

# Atrazine removal by preloaded GAC

*Utilities can use predictions of remaining GAC life to develop a GAC regeneration or replacement schedule.*

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**P**esticide pollution episodes, which typically occur in surface water sources during the spring runoff season, have become a major concern of drinking water suppliers. Granular activated carbon (GAC) adsorbers have been used either as the primary means of removing pesticides or as a secondary

barrier to remove pesticides that had escaped a previous treatment such as powdered activated carbon (PAC) adsorption or advanced oxidation. Because water treatment plants typically operate GAC adsorbers continuously, background organic matter (BOM) adsorbs on GAC even when the pollutant is absent in the source water. As a result, the GAC becomes loaded with or fouled by humic substances that adsorb irreversibly.<sup>1</sup> Both the GAC adsorption capacity for a micropollu-

The effect of granular activated carbon (GAC) service time on the remaining life of GAC adsorbers that are exposed to periodic pollutant episodes was evaluated. Equilibrium and kinetic parameters describing the adsorption of atrazine were determined for GAC that had been preloaded with background organic matter (BOM) for as long as 25 months. Furthermore, atrazine removal was measured in pilot tests employing GAC that had been preloaded for five and 20 months. Isotherm data showed that (1) preloaded BOM sharply reduced the remaining adsorption capacity of GAC for atrazine, (2) competitive adsorption was not important on the tested preloaded GAC samples, and (3) use of pulverized preloaded GAC led to an overestimate of remaining adsorption capacity. Preloading had the greatest effect on GAC capacity; adsorption kinetics were not affected as severely. The homogeneous surface diffusion model was used to predict atrazine removal in pilot tests and to predict remaining GAC life. For the given adsorbent and background water, remaining life predictions for atrazine removal are presented for scenarios that may be typical for utilities in the midwestern United States and in western Europe.

**For executive summary,  
see page 183.**

**TABLE 1** Pilot-scale test parameters

Attribute	Depth of Sample— <i>m</i> (ft)	Preloaded for Five Months	Preloaded for Twenty Months
Mean particle diameter			
Column 1	Surface	0.72 mm	0.79 mm
Column 2	1.2 (3.9)	1.11 mm	0.94 mm
Column 3	2.2 (7.2)	1.24 mm	1.18 mm
GAC mass			
Column 1	Surface	24.5 g (0.9 oz)	21.8 g (0.8 oz)
Column 2	1.2 (3.9)	29.7 g (1.0 oz)	31.8 g (1.1 oz)
Column 3	2.2 (7.2)	38.0 g (1.3 oz)	42.3 g (1.18 oz)
Bed depth			
Column 1	Surface	11 mm (4.3 in.)	95 mm (3.7 in.)
Column 2	1.2 (3.9)	135 mm (5.3 in.)	145 mm (5.6 in.)
Column 3	2.2 (7.2)	173 mm (6.7 in.)	192 mm (7.5 in.)
Bed porosity			
Column 1	Surface	0.59	0.58
Column 2	1.2 (3.9)	0.60	0.60
Column 3	2.2 (7.2)	0.60	0.60
Average approach velocity— <i>m/h</i> (gpm/sq ft)	NA*	2.92 (1.20)	3.08 (1.26)
Average influent atrazine concentration— $\mu\text{g/L}$	NA	3.98	4.31

\*NA—Not applicable

tant and the rate of contaminant adsorption are reduced by preloaded BOM.

### Equilibrium parameters

BOM preloading generally alters GAC's remaining capacity to adsorb micropollutants in two ways: capacity decreases rapidly during the initial weeks of preloading and more gradually thereafter,<sup>2–12</sup> and differences in capacity as a function of bed depth diminish as preloading time increases.<sup>5,12</sup> Preloaded BOM can lower GAC's subsequent capacity to adsorb micropollutants because it reduces high-energy adsorption sites and blocks pores.<sup>9</sup> At low humic substance loadings, the loss of high-energy adsorption sites explained most of the reduction in the remaining micropollutant capacity.<sup>13</sup> At higher humic substance loadings, isotherm data suggested that pores may have been blocked.<sup>9,13</sup> Furthermore, pore blockage was primarily responsible for reducing the atrazine capacity of preloaded activated carbon fibers, most of whose pores were  $\leq 0.8$  nm in diameter.<sup>14</sup> Because adsorption of humic substances on GAC is governed primarily by size exclusion effects and because the largest percentage of adsorption sites is contained in micropores ( $< 2$  nm in diameter), GAC preferentially adsorbs humic substances of lower molecular weight.<sup>15–18</sup> Consequently, preloading experiments with several humic acid-size fractions showed that the lowest molecular weight fraction most greatly reduced GAC's remaining capacity to adsorb micropollutants.<sup>13</sup>

**Competitive coadsorption.** Although GAC fouling by irreversibly adsorbed BOM components is commonly observed in fixed-bed adsorbers, it is unclear whether competitive, reversible coadsorption of BOM components and the target pollutant plays an impor-

tant role in the mass transfer zone of the micropollutant. Research with PAC has shown that competitive, reversible coadsorption of a target compound and BOM components results in a lower PAC adsorption capacity for the target compound as the initial concentration of the target compound decreases.<sup>19–23</sup> However, contradictory evidence exists for preloaded GAC. For example, the remaining trichloroethene (TCE) and 1,1,1-trichloroethane capacity of GAC that was preloaded with pretreated Rhine River water did not depend on the initial target compound concentration,<sup>7</sup> even though the metazachlor capacity of a GAC that was preloaded with bank-filtered Rhine River water did depend on the initial concen-

tration of metazachlor. The TCE and tetrachloroethene capacity of GAC that was preloaded for six months with clarified Mississippi River water was independent of the initial concentration of the target compound.<sup>20</sup> On the other hand, the atrazine capacity of a GAC that was preloaded for seven and a half months with Hudson River water did depend on the initial atrazine concentration.<sup>24</sup>

Lack of competitive adsorption on preloaded GAC suggests that the remaining adsorption sites are accessible to the target compound but not to competing BOM components. Thus, once the adsorption of BOM by diffusion-controlled processes ceases, competitive adsorption should no longer be observed in GAC adsorbers. GAC fouling may continue for a longer time, however, because long-term fouling appears to be controlled by processes independent of particle size, such as reorientation or chemical reaction of preloaded BOM on the GAC surface.<sup>5,6</sup> For example, oxidative polymerization of preloaded BOM may proceed in the presence of dissolved oxygen.<sup>25</sup>

**Effect of pulverizing preloaded GAC.** Typically, the GAC capacity for a target compound is determined from an isotherm experiment using pulverized GAC (PGAC) because equilibrium is attained more rapidly with smaller particles.<sup>26</sup> Pulverizing GAC after a preloading time of 16 weeks, PGAC isotherms yielded a *cis*-1,2-dichloroethene capacity similar to that observed in GAC pilot-column tests.<sup>8</sup> Furthermore, dichloroethene capacities were the same for dried or nondried PGAC samples that were crushed after 16 weeks of preloading. However, different TCE capacities have been obtained for preloaded GAC and pulverized, preloaded GAC, suggesting that pulverizing preloaded GAC might open up pores that

had been blocked by preloaded organic matter.<sup>9</sup>

## Kinetic parameters

### External mass transfer.

The film mass transfer coefficient ( $k_f$ ) decreases as preloading time increases.<sup>8,11,24</sup> GAC that was preloaded for four weeks had a  $k_f$  value describing TCE adsorption from Huron River water that was only 29 percent of the value for virgin GAC.<sup>11</sup> Furthermore, GAC preloaded for 32 weeks had a  $k_f$  value describing atrazine adsorption from Hudson River water that was 45 percent of that for virgin GAC.<sup>24</sup> It may appear surprising that  $k_f$  declines with increasing preloading time, given that the  $k_f$  value for a given adsorbate should depend only on the adsorbent geometry and the interstitial fluid velocity in an aqueous system. However, BOM may accumulate near the outer surface of the adsorbent particles as a result of slow adsorption kinetics.<sup>27</sup> Consequently, the local fluid viscosity at the external GAC surface may increase, or the effective surface area for mass transfer may decrease, which would lower  $k_f$  values in the presence of preloaded BOM.<sup>11</sup>

**Internal mass transfer.** Several researchers have studied the effect of preloaded BOM on internal mass transfer.<sup>2,4,8,11</sup> For TCE adsorption from natural water sources, a reduction in the effective surface diffusion coefficient of about one order of magnitude was observed after a preloading time of five weeks.<sup>2,4</sup> As a result of the decreased importance of surface diffusion, both studies subsequently used the pore diffusion model to describe the removal rate of TCE in GAC columns. To model the effect of preloading, the value of GAC's particle tortuosity was increased over time, which led to a successful simulation of the experimental data.<sup>2,4</sup> GAC's removal of TCE from Huron River water was also described by the pore diffusion model.<sup>11</sup> The researchers incorporated an empirical correlation into the pore diffusion model that simulated the transient behavior of the impedance, a factor that described the increased intraparticle mass transfer resistance as BOM accumulated inside GAC pores. During a preloading period of four weeks, the impedance increased by a factor of five compared with virgin GAC.<sup>11</sup>

### Predicting remaining GAC life

Little information is available about predicting the performance of operating GAC adsorbers that are subjected to periodic pollutant episodes.<sup>6,28,29</sup> Rapid small-scale column tests (RSSCTs) successfully predicted atrazine breakthrough curves following short preloading times (about five months), but long-term

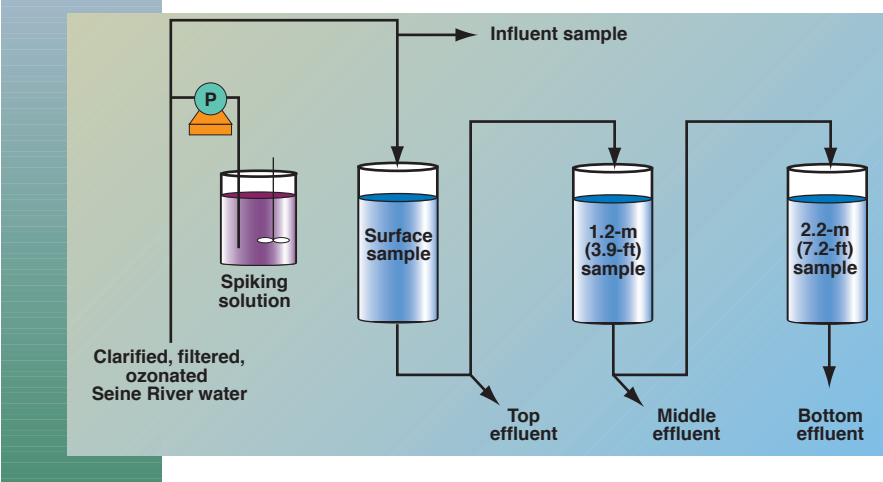
fouling mechanisms were not captured by RSSCTs.<sup>29</sup> In practice, many utilities rely on iodine number determinations to monitor the degree of GAC exhaustion. However, this test does not provide a direct measure of the remaining life of GAC for a given micropollutant. This study evaluated the utility of a dual-resistance mass transfer model for predicting the remaining life of operating GAC adsorbers. The objectives of this research were to (1) determine the effect of preloaded BOM on the adsorption capacity of GAC in adsorber columns as a function of bed depth and preloading time, (2) determine the effect of preloaded BOM on the rate of atrazine adsorption as a function of bed depth and preloading time, (3) predict atrazine removal in pilot-scale GAC adsorbers after various preloading times using a dual-resistance mass transfer model with the equilibrium and kinetic parameters determined from bench-scale studies, and (4) predict the remaining life of GAC adsorbers after various service times.

## Materials

**Organic-free water.** Organic-free water was obtained by deionizing and distilling Urbana, Ill., tap water. After passage through a mixed-bed ion exchange column that contained strong acid cation and strong base anion exchange resins, the water had a conductivity of  $\leq 0.2 \mu\text{S}/\text{cm}$ . Following distillation, the dissolved organic carbon (DOC) concentration of the water was  $\leq 0.3 \text{ mg}/\text{L}$ . For experiments conducted in organic-free water, a  $10^{-3} \text{ M}$  phosphate buffer was added to maintain a neutral pH.

**Seine River water.** Seine River water from the Choisy-le-Roi Water Treatment Plant outside of Paris, France, was used to study the adsorption of atrazine from natural water. Water for bench- and pilot-scale experiments was sampled at the influent to the full-scale GAC filters, at which point it had been pretreated by coagulation, sedimentation, sand filtration, and ozone-hydrogen peroxide oxidation.

**FIGURE 1** Pilot column used to determine remaining life of preloaded granular activated carbon



**TABLE 2** Short-bed adsorber test parameters

Attribute	Virgin	Preloaded for Five Months		Preloaded for Twenty Months
Sample depth—m (ft)	NA*	Surface	2.2 (7.2)	1.2 (3.9)
Mean GAC diameter—mm	1.01	0.72	1.24	0.94
GAC mass—g (oz)	0.252 (0.009)	0.390 (0.013)	0.500 (0.02)	0.440 (0.015)
Bed depth—mm (in.)	14 (0.06)	28 (1.1)	24 (0.9)	24 (0.9)
Bed porosity	0.50	0.66	0.49	0.55
Approach velocity—m/h (gpm/sq ft)	9.48 (3.88)	2.90 (1.19)	2.90 (1.19)	3.10 (1.27)
Influent atrazine concentration—µg/L	101.6	49.9	49.8	49.1

\*NA—Not applicable

Following pretreatment, the GAC influent had an average DOC concentration of about 2.1 mg/L. Water for bench-scale tests was stored at 4°C.

**GAC.** Wood-based GAC\* (1.01-mm geometric mean diameter, 12 X 30 US mesh) with a BET surface area of 1,690 m<sup>2</sup>/g and an iodine number of 915 mg/g was used in this study. At the beginning of the research project, a full-scale postfilter adsorber containing this GAC was put into service at the Choisy-le-Roi Water Treatment Plant. To determine the effect of preloading time on equilibrium and kinetic parameters, core samples were taken from the full-scale adsorber after preloading times of eight weeks, five months, 20 months, and 25 months. To evaluate the effect of bed depth, GAC was sampled at the adsorber surface and at bed depths of 1.2 and 2.2 m (3.9 and 7.2 ft). Mean particle sizes at the three bed depths for samples that were preloaded for five months and 20 months are summarized in Table 1. Preloaded GAC was stored nondried at 4°C before use.

PGAC used in isotherm experiments was obtained by grinding† about 2 g of oven-dried GAC‡ until ≥ 95 percent of the sample passed a 52-µm (270-mesh) sieve. After being sieved, the carbon retained on the sieve was recombined with the carbon that passed through the sieve and stored in a desiccator until further use.

**Atrazine.** Bench-scale tests used <sup>14</sup>C-labeled atrazine§ to facilitate quantitation. Stock solutions were prepared by dissolving about 10 mg of atrazine directly into 2 L of organic-free water or natural water. After the solution was stirred for 24 h, it was filtered through a 0.45-µm membrane to remove any remaining solid atrazine. The filtrate was then stored at 4°C for up to two months. To analyze atrazine samples, 2.5-mL aliquots were mixed with 18 mL of scintillation cocktail\*\* in scintillation vials. The emitted radiation was then measured in a liquid scintillation analyzer.†† For a specific activity of 7.8 mCi/mM or greater, 0.1 µg/L could be detected without concentrating the sample. Samples from pilot tests were analyzed for atrazine by solid-phase extraction,‡‡ high-performance liquid chromatography (HPLC), and ultraviolet detection at 220 nm.

## Methods

**Bottle-point isotherms.** The bottle-point isotherm technique was used to determine the equilibrium capacity of activated carbon for atrazine.<sup>26</sup> Various amounts of carbon were added to amber glass isotherm bottles. A known volume of a solution containing atrazine was then transferred into the isotherm bottles through a 100-mL dispensing pipette.§§ Isotherm bottles containing PGAC were placed on a shaker table for one week to reach equilibrium. For

GAC isotherms, the 0.5-mm geometric-mean-diameter (30 X 40 US mesh) fraction was used, and the mixing time was increased to four weeks to ensure equilibration. Three blanks were included with each isotherm experiment;

**TABLE 3** Effect of preloading time on Freundlich isotherm parameters

Preloading Time	Organic-free Water (Pulverized Granular Activated Carbon)	Seine River Water	
		Pulverized Granular Activated Carbon	Granular Activated Carbon
Virgin	$K = 5.02^*$ $1/n = 0.543$	NA†	NA
Eight weeks	$K = 3.26$ $1/n = 0.454$	NA	NA
Five months	$K = 2.46$ $1/n = 0.466$	$K = 0.898$ $1/n = 0.587$	$K = 0.304$ $1/n = 0.676$
Twenty months	$K = 1.28$ $1/n = 0.491$	$K = 0.665$ $1/n = 0.582$	$K = 0.220$ $1/n = 0.689$
Twenty-five months	$K = 1.46$ $1/n = 0.504$	$K = 0.505$ $1/n = 0.617$	$K = 0.188$ $1/n = 0.668$

\*K values have units of (mg/g)(L/µg)<sup>1/n</sup>.

†NA—Not analyzed

\*PICA B, PICA, Levallois, France  
†8000 Mixer/Mill, SPEX, Edison, N.J.

‡PICA B, PICA, Levallois, France  
§Ciba-Geigy, Greensboro, N.C., and Sigma Chemical Co., St. Louis, Mo.

\*\*Ecoscint, National Diagnostics, Manville, N.J.

††Tri-Carb Model 1600CA, Packard Instrument Co., Downers Grove, Ill.

‡‡Sep-Pak, Waters Corp., Milford, Mass.

§§Brinkman, Westbury, N.Y.



none showed any loss of atrazine during the equilibration period. After equilibrium was reached, the remaining liquid-phase atrazine concentration was measured, and the solid-phase concentration was calculated by use of a mass balance.

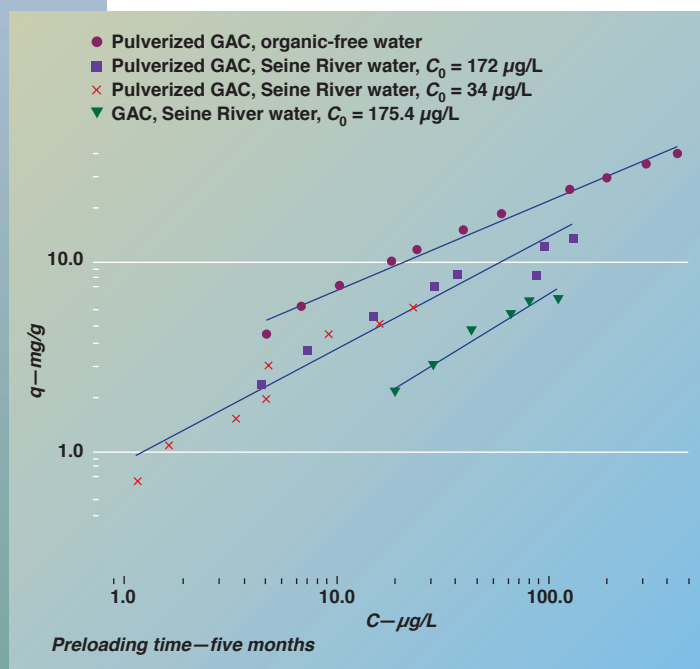
**Short-bed-adsorber tests.** A short-bed adsorber (SBA) was used to determine kinetic parameters describing the rate of atrazine adsorption. The glass column containing the GAC bed for these tests had an inside diameter of 11 mm (0.43 in.) and a length of 350 mm (1.15 ft), and each column end was sealed by PTFE plugs.\* Two porous glass plates centered in a bed of glass beads contained the GAC bed. GAC bed depths were sufficiently shallow to obtain immediate breakthrough of atrazine (Table 2). Constant flow rates were maintained by a double-plunger HPLC pump.†

The kinetics of atrazine adsorption were then determined. Tests run with organic-free water on virgin GAC used the 1.01-mm geometric-mean-diameter (16 X 20-mesh) fraction of GAC samples. Tests run with preloaded GAC used non-dried portions of core samples that had been taken from the full-scale filter (see Table 2 for mean particle diameters).

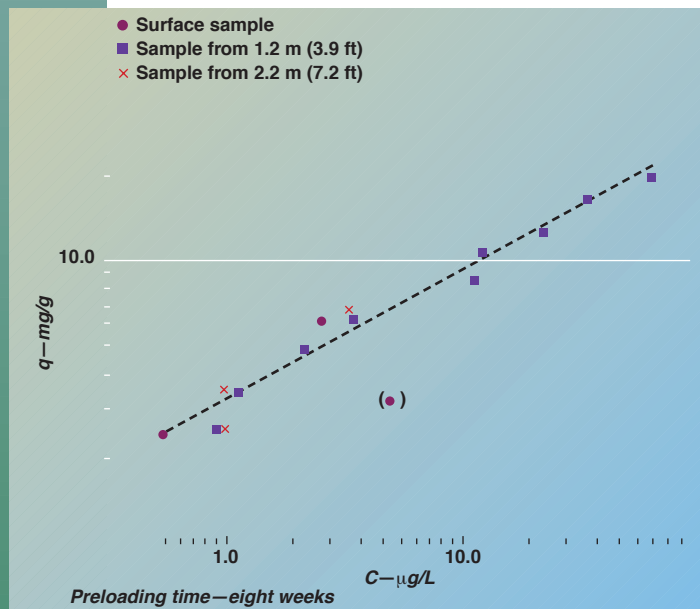
In this study, the ratio of the column diameter to the particle diameter ranged from 8.9 to 15.3, depending on the mean particle diameter of the GAC sample. Although the ratios of column diameter to particle diameter used in this study were smaller than those used in previous studies,<sup>11,30,31</sup> ratios > 8–10 are sufficiently large that wall effects on mass transfer can be neglected.<sup>32,33</sup> Before the SBA test, preloaded GAC samples were stored overnight under vacuum in about 5 mL of natural water to ensure wetting of all pores. No changes in the adsorptive characteristics of the GAC were expected as a result of this treatment because the capacity of the GAC for BOM had been exhausted at the tested preloading times.<sup>29</sup>

**Pilot studies.** Pilot tests were performed at Choisy-le-Roi, France, to determine the remaining atrazine adsorption effectiveness of GAC after various preloading times. Core samples were tested after preloading times of five months and 20 months (Figure 1 and Table 1). The inside diameter of the pilot columns was 40 mm (1.57 in.), and the approach velocity was about 3.0 m/h (1.23 gpm/sq ft). The total GAC bed depth was

**FIGURE 2** Atrazine isotherms on granular activated carbon (GAC) and pulverized GAC in two types of water



**FIGURE 3** Effect of bed depth on pulverized granular activated carbon capacity



about 400 mm (1.31 ft), leading to a total empty bed contact time (EBCT) of about 8 min.

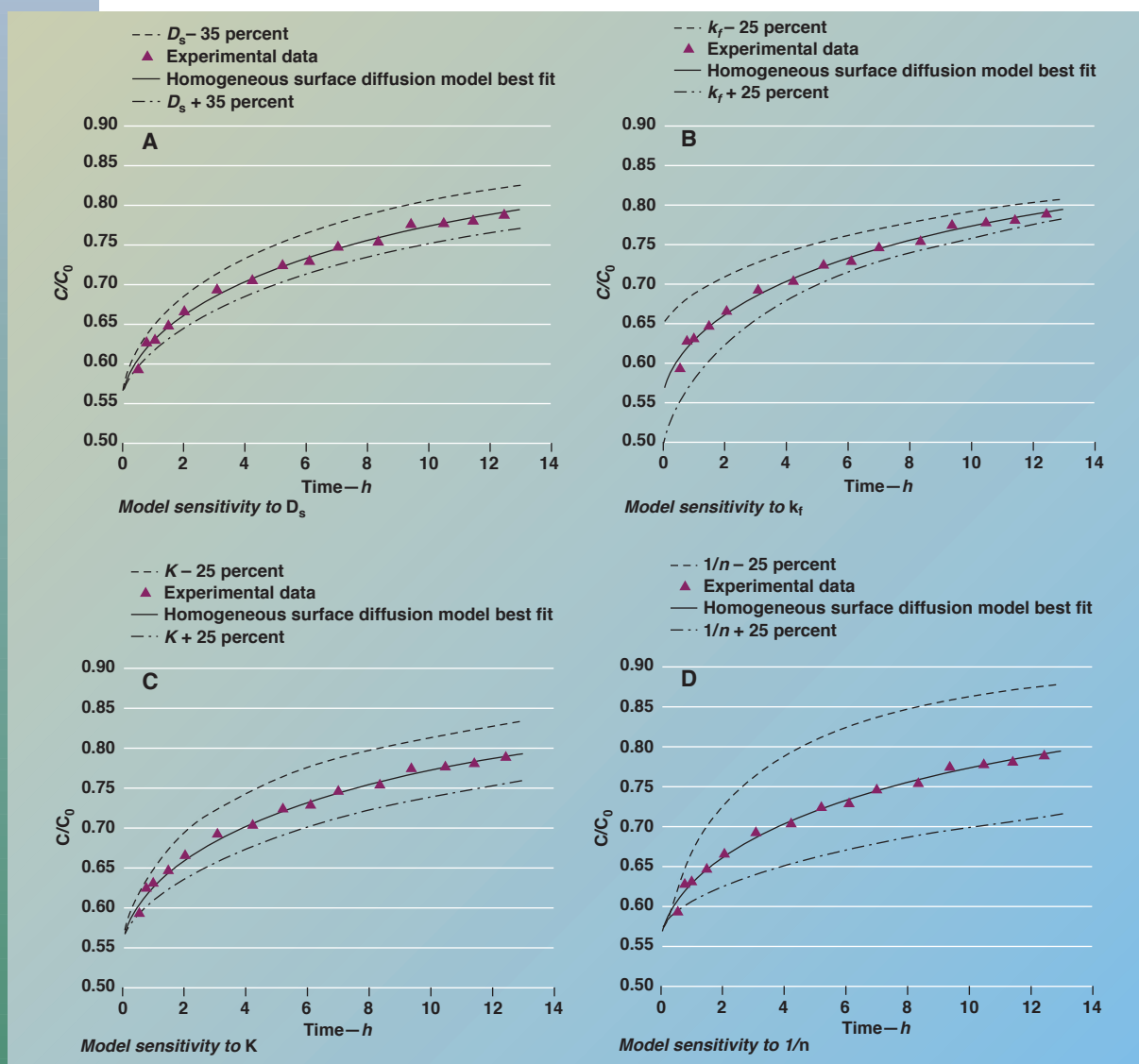
## Results and discussion

**Adsorption equilibria.** Atrazine isotherm experiments were conducted in organic-free water and in Seine River water to monitor the effect of preloaded BOM on the remaining capacity of GAC to adsorb atrazine. Furthermore, atrazine adsorption equilib-

\*Ace Glass Inc., Vineland, N.J.

†Waters Corp., Milford, Mass.

**FIGURE 4** Atrazine adsorption kinetics from Seine River water on granular activated carbon preloaded for 20 months and model sensitivity to four factors



ria were measured at two initial concentrations in the natural water to study whether competitive, reversible coadsorption was important on the preloaded GAC. Finally, the effect of grinding on the atrazine capacity of preloaded GAC was evaluated.

**Effect of preloading time.** Initially, atrazine isotherm experiments were conducted in organic-free water with virgin PGAC and with GAC that was pulverized after preloading times of eight weeks, five months, 20 months, and 25 months. The corresponding Freundlich  $K$  values for each isotherm (Table 3) show that the atrazine capacity decreased with increasing preloading time. After a preloading time of eight weeks, the PGAC capacity for atrazine in organic-free water, as measured by the Freundlich  $K$  value, was about 65 percent of the virgin PGAC capacity. After five months of preloading, the remaining

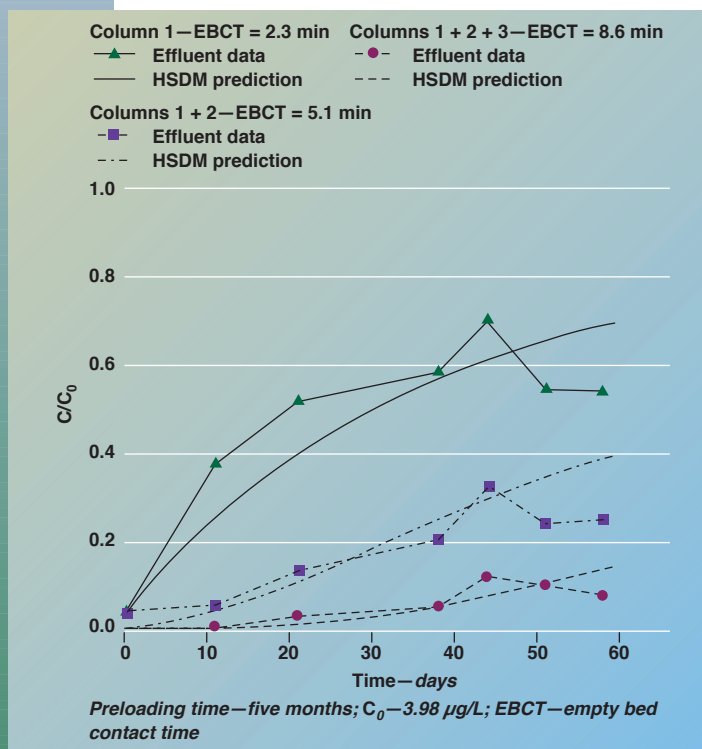
atrazine capacity had decreased to about 50 percent of the virgin PGAC capacity, and only about 25–30 percent of the virgin PGAC capacity remained after 20 and 25 months of preloading. The rapid initial capacity loss followed by a more gradual capacity decrease agrees with results from prior preloading studies.<sup>2–12</sup>

After the effect of BOM preloading on atrazine capacity in organic-free water was established, the potential for competitive coadsorption of atrazine and BOM components was investigated next. This potential was assessed with GAC samples that were pulverized after preloading times of five, 20, and 25 months. Atrazine isotherm experiments were conducted with Seine River water at two initial atrazine concentrations. Isotherms determined in organic-free water and in natural water were compared for carbon sampled after a preloading time

of five months (Figure 2). Although the Freundlich  $K$  value for the natural water isotherms was only 37 percent of that obtained in organic-free water (Table 3), no effect of initial concentration was discerned. That is, the data for the two atrazine isotherms derived in PGAC tests using Seine River water could be described by the same Freundlich parameters. Similar observations were made for PGAC isotherms obtained after preloading times of 20 and 25 months.<sup>22</sup> This lack of competition suggests that the available adsorption sites on preloaded GAC were accessible to atrazine molecules but not to BOM. This lack agrees with the observation that the GAC capacity for BOM as measured by total organic carbon (TOC) had been exhausted after a preloading time of five months.<sup>29</sup> As a result, coadsorbing BOM constituents were not able to compete with atrazine for the remaining adsorption sites. The difference in capacity between the isotherms in organic-free water and in Seine River water in the absence of competitive adsorption suggests that some of the preloaded BOM may have reoriented in the presence of organic-free water. This reorientation made additional adsorption sites, possibly in previously blocked micropores, accessible to atrazine. A small amount of BOM may have also desorbed from the preloaded carbon. However, evidence of irreversible adsorption of humic substances inside of activated carbon pores does not favor BOM desorption as a likely explanation for the observed results.<sup>1</sup>

**Effect of bed depth.** To evaluate the effect of bed depth on remaining GAC adsorption capacity for atrazine, GAC samples were obtained from the full-scale adsorber at three bed depths after eight weeks of preloading. The GAC was pulverized and then used in atrazine isotherm experiments in organic-free water. Preloaded BOM reduced GAC capacity uniformly throughout the depth of the filter (Figure 3). Compared with the results of other studies,<sup>5,12</sup> this result was unexpected after only eight weeks of preloading. It might be expected that the capacity at the bottom of the filter would not be as severely affected by preloaded BOM as the capacity at the top of the filter. However, TOC breakthrough data obtained for virgin GAC in a pilot-scale adsorber with an EBCT of 14 min showed that no TOC was removed in the lower half of the bed after about seven weeks of operation. Exhaustion of the capacity of GAC to adsorb TOC after about seven weeks of operation supports the finding that the remaining atrazine adsorption capacity was independent of bed depth after a preloading time of eight weeks. Similarly, the remaining atrazine capacity was uniformly reduced throughout the entire depth of the GAC bed after a preloading time of 20 months.<sup>22</sup>

**FIGURE 5** Pilot-column results and homogeneous surface diffusion model (HSDM) predictions of atrazine removal from Seine River water after five month's preloading



**Effect of grinding.** To test whether grinding affected the results of isotherm experiments, atrazine isotherm data were collected with pulverized, preloaded GAC and the 0.5-mm geometric-mean-diameter (30 X 40-mesh) fraction. For GAC sampled after a preloading time of five months, PGAC isotherms in Seine River water show a greater remaining capacity for adsorbing atrazine than the GAC isotherm (Figure 2). Activated carbons that were sampled after preloading times of 20 and 25 months produced similar results. Freundlich  $K$  values for the GAC isotherms were about 33–37 percent of those for the PGAC isotherms in Seine River water (Table 3). In addition, the GAC isotherms possessed steeper slopes (represented by larger  $1/n$  values).

The results of the current study agree with those of an earlier study that compared TCE isotherms of GAC and PGAC after GAC preloading for four weeks in Huron River water.<sup>9</sup> In that study, crushing of preloaded GAC apparently opened pores that had been blocked by preloaded BOM. Thus, more adsorption sites were available after crushing, as expressed by a larger Freundlich  $K$  value.<sup>9</sup> Furthermore, pulverizing preloaded GAC led to a greater heterogeneity of adsorption site energies as evidenced by a lower  $1/n$  value.<sup>9</sup>

On the basis of the effects of pulverizing preloaded GAC, the isotherm capacities determined with the

**TABLE 4** Effect of preloading time and bed depth on adsorption kinetics

Water Source and Preloading Time	Sample Depth <i>m</i> (ft)	Surface Diffusion Coefficient— <i>cm</i> <sup>2</sup> / <i>s</i>	Film Mass Transfer Coefficient— <i>cm</i> / <i>s</i>
Organic-free water Virgin	NA*	2.65 X 10 <sup>-11</sup>	2.81 X 10 <sup>-3</sup>
Pretreated Seine River water			
Five months	Surface	2.70 X 10 <sup>-11</sup>	7.69 X 10 <sup>-4</sup>
Five months	2.2 (7.2)	2.89 X 10 <sup>-11</sup>	7.42 X 10 <sup>-4</sup>
Twenty months	1.2 (3.9)	1.78 X 10 <sup>-11</sup>	7.27 X 10 <sup>-4</sup>

\*NA—Not applicable

**TABLE 5** Effect of preloaded background organic matter on the film mass transfer coefficient

Preloading Time and Depth of GAC Sample	<i>k<sub>f</sub></i> — <i>cm</i> / <i>s</i>	<i>k<sub>fL</sub></i> — <i>cm</i> / <i>s</i>	<i>k<sub>fBOM</sub></i> — <i>cm</i> / <i>s</i>
Five months			
Surface	7.69 X 10 <sup>-4</sup>	1.57 X 10 <sup>-3</sup>	1.51 X 10 <sup>-3</sup>
2.2 m (7.2 ft)	7.42 X 10 <sup>-4</sup>	1.50 X 10 <sup>-3</sup>	1.47 X 10 <sup>-3</sup>
Twenty months			
1.2 m (3.9 ft)	7.27 X 10 <sup>-4</sup>	1.64 X 10 <sup>-3</sup>	1.31 X 10 <sup>-3</sup>

0.5-mm-size fraction of preloaded GAC were used in subsequent mathematical modeling that determined kinetic parameters and predicted the performance of pilot-scale GAC adsorbers. It was assumed that the 0.5-mm-size fraction of preloaded GAC had the same adsorption capacity for atrazine as the entire core sample. This assumption was reasonable because the degree of GAC fouling has been shown to be independent of particle size.<sup>5,6,9</sup>

**Adsorption kinetics.** Initially, it was necessary to establish a baseline for the subsequent determination of kinetic parameters on preloaded GAC. To this end, the film mass transfer coefficient (*k<sub>f</sub>*) and the surface diffusion coefficient (*D<sub>s</sub>*) for the adsorption of atrazine from organic-free water on virgin GAC were determined. The homogeneous surface diffusion model (HSDM) was used to mathematically describe the kinetic data.<sup>34,35</sup> The minimum difference between the SBA data and the HSDM output was obtained for a *k<sub>f</sub>* value of 2.81 X 10<sup>-3</sup> *cm*/*s* and a *D<sub>s</sub>* value of 2.65 X 10<sup>-11</sup> *cm*<sup>2</sup>/*s* (Table 4).

SBA tests were also performed in Seine River water to evaluate atrazine adsorption kinetics on preloaded GAC samples. Physical parameters for SBA tests closely matched those used in the corresponding pilot-scale adsorbers (Tables 1 and 2). After a preloading time of five months, the effect of bed depth on mass transfer coefficients in the full-scale GAC adsorber was evaluated. Samples were obtained from two depths—the surface and 2.2 m (7.2 ft) below the surface—and resulting *k<sub>f</sub>* and *D<sub>s</sub>* values were determined (Table 4). These kinetic parameters were similar at the two depths. In agreement with the isotherm results, the SBA data showed that BOM uniformly affected the adsorption of atrazine throughout the depth of the full-scale GAC adsorber once the adsorp-

tion capacity for TOC had been exhausted.

Next, the effect of a longer preloading time on the kinetics of atrazine adsorption was determined. The *k<sub>f</sub>* value for the GAC preloaded for 20 months was similar to that for GAC preloaded for only five months (Table 4). However, after a preloading time of 20 months, the *D<sub>s</sub>* value was about 36 percent smaller than the average value obtained after a preloading time of five months. A sensitivity analysis showed that HSDM results were sensitive to a 35 percent change in *D<sub>s</sub>* (Figure 4, part A), especially in the latter stages of the test, when intraparticle diffusion was the rate-limiting adsorption step. The initial region of the SBA test was more sensitive to

changes in *k<sub>f</sub>* (Figure 4, part B). The sensitivity of the model to *k<sub>f</sub>* in the early stages and to *D<sub>s</sub>* in the latter stages of the SBA test showed that the experimental design was suitable to determine both kinetic parameters accurately. However, HSDM results were also sensitive to changes in the equilibrium parameters (Figure 4, parts C and D). For example, a *K* value of 0.190 (mg/g)(L/μg)<sup>1/*n*</sup> (14 percent smaller than the value determined from the GAC isotherm) and a 1/*n* value of 0.670 (2.8 percent smaller than the value determined from the GAC isotherm) produced a *D<sub>s</sub>* value of 2.74 X 10<sup>-11</sup> *cm*<sup>2</sup>/*s*, which closely matched the average *D<sub>s</sub>* value for GAC that had been preloaded for five months. Consequently, the significance of the 36 percent decrease in the *D<sub>s</sub>* value between preloading times of five and 20 months depends on the accuracy of the equilibrium parameters.

The kinetic parameters for the virgin GAC and preloaded GAC are compared in Table 4. Surprisingly, the *D<sub>s</sub>* value that best described the rate of atrazine adsorption from Seine River water on a

**TABLE 6** Equilibrium and kinetic parameters used in predictions of pilot-column performance

Parameter	Preloaded for Five Months	Preloaded for Twenty Months
<i>K</i> —(mg/g)(L/μg) <sup>1/<i>n</i></sup>	0.304	0.220
1/ <i>n</i>	0.676	0.689
<i>D<sub>s</sub></i> — <i>cm</i> <sup>2</sup> / <i>s</i>	2.80 X 10 <sup>-11</sup> *	1.78 X 10 <sup>-11</sup>
<i>k<sub>f</sub></i> — <i>cm</i> / <i>s</i>	7.56 X 10 <sup>-4</sup> *	7.27 X 10 <sup>-4</sup>

\*Average of surface sample and 2.2-m (7.2-ft) sample values reported in Table 4



GAC preloaded for five months was similar to the value that best described the rate of atrazine adsorption from organic-free water on the virgin GAC. The results of this research show a small to negligible effect of BOM preloading on  $D_s$ . This result differs from results of prior studies on the effect of preloading on intraparticle mass transfer.<sup>2,4,11,24</sup> Large humic molecules inside GAC pores may retard intraparticle diffusion rates of micropollutants.<sup>36</sup> However, this effect may not be as pronounced for the wood-based GAC used in this study, whose large volume of mesopores (2–50-nm pore diameter) can facilitate intraparticle mass transfer. After 20 months of preloading, the mesopore volume of this GAC was 0.253 cm<sup>3</sup>/g.<sup>22</sup> In addition, the molecular size of the adsorbed BOM may have been comparatively small given that an advanced oxidation process preceded the full-scale GAC adsorbers. Given the similarity of the surface diffusion coefficients that were determined for atrazine adsorption on virgin and pre-

**TABLE 7** Predictions of GAC's remaining life after two preloading times

Influent Atrazine Concentration	Remaining Life*	
	Preloaded for Five Months	Preloaded for Twenty Months
Target effluent concentration: 3.0 µg/L C <sub>0</sub> = 5 µg/L C <sub>0</sub> = 10 µg/L C <sub>0</sub> = 50 µg/L	10.9 months 4.8 months 1 month	4.6 months 1.4 months 7 days
Target effluent concentration: 0.1 µg/L C <sub>0</sub> = 0.5 µg/L C <sub>0</sub> = 1 µg/L C <sub>0</sub> = 2 µg/L	14.9 months 9.2 months 5.5 months	4.9 months 2.6 months 1.4 months
*To reach target effluent concentration, empty bed contact time = 15 min		

loaded GAC, the HSDM was used to describe atrazine adsorption in pilot-scale adsorbers containing preloaded GAC.

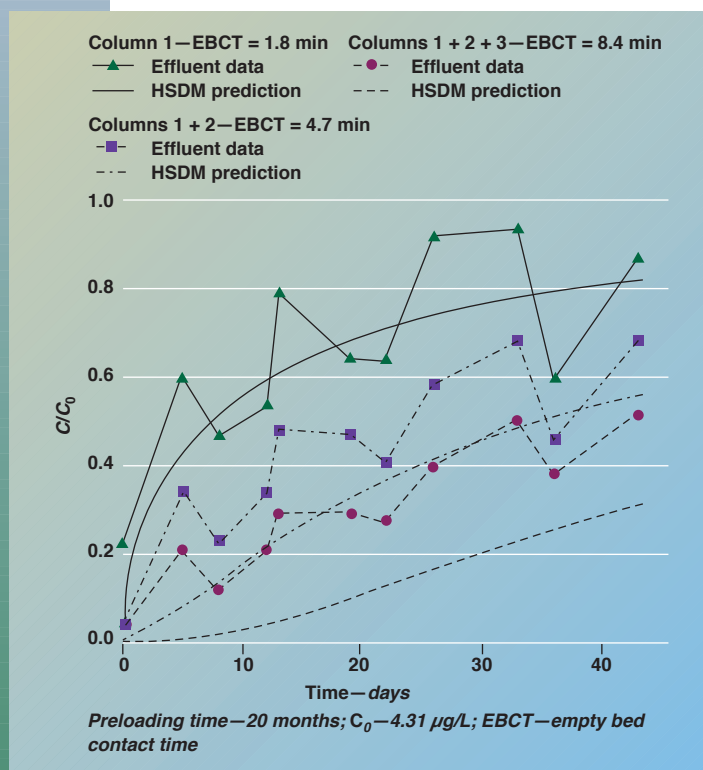
Smaller  $k_f$  values were determined for preloaded GAC than for virgin GAC (Table 4). Reductions in  $k_f$  as a result of BOM preloading agree with prior studies.<sup>8,11,24</sup> In the current study, the decrease in  $k_f$  during the SBA tests that used preloaded GAC can be partially explained by different hydrodynamic conditions—lower interstitial velocity, different particle diameters, and different bed porosities (Table 2).

However, hydrodynamic conditions alone could not fully explain the observed decrease in  $k_f$  value as predicted by the Gnielinski correlation.<sup>3,31</sup> It is possible BOM that had accumulated at or close to the external surface of preloaded GAC added some resistance to mass transfer, which was expressed in the  $k_f$  value for preloaded GAC. Thus, a series-resistance model was used to estimate the relative contributions of the liquid film ( $k_{f,L}$ ) and the BOM at the external surface of the GAC ( $k_{f,BOM}$ ) to the overall film mass transfer coefficient ( $k_f$ ) determined from the SBA tests:

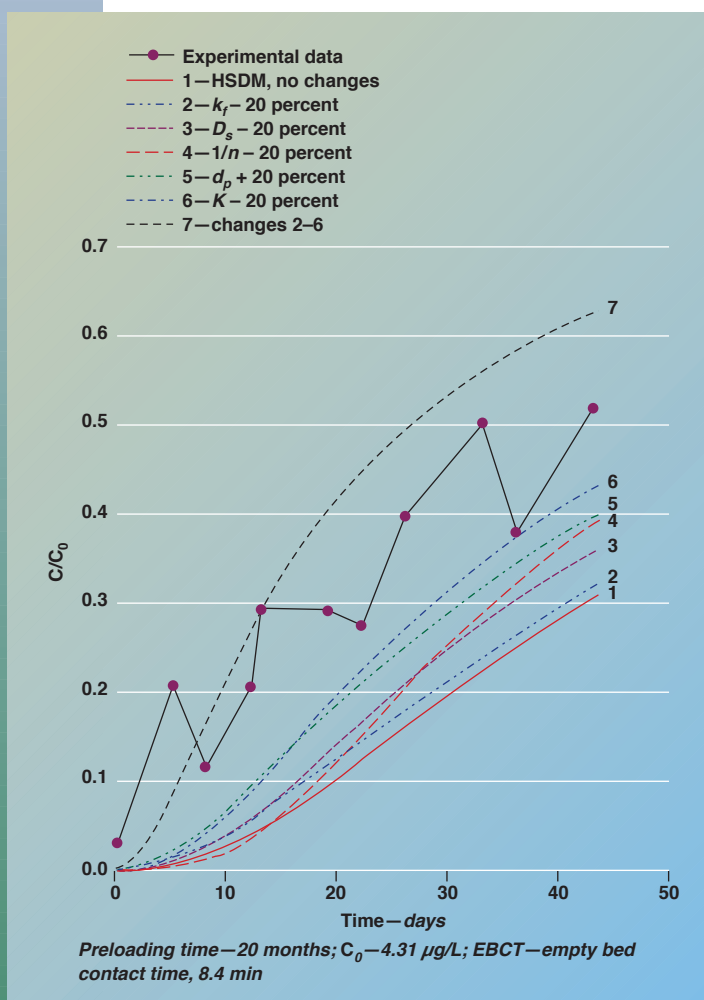
$$\frac{1}{k_f} = \frac{1}{k_{f,L}} + \frac{1}{k_{f,BOM}} \quad (1)$$

To calculate  $k_{f,L}$  for preloaded GAC, the  $k_f$  value from the SBA test with virgin GAC was used. This value was multiplied by the ratio of  $k_f$  values predicted by the Gnielinski relationship<sup>3,31</sup> for preloaded and virgin GAC with the hydrodynamic conditions of the respective SBA tests (Table 2). The resulting  $k_{f,L}$  values are shown in Table 5. Once  $k_f$  was determined from the SBA tests,  $k_{f,BOM}$  could then be calculated using Eq 1. The  $k_{f,L}$  value was more than twice as large as the overall  $k_f$  value obtained from the

**FIGURE 6** Pilot-column results and homogeneous surface diffusion model (HSDM) predictions of atrazine removal from Seine River water after 20 months' preloading



**FIGURE 7** Sensitivity analysis of homogeneous surface diffusion model (HSDM) predictions



SBA tests (Table 5). Thus, preloaded BOM must have been responsible for the additional resistance to mass transfer. The  $k_{f,BOM}$  values for the GAC preloaded for five months were similar at the two bed depths, and the  $k_{f,BOM}$  value for the GAC preloaded for 20 months was only slightly smaller (Table 5), indicating that the additional preloading time had only a negligible effect on external mass transfer. At the tested flow rates, the resistance to mass transfer produced by preloaded BOM accounted for more than 50 percent of the overall film mass transfer resistance.

**Pilot-column tests.** Pilot-column tests at the Choisy-le-Roi Water Treatment Plant evaluated the remaining GAC life after preloading times of five and 20 months (Table 1). Atrazine breakthrough curves were measured for GAC preloaded for five months (Figure 5). Superimposed on the measured curves are HSDM predictions obtained with the equilibrium and kinetic parameters for GAC that was preloaded for five months (Table 6). HSDM predictions agreed well with the experimental data (Figure 5). Thus, for a preloading time of five months, determination of

one set of equilibrium and kinetic parameters from bench-scale experiments was sufficient to successfully describe atrazine removal at three EBCTs in the pilot test. Obtaining a good prediction with equilibrium and kinetic parameters independent of GAC depth further showed that preloaded BOM uniformly affected atrazine adsorption at all tested bed depths.

A separate pilot test evaluated the atrazine removal efficiency of GAC that had been preloaded for 20 months. Experimental data were compared with HSDM predictions (Figure 6) obtained with the GAC equilibrium and kinetic parameters for a preloading time of 20 months (Table 6). Especially at longer EBCTs, the predicted atrazine breakthrough curves did not describe the experimental data well. A sensitivity analysis assessed how uncertainty in the determined equilibrium and kinetic parameters affected the predictions.

Atrazine breakthrough data measured at an EBCT of 8.4 min were compared with the HSDM predictions (Figure 7) obtained with 20-month equilibrium and kinetic parameters (Table 6). In addition, further HSDM predictions were obtained by varying individual model parameters by 20 percent (Figure 7). The model was more sensitive to changes in the equilibrium parameters than to changes in the kinetic parameters (Figure 7). A 20 percent decrease in the Freundlich  $K$  value had the greatest overall effect, although a 20 percent decrease in the  $1/n$  value caused the greatest

change in the shape of the predicted breakthrough curve. Uncertainty associated with the equilibrium parameters may have been a result of collecting isotherm data at equilibrium liquid-phase concentrations that were in the 10–100- $\mu\text{g/L}$  range; this range was higher than those in pilot-scale tests.

The isotherms were not completely linear throughout several orders of magnitude on a log-log plot. Better estimates of the Freundlich  $K$  and  $1/n$  values might be obtained with an isotherm experiment that investigated the liquid-phase concentration range of the pilot-scale test. In addition, preloaded BOM may have reoriented during storage of the GAC. However, the resulting effect on remaining atrazine capacity should have been small. In an evaluation of the effectiveness of bioregeneration of preloaded GAC, the atrazine adsorption capacity of preloaded GAC did not change for 16 months.<sup>12</sup>

The sensitivity analysis further showed that the model was more sensitive to a 20 percent increase in the GAC particle diameter than to a 20 percent decrease in the kinetic parameters. Uncertainty asso-

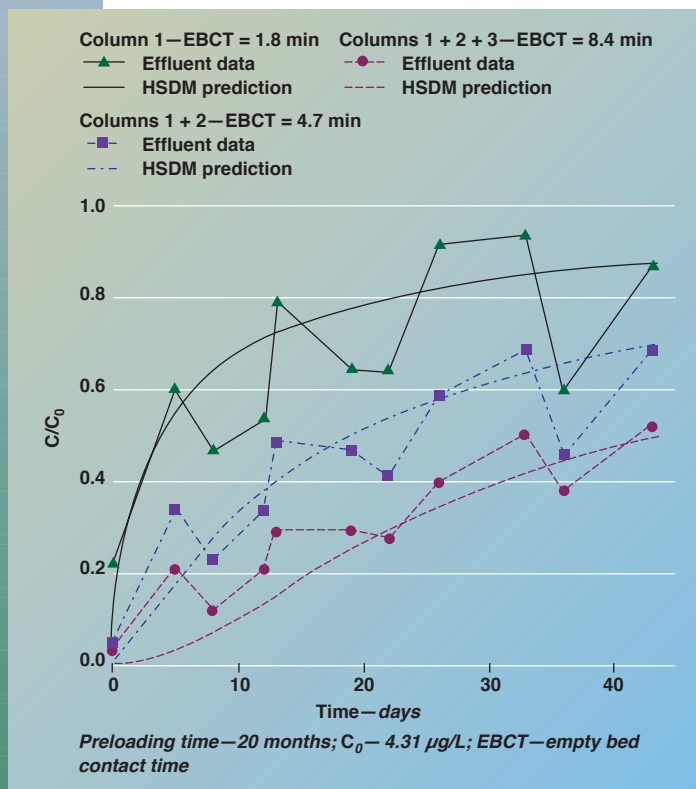
ciated with the particle diameter determination of GAC in service for 20 months could have been a result of sieving, which could have abraded or broken GAC particles. Finally, the combined effect of a 20 percent change of all evaluated parameters produced a breakthrough curve that underpredicted the measured performance of the GAC (Figure 7).

Overall, the sensitivity analysis showed that smaller Freundlich  $K$  values, smaller  $D_s$  values, and larger GAC particle diameters all led to HSDM results that matched the experimental data more closely. Assuming that the Freundlich  $K$  value was overestimated from isotherm experiments, and that all other parameters were determined correctly, HSDM results closely matched the pilot data when the Freundlich  $K$  value was lowered by 30 percent (from  $0.220 \text{ [mg/g][L/}\mu\text{g]}^{1/n}$  to  $0.154 \text{ [mg/g][L/}\mu\text{g]}^{1/n}$ ) (Figure 8).

**Remaining-life predictions.** To show how results from GAC isotherm and SBA tests can be used to obtain point estimates of remaining GAC life, atrazine episodes were simulated. The episodes used initial atrazine concentrations commonly encountered in surface water sources of the midwestern United States and western Europe. Median atrazine concentrations of about  $5 \mu\text{g/L}$  have been reported for Midwestern streams during the postplanting season,<sup>37</sup> and peak atrazine concentrations have exceeded  $100 \mu\text{g/L}$ .<sup>37–39</sup> Atrazine concentrations in excess of  $3 \mu\text{g/L}$  tend to appear briefly (< two months) in uncontrolled streams and during longer periods (four to five months) in controlled rivers.<sup>40</sup> Peak atrazine concentrations in major European rivers are typically one to two orders of magnitude lower than those observed in Midwestern streams. In the period April 1989–November 1990, atrazine concentrations in Seine River water outside of Paris, France, peaked in June near  $0.8 \mu\text{g/L}$ . Atrazine concentrations in the Dutch reaches of the rivers Rhine and Meuse tend to be  $< 1 \mu\text{g/L}$ .<sup>41</sup>

For remaining-life predictions, treatment goals were to meet the atrazine standards of  $3 \mu\text{g/L}$  in the United States<sup>42</sup> and  $0.1 \mu\text{g/L}$  for member countries of the European Union.<sup>43</sup> Influent atrazine concentrations of 5, 10, and  $50 \mu\text{g/L}$  were used for US scenarios and 0.5, 1, and  $2 \mu\text{g/L}$  for European scenarios. Predictions were made for operating times at which a breakthrough concentration corresponding to the treatment goal would be reached (Table 7). All but one of the equilibrium and kinetic parameters were those presented in Table 6. The one exception was the Freundlich  $K$  value for GAC preloaded for 20 months, which was reduced by 30 percent on the basis of pilot-scale results. Mean GAC parti-

**FIGURE 8** Pilot-column breakthrough curves and modified homogeneous surface diffusion model (HSDM) predictions



cle diameter was assumed to be 1 mm, bed porosity was 0.6, and EBCT was 15 min.

At a preloading time of five months, the predicted remaining GAC life was one month for an influent atrazine concentration of  $50 \mu\text{g/L}$ ; it was five months or more for all other tested scenarios. The predicted remaining GAC life in excess of five months cannot be taken at face value, because fouling will reduce the performance of the GAC adsorber during additional operation. Instead, such a point estimate should be interpreted as one that is sufficiently long to assure regulatory compliance through one spring runoff season.

For a preloading time of 20 months, remaining-life predictions ranged from seven days to 4.6 months for US scenarios and 1.4–4.9 months for European scenarios. The predicted values for the European examples should still be sufficiently long to meet regulatory standards for one spring runoff season. However, predicted remaining life for some US scenarios may be too short to achieve adequate atrazine removal for one spring runoff season, implying that annual regeneration or replacement may be necessary for the tested GAC and background water. Although these remaining-life predictions (Table 7) should not be interpreted as generally applicable to any GAC and natural water source, they show how utilities can use this procedure to develop a GAC regeneration or replacement schedule.

## Conclusions

Results obtained from equilibrium and kinetic tests in this study showed how preloaded BOM affects atrazine adsorption on GAC sampled from a full-scale adsorber over 25 months. Preloaded BOM uniformly reduced the remaining GAC adsorption capacity for atrazine through the 2.2-m (7.2-ft) depth of the filter, because the TOC adsorption capacity of the GAC had been exhausted at all tested preloading times. The remaining capacity to adsorb atrazine decreased rapidly during the first five months of preloading and more gradually thereafter. At the tested preloading times, the remaining adsorption capacity for atrazine was not a function of initial atrazine concentration in the natural water. Thus, competitive coadsorption of atrazine and BOM components was not observed on the preloaded carbon; this result was consistent with its exhausted TOC adsorption capacity. Use of pulverized, preloaded GAC overestimated the remaining atrazine adsorption capacity, as measured by the Freundlich  $K$  value, by as much as a factor of three. Overall, preloaded BOM greatly reduced the atrazine capacity of GAC; after a preloading time of 25 months, the Freundlich  $K$  value was only 4 percent of the value describing the virgin single-solute isotherm data.

Kinetic parameters were unaffected by bed depth after a preloading time of five months. In a comparison of kinetic and equilibrium parameters of virgin and preloaded GAC, preloaded BOM more strongly influenced equilibrium parameters than kinetic parameters. After a preloading time of five months, the  $D_s$  value was about the same as that describing atrazine adsorption by virgin GAC from organic-free water. However, the  $k_f$  value, which, for a given adsorbate, should be affected only by hydrodynamic conditions, was more than 50 percent smaller than could be expected from the hydrodynamic conditions alone. Thus, the  $k_f$  value for preloaded GAC expressed an additional resistance to mass transfer that resulted from preloaded BOM that must have accumulated at or close to the external GAC surface.

Remaining GAC life was predicted using the HSDM and equilibrium and kinetic parameters from GAC isotherm and SBA tests. The resulting breakthrough curve predictions were verified in pilot tests. Excellent agreement between predicted and measured atrazine breakthrough curves was obtained after a preloading time of five months. Discrepancies were observed between model predictions and experimental data after a preloading time of 20 months. These discrepancies were primarily attributed to uncertainty associated with the equilibrium parameters and GAC particle size. For the GAC and background water used in this study, examples of point estimates of remaining GAC life were presented to show how the obtained information can be used to develop a GAC regeneration or replacement schedule.

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