of preloading by whole humic acid and by the <3-K fraction were expected to be similar, and the data are consistent with this expectation (Figure 9).

In contrast, at lower humic acid loadings the percentage of DOC removed was greater than the percentage of low-molecular-weight components. At a loading of about 12 mg/g, for example, less than half the DOC removed from solution was composed of low-molecular-weight components. Thus, it was expected that the effect of preloading by the <3-K
fraction would be greater than that obtained by preloading whole humic acid. However, the observed effects were similar. The reasons for this behavior are not apparent, but several possibilities can be put forth. It is also possible that there is some synergistic effect that makes the mixture more reactive than the sum of its parts. One such effect might be attributed to a higher packing density of humic components adsorbed from a mixture as compared with isolated fractions. On the other hand, because the effects at low humic loadings are not large, it may not be possible to estimate isotherm parameters with sufficient precision to clearly distinguish preloading effects of whole humic solutions from those of isolated low-molecular-weight fractions.

Conclusions

TCE adsorption on carbon preloaded with humic acid molecular-weight fractions demonstrated the importance of molecular weight on the effect of preloading. Uptake by carbon preloaded with the <3 K fraction (molecular weight = 1,380 g/mol as PSS) was significantly reduced compared with adsorption by as-received carbon; however, TCE adsorption by carbon preloaded with larger-molecular-weight fractions (molecular weight > 3,000 g/mol as PSS) was statistically similar. Trends in Freundlich isotherm parameters were consistent with experimental results reported for TCE adsorption on carbon preloaded with Huron River water and synthetic polymaleic acid. Changes in computed site-energy distributions suggest that at preloading concentrations, almost all of the loss in capacity occurred because of a reduction in the number of high-energy sites and is reflected in an increase in the isotherm heterogeneity parameter $n$. The decrease in high-energy sites tended to reduce uptake in the low-concentration region of the isotherm, as reflected in a decrease in the Freundlich $K_F$ value. As preloading concentrations increased, sites were lost throughout the entire range of site energies.

In sequential adsorption experiments, when the low-molecular-weight components were loaded first, they exerted a marked preloading effect; furthermore, they were not displaced by larger-molecular-weight components present in the 10–30-K fraction. However, when the 10–30-K fraction was loaded first, it was not displaced by the <3-K fraction, and no preloading effect was observed. Preloading experiments with synthetic mixtures of UF fractions demonstrated that the effects of preloading were independent of the initial molecular-weight distribution as long as the amount of the <3-K fraction per mass of adsorbent was held constant. These results show that the smaller-molecular-weight fraction is preferentially adsorbed from mixtures and that the effects of preloading were caused primarily by this fraction. Adsorptive fractionation experiments using whole humic and fulvic acid solutions confirmed the effects of preloading from synthetic mixtures. The greatest reductions in TCE capacity occurred at the highest humic loadings, which correspond to high $C_e/D_0$ ratios and a shift in the molecular-weight distribution of preloaded humic substances to smaller weights.

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