Preloading of GAC by natural organic matter in potable water treatment systems: Mechanisms, effects and design considerations*

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ABSTRACT

The existence of complex and highly variable natural organic materials (NOMs) in virtually all potable supply source waters is broadly recognized. It is also general knowledge that granular activated carbon (GAC) adsorbers, integral parts of many potable supply treatment systems, effectively adsorb various molecular fractions of such NOMs. There is strong evidence that the phenomenon of 'preloading' of GAC by NOM can have profound effects on its subsequent ability to remove organic contaminants. Such effects on the performance of adsorbers in their primary role of contaminant removal are, nonetheless, seldom factored adequately into their initial design. The objective of this paper is to present a rational approach, a blend of mechanistic modelling and empirical parameter estimation, by which the impacts of NOM preloading can be incorporated into the design of GAC systems on a source-water specific basis. The results of a series of investigations from which a quantitative approach to the integration of preloading effects in the design of such adsorbers has evolved are detailed, and a specific case study application of the approach is described.

Key words | activated carbon, adsorption, design, natural organic matter, preloading

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INTRODUCTION

This is one of a number of invited papers presented at the IWA sponsored Workshop on Biological Activated Carbon Filtration held at Delft University of Technology in the Netherlands in May 2002. The focus of that workshop was, as its title indicates, the design and operation of biologically active carbon (BAC) systems for potable water treatment. This particular paper does not specifically address the issue of BAC design. Rather, it goes to a more fundamental issue underlying the reason why granular activated carbon (GAC) treatment units can in fact be operated as BAC systems; that is, prolific adsorption of the background natural organic matter (NOM) that functions as a primary substrate for microbial growth in GAC

adsorbers. Many different molecular types of NOM are indeed adsorbed well by activated carbon. It is not surprising then that the sorption of such complex background organic matter has major, although highly variable, effects on the ability of the carbon to remove other compounds more specifically targeted for removal.

This paper presents one approach to the assessment and modelling of precisely what effects can be anticipated in any specific application, and to the incorporation of that information in the design of GAC adsorbers. While references are made to and results incorporated from pertinent elements of the significant body of literature describing research by others on this important topic, the paper is not intended as a global review. Rather, in the tone of the workshop at which it was presented, it focuses on a consistent and systematic approach, one that has evolved from a comprehensive sequence of investigations

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ranging from fundamental science to engineering design conducted jointly over a number of years by the GAC and NOM research groups at the University of Michigan. It logically includes extensions of that work at other institutions where graduate students and post-docs have continued pursuit of the subject.

Figure 1 | Adsorption wave front behaviours leading to preloading.

GAC SYSTEMS IN WATER TREATMENT

The principal purpose of GAC systems in water treatment operations is to adsorb specific types of undesirable organic compounds (e.g. nuisance compounds that cause tastes and odours, and compounds that pose threats to human health). GAC performs this function by providing a large surface area populated by a variety of different types of functional groups generated in the activation process. Nuisance and potentially harmful organic compounds are generally present at relatively small concentrations (i.e. ppb levels) in most potable water sources. Conversely, a heterogeneous array of dissolved organic compounds of natural origin (e.g. humic and fulvic acids) are commonly present in the same source waters at much higher concentrations (i.e. ppm levels). While the compounds constituting this heterogeneous natural organic matter (NOM) are not necessarily harmful to public health on their own accord, some of their constituents interact with halogen-based disinfectants to form potentially harmful 'disinfection by-products' (e.g. chlorine and bromine substituted aliphatic and aromatic compounds).

By design, activated carbon is a highly effective adsorbent for removing a broad range of different types of undesirable organic compounds targeted for removal during water treatment (i.e. 'target' compounds). Given these inherent properties, GAC is thus effective also in removing many of the compounds that constitute NOM in source waters. This is desirable from one perspective: GAC reduces the number of NOM components available to colour water, cause odours or tastes, and function as precursors for formation of disinfection by-products. From a different perspective, it is undesirable: the diverse array of chemical moieties composing NOM compete
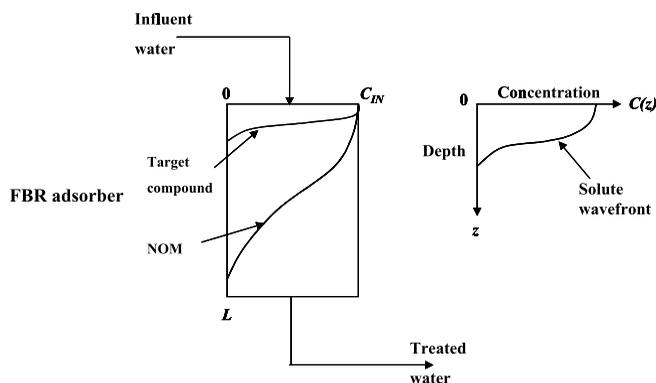
effectively with target compounds for the surfaces and reactive sites of activated carbon, thus interfering with and diminishing its adsorption of target compounds.

PRELOADING PHENOMENA

On a one-to-one 'molecular' basis, NOM moieties are generally not adsorbed as effectively as target contaminants. However, their presence in order-of-magnitude higher concentrations makes them effective competitors for adsorption sites on GAC. Another less obvious, and somewhat ironic, reason why NOM moieties compete effectively for GAC sites is that most of them are in fact not as effectively adsorbed as most target contaminants. This behaviour allows them more rapid access than target compounds to the fresh activated carbon regions of a typical fixed bed reactor (FBR), as depicted by the adsorption wave front behaviours shown in Figure 1. In accessing the fresh GAC more rapidly, the NOM moieties 'preload' and 'precondition' the fresh GAC in ways that potentially change its properties and reduce its effectiveness for adsorption of target contaminants that come along later. In other words, the fresh GAC intended for target compound removal rapidly becomes a 'used' GAC of unknown, but generally lower, effectiveness for subsequently removing target compounds.

It would seem at first consideration a relatively simple, albeit costly, matter to add more carbon to account for the
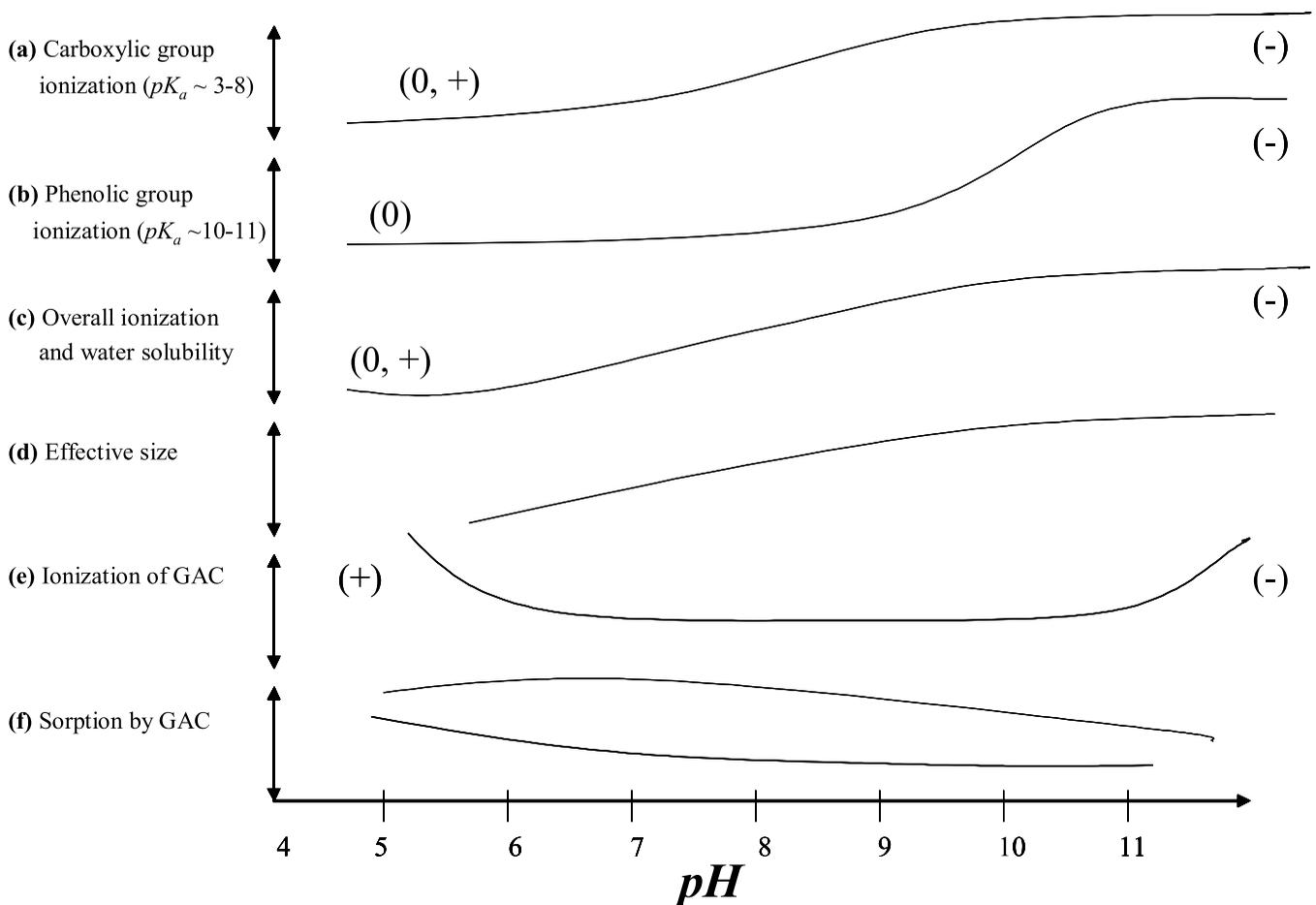
Figure 2 │ Parameters affecting NOM sorption (after Karanfil *et al*. 1998).

decreases in its capacity caused by adsorption of the NOM compounds. However, it is impossible to do this in a rigorous engineering manner without knowing the nature and magnitude of the effects of the NOM on the abilities and capacities of the GAC for target compound removal. Unfortunately, these effects can neither be predicted from any available adsorption theories nor can they be assessed by simple lumped-parameter NOM concentration measurements (e.g. total organic carbon). This is the case because: (i) the water containing the NOM and the target compounds is markedly changed in character once it moves a short distance in the GAC bed; and (ii) the character of the GAC once so contacted is changed from what it was initially. To make the situation even more complicated, the changes in each of these two media

relate to the specific changes that occur in the other as functions of time and position in the FBR. Such changes in turn relate to the chemical composition of the water being treated and to the flow characteristics of the FBR.

ADSORPTION OF NOM

Figure 2 presents a schematic representation of the effects of various parameters that impact the adsorption of NOMs by GAC. More specifically, the graphical representations given in Figure 2 illustrate expected trends in such parameters as functions of pH, an important background water quality control parameter. Variations in pH are

Table 1 | NOM characteristics (after Karanfil *et al.* 1996)

| NOM | Carbon/oxygen contents (%) | | Atomic ratios O/C | Aromaticity (%) | Phenolic acidity (meq/g TOC) | Carboxylic acidity (meq/g TOC) | Weight average MW |
	C	O					
Aldrich HA	50.7	31.4	0.47	57.7	3.6	7.9	4006
Soil HA (IHSS)	58.0	33.7	0.44	50.0	2.8	5.9	6202
Peat HA (IHSS)	56.6	35.4	0.47	47.0	3.5	7.0	5584
Leonardite HA (IHSS)	63.1	31.0	0.37	58.0	4.4	5.5	5867
Suwannee River FA (IHSS)	53.5	41.3	0.58	24.8	3.3	8.1	1920
Laurentian HA	51.9	39.9	0.58	33.4	5.7	8.9	3982
Laurentian FA	45.1	49.7	0.83	28.2	9.3	11.7	2402

known to affect the degree of NOM ionization, its solubility in water and the effective sizes of its various macromolecular constituents. Changes in pH also influence GAC surface charges, which in turn impact the adsorbabilities of charged NOM species. As the pH of a water is lowered, net GAC surface charge becomes more positive, and NOM acidic functional groups become more protonated. As a result, electrostatic interactions between carbon surfaces and charged macromolecules change. The extent to which such changes influence adsorption in any system depends on the distributions of acid functional groups on the sorbent surfaces and sorbate molecules in any particular GAC/NOM system. Protonation of acid groups on NOM also changes its hydrophobicity, and thus may reduce its effective size by inducing coiling or folding of its macromolecular constituents.

The net effect of such complex interactions is that the sorption of NOM species generally decreases with increasing pH, as indicated in part (f) of Figure 2. By presenting two lines that figure is also meant to indicate that the exact pattern of this decreasing trend can vary from one system to another. As qualitative and general as the trends represented in Figure 2 are, they do not necessarily represent the behaviour patterns of all GAC/NOM systems. The trend for GAC surface charge, for example, is an approximation of that expected for the particular GAC

used throughout the studies described in this paper. Thus, no relative effects or scales are implied, and no particular significance should be assigned to the relative magnitudes of the variations depicted.

To provide some quantitative examples of the qualitative effects shown in Figure 2, consider the equilibrium adsorption behaviours of the seven NOMs identified and characterized in Table 1. To characterize equilibrium conditions for this example, we use the following modified Freundlich equation to represent the adsorption isotherm

$$q_e = K_{F,M} \, (C_e/D_o)^n \tag{1}$$

where q_e is the solid phase concentration of NOM at equilibrium expressed as milligrams of total organic carbon (TOC) per gram of GAC, C_e is the corresponding solution phase concentration (mg TOC l^{-1}), D_o is the initial GAC dosage (g l^{-1}), $K_{F,M}$ is a Freundlich 'affinity' parameter for the chemically heterogeneous NOM, and n is related to the magnitude of the adsorption driving force and to the distribution of energy sites on the GAC (Weber and DiGiano 1996). The ratio C_e/D_o is the GAC-dosage normalized residual NOM concentration; that is, the amount of unadsorbed NOM per unit of carbon mass present in the reactors used to collect individual q_e and C_e
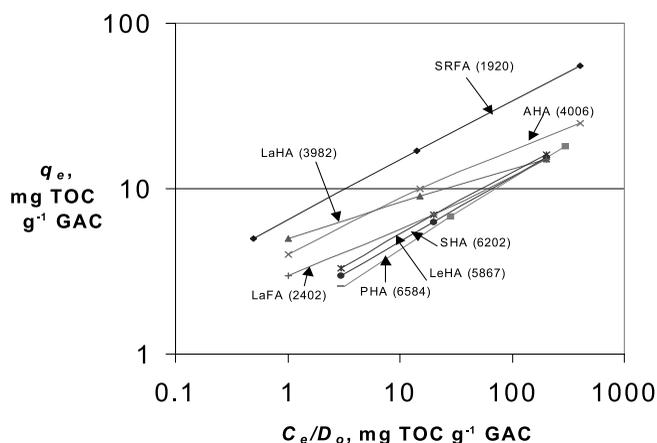
Figure 3 | Humic and fulvic acid sorption isotherms (after Karanfil et al. 1996).

Figure 4 | Laurentian HA component size fractions (after Karanfil et al. 1996).

data points for isotherm plotting and fitting with Equation (1). This modification of the conventional Freundlich equation, which is identical to Equation (1) but does not normalize C_e for D_o, has been found suitable for characterizing the isotherms of heterodisperse polymers.

Both the modified and conventional Freundlich equations have been used in different research projects described in this paper; the modified form given in Equation (1) has been used for the most part in the NOM adsorption equilibrium work described in the first half of the paper. The conventional form was employed in the case study example of preloading effects on target compound removal. Data obtained by Karanfil et al. (1996) for the individual isotherms for the seven NOMs identified in Table 1 are plotted in Figure 3, along with the best fit of the modified Freundlich model to each set of data. Values of $K_{F,M}$ and n for these different NOMs range from 6.6 to 1.7 (mg TOC g^{-1} GAC)$^{1-n}$ and from 0.43 to 0.22, respectively, the relative adsorption capacities of the GAC for the NOMs decline in the order SRFA (1920)>AHA (4006)>LaHA (3982)>LaFa (2402)>LeHa (5867)~SHA (6202) where the quantities in parentheses are the number-average molecular weights of the NOMs determined by size exclusion chromatography.

Figure 4 depicts the different adsorption behaviours of various size fractions of one of the NOMs identified in Table 1, the Laurentian humic acid (LaHA). Values of $K_{F,M}$ and n for the different size fractions of this LaHA
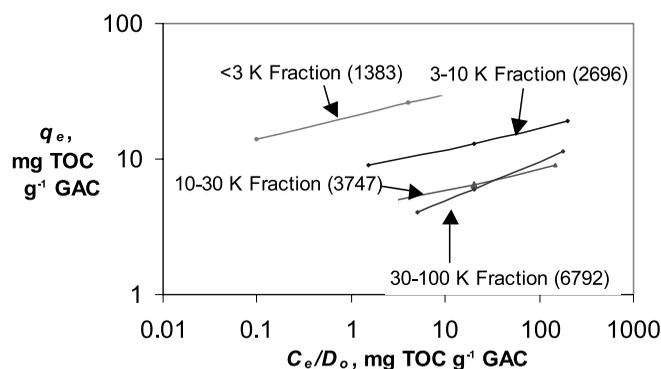
were found to range from 18.9 to 3.5 (mg TOC g^{-1} GAC)$^{1-n}$ and from 0.12 to 0.25, respectively, compared with values of 5.3 (mg TOC g^{-1} GAC)$^{1-n}$ and 0.22 for the whole LaHA. It is clear from Figure 4 that, for the constituents of a given NOM mixture, the relative adsorption capacity of the GAC decreases with increasing molecular size. Figure 3, however, just as clearly indicates that other properties of NOM mixtures are also important determinants of adsorption, as suggested earlier in Figure 2.

To draw the discussion relating to factors affecting NOM adsorption behaviour to a close, Figures 5 and 6 after Karanfil et al. (1998) show the relative effects of three general solution properties on the adsorption of the Laurentian fulvic acid (LaFA) identified in Table 1. Figure 5a and b shows isotherms for adsorption of the LaFA for three different solution pH values and three different ionic strengths, respectively. Figure 6a presents corresponding parametric trends of the ratio $(K_{F,M})_{oxic}/(K_{F,M})_{anox}$ for LaFA and the peat humic acid (PHA) as functions of solution pH, and Figure 6b illustrates the trend of this ratio for LaFA as a function of solution ionic strength.

PRELOADING MECHANISMS

The dual mechanism concept advanced by Carter et al. (1992) involving sequential occupation of high-energy surfaces and subsequent pore blocking as an explanation for
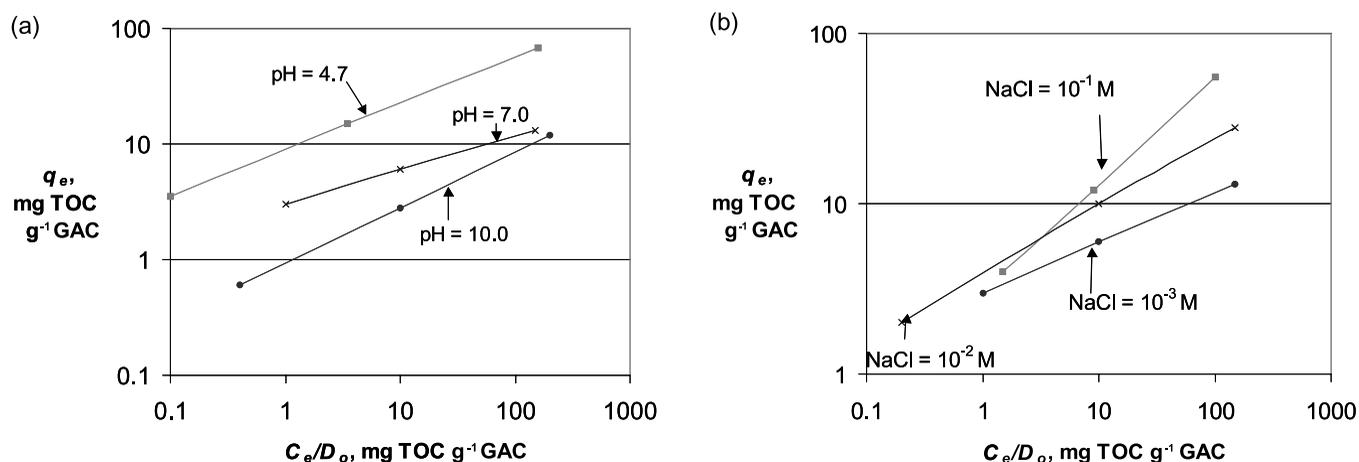
Figure 5 | LaFA isotherms as functions of pH and ionic strength (after Karanfil *et al*. 1998).
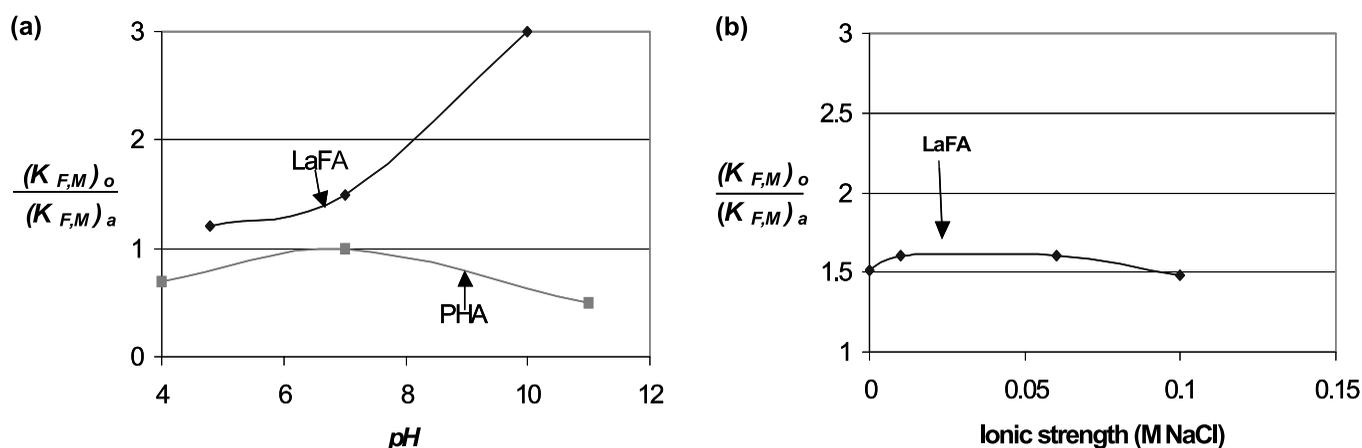

Figure 6 | pH and ionic strength effects on the oxygen sensitivity of Laurentian FA and peat HA sorption (after Karanfil *et al*. 1998).

preloading effects has more or less stood the test of time. This concept derives from observations of changes in the exponent n of the Freundlich isotherm model (modified or otherwise) as a function of increasing time of preloading of GAC in completely mixed batch reactors (CMBRs) and short-bed adsorbers (SBAs). As noted earlier in discussion of Equation (1), the parameter n is representative of the distribution of energy sites on solid adsorbents. The concept is depicted schematically in the series of four panels shown in Figure 7; the n values given in the panels are actual experimental values measured for adsorption of NOM from Huron River water, a raw water source for the city of Ann Arbor, Michigan.

Panel I in Figure 7 represents an initial non-preloaded carbon reference state in which the surfaces and pores are free from NOM. In this state the GAC has highest energy site heterogeneity and lowest n value along with the corresponding hypothetical site energy distribution shown in Figure 7. Panel II depicts early preloading effects, with certain NOM species rapidly moving through the larger pores and occupying the most readily accessible high-energy sites on the GAC. The resulting site energy distribution is thereby narrowed from that of non-preloaded carbon, with losses occurring especially in high-energy regions. This is reflected in a rapid initial increase in n for early preloading. Panel III represents an intermediate
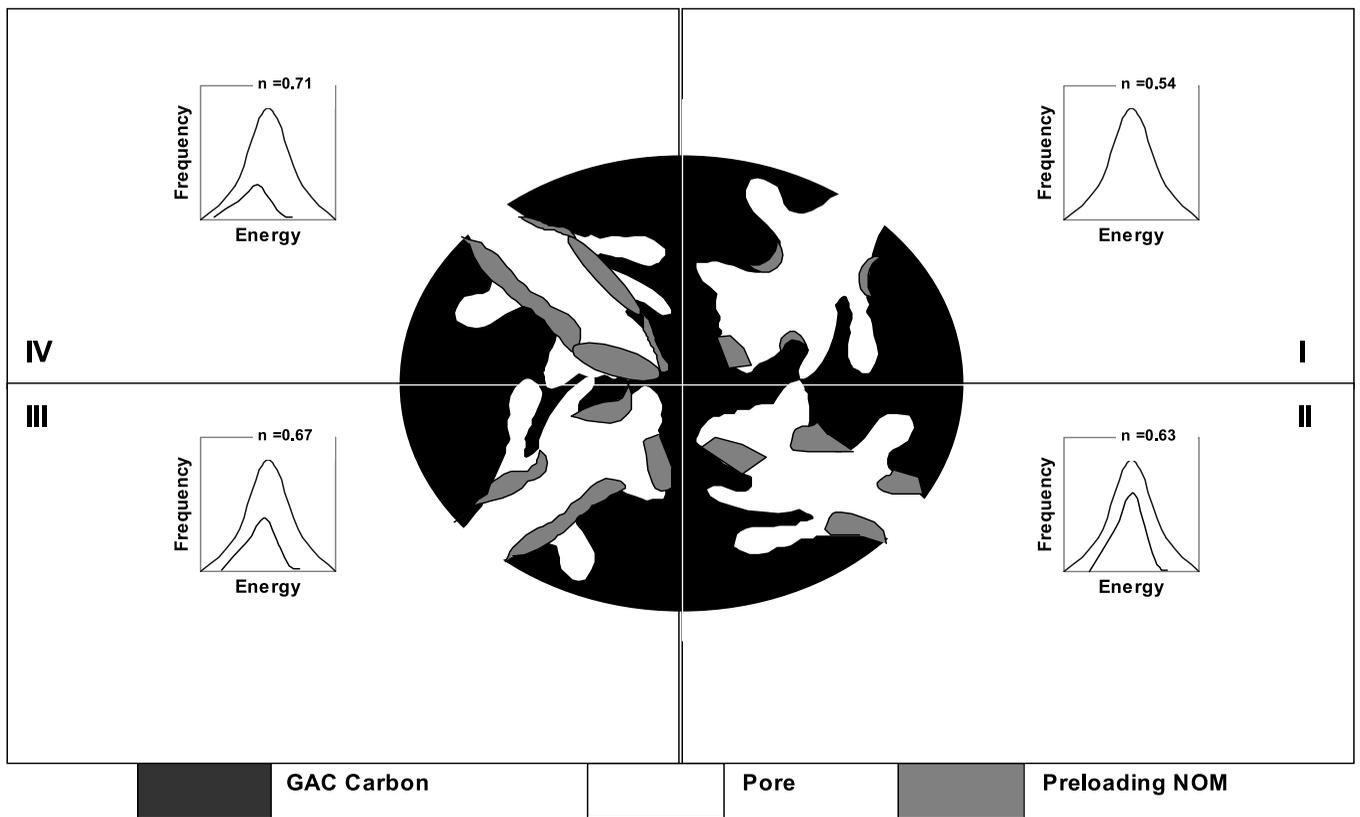
Figure 7 | Schematic representation of preloading mechanisms (after Carter *et al*. 1992).

stage in the preloading process as the smaller pore openings begin to be blocked and the remaining readily accessible high-energy sites are lost.

Losses in numbers of sites then begin to occur more evenly across all energy levels, resulting in a gradual levelling off of K_F (or $K_{F,M}$) and n values at extended preloading times. This plateauing or levelling off of parameter values suggests that most of the readily accessible high-energy sites have been exhausted, and that further decreases in capacity occur more slowly via ongoing pore blockage. Panel IV in Figure 7 represents the state of an extensively preloaded carbon. Primary capacity reduction at and beyond this state is mechanistically attributable principally to pore blockage, and all isotherms tend towards parallel slopes (i.e. equal n values).

The above mechanism is consistent with a distributed reactivity model (DRM) concept advanced to explain the observed sorption behaviours of heterogeneous soils and sediments in subsurface systems (Weber *et al*. 1992). In the context of the present discussion, this model projects a sequential compression of an initially wide distribution of sites having different adsorption energies to a more narrowly distributed range by virtue of an initial and uncontested occupation of higher-energy sites on the GAC by selected NOM moieties, followed by a gradual shifting of the dominant capacity reduction mechanism to one of pore blockage by different NOM constituent species. The concept visualizes complex sorption phenomena as comprising one or more typically linear absorption processes, and one or more typically non-linear adsorption processes. Each absorption and adsorption contribution to the overall process manifests a different level of reactivity. For such situations, the sum of absorptive processes increases with increasing saturation of surfaces and pore volumes by organic matrices.

An initially fresh (non-preloaded) activated carbon accordingly may act to remove organic compounds primarily by high energy and highly non-linear adsorptive mechanisms that exhibit n values much lower than unity. This is shown in panel I of Figure 7. As the carbon is preloaded, however, NOM molecules begin to coat the surfaces of the pores, and perhaps even begin to fill some pore spaces completely, essentially forming an organic phase into which absorption now occurs. Panels II through IV of Figure 7 depict this progression of organic accumulation within the carbon pores. As the organic saturation of the carbon increases, the sorption balance shifts away from surface adsorption mechanisms and more towards absorption or 'partitioning' mechanisms, with corresponding increases in n values. At infinite preloading time, all pore volumes would presumably be filled with NOM organic matrix, and the removal of the target compounds would occur primarily by a nearly linear absorption-like process.

Thus, as a GAC adsorber becomes essentially exhausted with respect to the *specific* removal of a target compound because of a gross overload of NOM, the overall sorption process tends to linear behaviour, yielding a simple equilibrium relationship of the form $q_e = K_D C_e$. At this point the target compound is being removed primarily by absorption into the sorbed NOM rather than by adsorption onto the activated carbon, generally an inefficient way to operate a GAC system.

REMOVAL EFFECTS ON TARGET COMPOUNDS: A CASE STUDY

As noted earlier and depicted in Figure 1, the most common reactor configuration for GAC applications in water and wastewater treatment is that of a fixed-bed reactor (FBR). To illustrate the effects of preloading on FBR adsorption behaviour with respect to target organic compounds we will examine a specific case study based on work by Carter and Weber (1994) involving a water treatment grade carbon (Filtrasorb 400, Calgon Corp., Pittsburgh, Pennsylvania), a common chlorinated solvent target contaminant (trichloroethylene, TCE) and a public

surface water supply source (Huron River water, Ann Arbor, Michigan) having a reasonably representative background NOM level.

FBR MODEL

A pore diffusion model was used for calibration of rate data and simulation of all FBR breakthrough data. The model equations and solutions are based upon earlier work by Crittenden *et al.* (1986). The model was reduced to a set of simultaneous ordinary differential equations (ODEs) in time using the method of orthogonal collocation. The coefficients of the ODEs incorporate the isotherm and rate information provided by the equilibrium parameters K_F (note use of conventional Freundlich model form), n and the rate parameters k_f (external film mass transfer coefficient) and D_p (internal pore diffusion coefficient). The breakthrough simulation was then obtained by calling a general ODE solver for stiff equations (LSODE) to solve the ODEs through a series of time steps until the total run time was met. The validity of this approach and the ability of the pore diffusion model to describe adsorption in fixed beds have been widely demonstrated. The conventional constant parameter version of the pore diffusion model was used for calibration of SBA rate data and for simulation of deep bed adsorber (DBA) data. A second version of the pore diffusion model referred to here as the time-variable parameter model was developed in which each of the isotherm and rate parameters was input as a function of model run time, for example, $K_F = \varphi(t)$. The isotherm and rate parameters were then updated at each time step, resulting in ODE coefficients that changed over the model run time according to the parametric input expressions.

GAC PRELOADING

The general chemical characteristics of the Huron River water (HRW) used for preloading are given in Table 2. This water was collected in one batch, dosed to a level

Table 2 | Huron river water (from Carter and Weber 1994)

Parameter	Value
Total organic carbon (mg l^{-1})	7.4
pH	8.3
Alkalinity (mg l^{-1} as $CaCO_3$)	248
Calcium (mg l^{-1} as $CaCO_3$)	178
Hardness (mg l^{-1} as $CaCO_3$)	260
Ionic strength (mM as NaCl)	6.9
Mol wt of organic matter (amu) (peak weight)	1000–5000 (1860)

Table 3 | Isotherm and rate parameters (from Carter and Weber 1994)

Preloading time	K_F[1]	n[2]	k_f (cm $s^{-1} \times 10^3$)	τ[2]
None	1.4	0.54	3.5	1.2
1 week	–	–	–	–
2 weeks	0.49	0.63	1.4	5.0
3 weeks	0.41	0.67	1.2	8.0
4 weeks	0.29	0.71	1.0	6.0

[1]Based on $q_e = K_f C_e^n$ (with $q_e = (\mu g\ mg^{-1})$ and $C_e = (\mu g\ l^{-1})$)
[2]Dimensionless

of 100 mg l^{-1} with sodium azide, and stored under refrigerated conditions. Immediately prior to its use in both isotherm experiments and column studies the HRW was filtered through a 1.0-μm filter. A GAC of US Standard Sieve Size 30/40 (0.512 mm arithmetic mean diameter) was preloaded with HRW in FBR adsorbers at a nominal surface loading of approximately 6.6 m h^{-1}. The four parallel beds of GAC were preloaded for 1 week, 2 weeks, 3 weeks and 4 weeks, respectively. Breakthrough of TOC was measured as a function of time in each preloading bed. The mass of background NOM loaded onto the 4-week bed was 27 mg TOC g^{-1} GAC.

EQUILIBRIUM STUDIES

Conventional Freundlich isotherm constants for adsorption of TCE from HRW in CMBR systems for the cases of no preloading and preloading for 2, 3 and 4 weeks are presented in Table 3. The data indicate significant loss of equilibrium capacity with increased preloading time with the biggest drop occurring by the end of the second week. K_F values dropped from 1.4 to 0.29 over 4 weeks of preloading. Correspondingly, Freundlich n values increased from 0.54 to 0.71. With respect to rate parameters, indeed all parameters listed, the most significant change occurred in the tortuosity parameter, τ, which

increased from 1.2 to 8.0 in 3 weeks, before declining to 6.0 after 4 weeks.

RATE STUDIES

TCE rate parameters were gathered in the background waters for various levels of preloading using the short-bed adsorber (SBA) technique developed by Weber and Liu (1980). In the pore diffusion model described above the relevant rate parameters are k_f, the film transfer coefficient which characterize mass-transfer resistance across a hydrodynamic boundary layer surrounding a carbon particle, and D_p, the intraparticle pore diffusion coefficient which quantifies TCE diffusion through the liquid contained within internal particle pores. The SBA is designed to be sufficiently short so that virtually immediate solute breakthrough occurs. Thus, for early time data (i.e. before significant intraparticle mass transport occurs), simulations using the pore diffusion model are sensitive only to changes in the film transfer coefficient, k_f. By calibrating only early time data, an explicit determination of k_f is made. Once k_f is determined, it is held constant and the entire SBA breakthrough data set is then simulated by varying D_p until a best fit of the model output to the experimental data is obtained. The pore diffusivity, D_p, is incorporated here in terms of an impedance factor, τ, using the relationship $D_p = D_l/\tau$, where D_l is the free liquid diffusivity of the solute.

EXTERNAL FILM TRANSFER

The parameter values resulting from model calibrations of SBA data are also presented in Table 3. A statistically significant decrease in the external film transfer coefficient with increasing preloading was observed with k_f values dropping from 3.5×10^{-3} to 1.0×10^{-3} cm s^{-1} over 4 weeks of preloading. These findings suggest that preloading may impact diffusion processes on the surfaces of GAC particles. One possible explanation may be that the local fluid viscosity of the film surrounding a particle is increased by the presence of the relatively large molecular weight background organic matter preloaded on the particle surface, resulting in decreased rates of diffusion of TCE across the hydro-dynamic boundary layer. Another possibility is that some effective area for TCE mass-transfer flux into the carbon particle is lost owing to a partial blockage of external pores by preloaded background organic matter.

INTRAPARTICLE DIFFUSION

The values measured for the pore diffusion impedance factor, τ, can be related to changes in resistance to TCE diffusion with preloading. Impedances near unity imply that the total mass diffusion is on the order of that given by the free liquid diffusivity of the solute; that is, the carbon pore spaces are relatively open and free of obstruction. Impedances several factors greater than unity indicate that intraparticle diffusion of TCE is greatly restricted by the presence of preloaded background organic matter in the carbon pores.

The impedance factors presented in Table 3 can be interpreted within the above framework. For unpreloaded carbon, the τ value was 1.2. This indicates that significant intraparticle transport of TCE occurred in the unpreloaded carbon. For all of the Huron River water preloaded carbons, however, the impedance factors were found to be significantly greater than unity. Values of τ between 5 and 10 indicate that intraparticle diffusion was 5–10 times slower than that for TCE in pure water. This suggests that preloaded background organic matter posed

a significant resistance to TCE diffusion within the carbon pores. The high upper confidence limits of τ values greater than 3 were caused by an increasing insensitivity of the model to this parameter as intraparticle impedance became large.

TIME-VARIABLE PARAMETER MODEL SENSITIVITY

To assess the relative contribution of each isotherm and rate parameter to the overall shape of the breakthrough profile in the time-variable parameter modelling method, each parameter was varied individually from a constant baseline condition. The baseline case was produced by simulating breakthrough in the bench-scale fixed-bed adsorber using unpreloaded carbon isotherm and rate parameters based on the CMBR isotherms and corresponding SBA rate parameters for Huron River water over a period typical of the run times used in this research. For the time-variable parameter simulations, a non-linear regression software package (SYSTAT, Systat, Inc., Evanston, Illinois) was used to obtain continuous functions of the isotherm and rate parameter values with preloading time that were incorporated into the model. Exponential and linear expressions, which give parameter values as functions of pre-loading time, were fitted to the isotherm and rate data given in Table 3. The resulting equations for the Huron River water CMBR-based system are:

$$K_F(t) = 1.4 \, e^{0.44t} \tag{2}$$

$$n(t) = 0.042 \, t + 0.54 \tag{3}$$

$$k_f(t) = 0.0034 \, e - 0.37 \, t \tag{4}$$

$$\tau(t) = 7.2 - 6.1 \, e - 0.70 \, t \tag{5}$$

In the sensitivity analysis, parameter expressions were varied one at a time from the baseline condition, and the resulting simulations are plotted in Figure 8.

Examination of the breakthrough curves presented in Figure 8 reveals that the greatest impact on this profile was
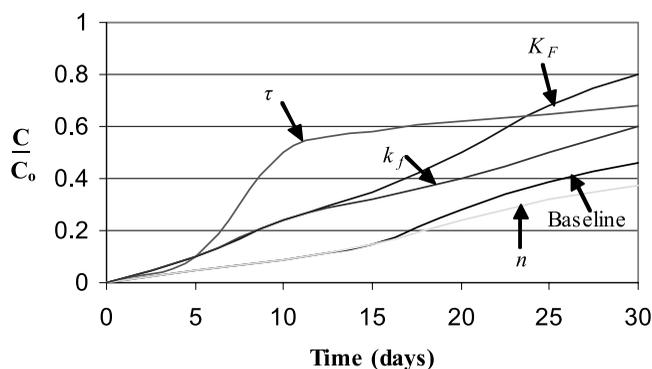
Figure 8 │ Time-variable modelling sensitivity to input parameters (after Carter and Weber 1994).

caused by changes in Freundlich K_F and impedance factor values. Decreases in the Freundlich K_F value caused a sharp rise in the latter portion of the breakthrough profile. This rapid rise was probably due to the coupled effect of an accelerated approach to equilibrium as the carbon became loaded with solute and a simultaneous lowering of capacity as K_F values declined. The effect produced by increasing impedance largely impacted intermediate time data. The decreasing rate of uptake of solute by the carbon as increased promoted faster breakthrough of solute. Smaller impacts were noted for variations in Freundlich n and film transfer coefficient (k_f) values. Increases in n actually produced a decrease in the breakthrough profile in the sensitivity analysis. This result is an artefact arising from changing τ while holding K_F constant which, in effect, results in an apparent increase in isotherm capacity. In actuality, increases in n are always accompanied by decreases in K_F. The notable feature of the curve resulting from the n variation is that the effect is relatively small, although it still would provide some offset to the impacts of declining K_F values.

The range of impact of decreasing film-transfer coefficient (k_f) values is surprising; changes in this parameter are significant over the entire period simulated. The mechanistic nature of this parameter would suggest that k_f variations would primarily impact early time data and diminish thereafter (Weber and Liu 1980). This behaviour may be due to the relatively large drop in k_f (~70%) that was seen with these data. It may also relate to the

portion of the breakthrough curve simulated, which reflected only about 50% breakthrough. As breakthrough approaches completion, the impact of changes in kf may very well decrease. In the sense that the two equilibrium parameters of the Freundlich isotherm model are by nature interrelated, one might question the significance of sensitivity analyses in which each is varied separately. While the parameters are in fact interdependent in both physical significance and their co-determination in regressions of isotherm data, each also has a very specific inference with respect to the dynamics operative in GAC preloading by, and/or direct competitive adsorption of NOM with, target solutes. The relative sensitivity of the model to each is therefore instructive.

FIXED-BED ADSORBER EXPERIMENTAL DATA AND MODELLING RESULTS

Breakthrough data were obtained for TCE in the background water over a period of 4 weeks using the bench-scale fixed-bed adsorber system operated at the same flow rate (6.6 m h^{-1}) as used in the preloading of the adsorbers. This then allowed the use of *time dependent* rather than *mass dependent* preloading model parameters. In this context, it is important to note that, for the approach described here, the preloading experiments should be conducted at the same flow rates and with the same background water(s) as anticipated for full-scale operating conditions. For each set of fixed-bed breakthrough data, both constant parameter and time-variable parameter simulations were made using the pore diffusion model. For the constant parameter simulations, parameter sets obtained at each of the individual preloading levels were used in the pore diffusion model to simulate bench-scale fixed-bed adsorber TCE breakthrough behaviour. The time-variable parameter pore diffusion model was used to ascertain whether better predictive capability could be achieved if equilibrium and rate parameters are made to vary with time of operation.

The data and the constant parameter predictions for TCE breakthrough in the Huron River system are presented in Figure 9. The data are bracketed by predictions from the unpreloaded carbon and 2-week preloaded
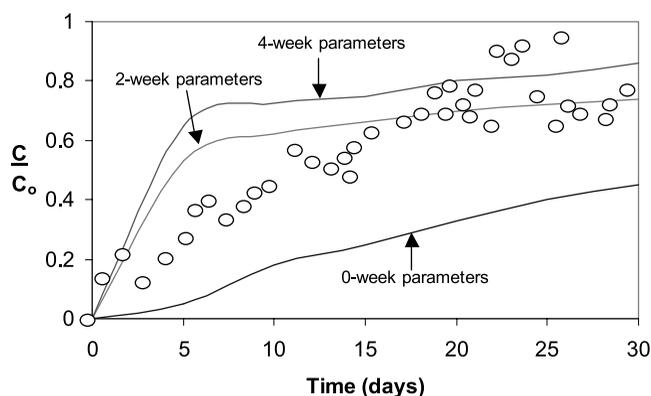
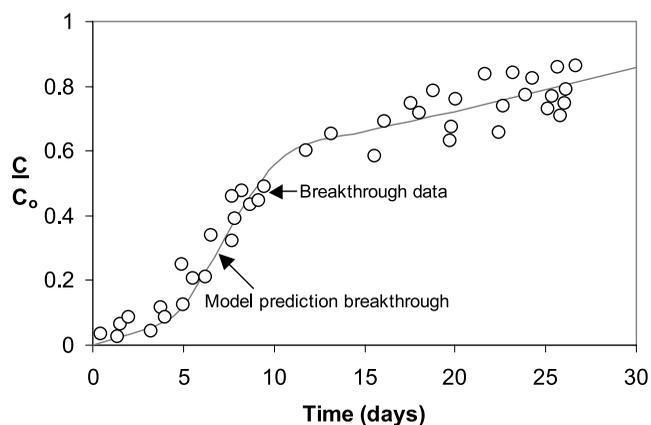**Figure 9** | Constant parameter predictions and data for TCE breakthrough (after Carter and Weber 1994).

Figure 10 | Time-variable model predictions and data for TCE breakthrough (after Carter and Weber 1994).

this region, while decreasing capacity (as measured by K_F) significantly impacted later time data. Individually, the unpreloaded carbon parameters estimated too much capacity and intraparticle mass transport, while the 2-week parameters gave levels that were too much reduced. With the time-variable parameter model, the impacts due to preloading appear to be apportioned over the run time in a manner representative of the changes in equilibrium capacity and rates of adsorption that occurred in the bed. Thus, the transition from low to high values for τ caused an acceleration of breakthrough owing to higher mass-transfer resistances when capacity was high over intermediate time data. At later times, when intraparticle resistance reached a limiting value, the enhanced upward trend of the breakthrough data was continued as the K_F capacity effects became more significant.

For systems in which adsorption rate and equilibrium parameters do not change markedly over run time, fixed-bed adsorber breakthrough data may be adequately simulated using a constant-parameter modelling approach and some representative 'average' parameter set.

Indeed, fixed-bed adsorber removal of target organic compounds in a background organic matter matrix has been successfully modelled using a single set of isotherm and rate parameters obtained on unpreloaded carbons (Smith and Weber 1989; Summers *et al*. 1989; Speth and Miltner 1989). These studies either used concentrations of target compounds at least an order of magnitude higher than those used in this work or were conducted over significantly shorter periods of time (a few days). Enhanced target compound adsorption rates from higher concentrations or a reduced time for preloading from the shorter run times would reduce the scope of any parameter changes which might occur, resulting in reasonably accurate fixed-bed adsorber modelling with a single parameter set. Conversely, in the time-variable-parameter modelling approach necessary for accurate predictions of TCE breakthrough data for the Huron River water, parameters varied a great deal over the period of study. Thus, a time-variable parameter modelling approach may be best suited when target compound concentrations are low relative to background organic matter and fixed-bed adsorber run times are long enough for significant preloading to occur.

parameters; the unpreloaded carbon set over-predicted removal and the 2-week set under-predicted removal. The close proximity of the 4-week CMBR set to the 2-week set prediction in Figure 9 suggests that preloading by the Huron River water was beginning to level off. Predictions resulting from use of the time-variable parameter expressions are shown in Figure 10. The predicted curve exhibited a sharper breakthrough profile, with more removal of TCE at early times.

The sensitivity analysis presented in Figure 8 can provide insight into the reasons why a time-variable parameter approach better fits the data. Intraparticle pore diffusion resistance was shown to primarily influence intermediate time data, causing a rapid breakthrough over

SUMMARY

The HRW case study breakthrough data presented and discussed in the preceding section were observed to lie between model simulations based on parameters derived from unpreloaded carbon data and those based on preloaded carbons. This suggests that competition posed by background organic matter to target solute adsorption will be neither simultaneous nor preloading in nature during practical GAC system operations. For background waters that do not cause extensive changes in parameter values with preloading, the use of parameters obtained on either a non-preloaded or intermediately preloaded carbon may provide reasonable simulations of anticipated fixed-bed adsorber behaviour. An observation that the operational intraparticle diffusion coefficient for the target solute in a preloaded carbon sample is not substantially diminished from its free liquid value would be an indication that this may be an appropriate approach. In cases where isotherm and rate parameters are observed to change significantly with preloading over the time period of interest, the time-variable parameter approach is the likely candidate for accurate predictions. An intraparticle diffusion coefficient several factors lower than free liquid diffusion of the target solute would be an appropriate indicator of this condition.

The tendency observed in the Huron River water data for preloading effects to approach limiting values suggests a third modelling regime; that is, the use of one set of constant parameters representative of a highly preloaded state. This approach was investigated by simulating breakthrough from a 1-m long column over a period of 1 year by both time-variable and constant parameter methods, using parameters representative of the preloading effects found in the Huron River treatment system. In the time-variable simulation, parameters were allowed to vary over the first 4 weeks of preloading in the same fashion as for the shorter time predictions discussed earlier. After 4 weeks of simulation, the values were fixed at those levels. In the constant parameter approach, the parameters were set at the 4-week preloading level over the entire simulation time. A breakpoint of 10% of influent concentration was chosen for comparison purposes. The constant parameter modelling approach gave a time to breakpoint of 107 days while the time-variable parameter simulation predicted 143 days. The 'extra' capacity afforded by the time-variable parameter simulation over the first 4 weeks of preloading (i.e. before the model parameters became equivalent) is surprisingly large given the 1-year simulated run time. Nonetheless, use of a constant parameter approach with parameters representative of an extensively preloaded state would, in practice, provide a conservative estimate of overall adsorber capacity that would be acceptable for preliminary design calculations.

While three possible modelling regimes have been proposed, the uniqueness of each adsorption system precludes determination of which predictive approach is most appropriate without performing some isotherm and rate parameter measurements. This is essentially the message given in the Abstract, above, regarding the nature of the predictive modelling methodology described herein: a blend of mechanistic modelling and empirical parameter estimation. Because of the heterogeneous characteristics of background organic matter, the amount of TOC preloaded onto a given mass of carbon is not a reliable indicator of the resulting preloading effect on adsorption of a target compound. Moreover, characteristics of the solute itself will influence the impact of preloading on its adsorption equilibria and rates. The impact of preloading may be more severe for a weakly hydrophobic compound such as TCE than for a highly hydrophobic solute that would tend to sorb to preloaded organic matter. Exact identification of the mechanisms of the preloading process, assessment of key properties that can be used to quantify the preloading potential of a background organic material, and an understanding of how solutes interact with preloaded organic matter in the preloaded state are areas requiring further research.

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NOMENCLATURE

n	Freundlich isotherm exponent*
K_D	linear phase distribution coefficient (l mg^{-1} or µg)
K_F	Freundlich isotherm capacity factor*
$K_{F,M}$	modified Freundlich isotherm capacity factor**
k_f	film mass transfer coefficient (cm s^{-1})
C_e	equilibrium solution-phase concentration (mg or µg l^{-1})
D_o	initial sorbent dosage (g l^{-1})
D_P	pore diffusion coefficient (cm^2 s^{-1})
D_l	free liquid diffusion coefficient (cm^2 s^{-1})
q_e	equilibrium solid-phase concentration (mg or µg g^{-1})
$\varphi(x)$	function of x
τ	diffusion impedance (dimensionless)
*	units dependent upon units of q_e and C_e
**	units dependent upon units of q_e, C_e and D_o

ABBREVIATIONS

CMBR	completely mixed batch reactor
DBA	deep bed adsorber
FBR	fixed bed reactor
GAC	granular activated carbon
HRW	Huron River water
NOM	natural organic matter
ppb	parts per billion
ppm	parts per million
SBA	short bed adsorber
TCE	trichloroethylene
TOC	total organic carbon

REFERENCES

Carter, M. C. & Weber, W. J. Jr 1994 Modeling adsorption of TCE by activated carbon preloaded by background organic matter. *Environ. Sci. Technol.* **28**(4), 614–623.

Carter, M. C., Weber, W. J. Jr & Olmstead, K. P. 1992 Effects of background dissolved organic matter on TCE adsorption by GAC. *J. Am. Wat. Wks Assoc.* **84**(8), 81–89.

Crittenden, J. C., Hutzler, N. J., Geyer, D. G., Oravitz, J. L. & Friedman, G. 1986 Transport of organic compounds with saturated groundwater flow: Model development and parameter sensitivity. *Wat. Resour. Res.* **22**, 271–284.

Karanfil, T., Kilduff, J. E., Schlautman, M. A. & Weber, W. J. Jr 1996 Adsorption of organic macromolecules by granular activated carbon. 1. Influence of molecular properties under anoxic solution conditions. *Environ. Sci. Technol.* **30**(7), 2187–2194.

Karanfil, T., Kilduff, J. E., Schlautman, M. A. & Weber, W. J. Jr 1998 The oxygen sensitivity of organic macromolecule sorption by activated carbon: Effects of solution chemistry. *Wat. Res.* **32**(1), 154–164.

Smith, E. H. & Weber, W. J. Jr 1989 Evaluation of mass transfer parameters for GAC adsorption from complex organic matrices. *Environ. Sci. Technol.* **23**, 713–722.

Speth, T. F. & Miltner, R. J. 1989 Effect of preloading on the scale-up of GAC microcolumns. *J. Am. Wat. Wks Assoc.* **81**(4), 141–148.

Summers, R. S., Haist, B., Koehler, J., Ritz, J., Zimmer, G. & Sontheimer, H. 1989 The influence of background organic matter on GAC adsorption. *J. Am. Wat. Wks Assoc.* **81**(5), 66–74.

Weber, W. J. Jr & DiGiano, F. A. 1996 *Process Dynamics in Environmental Systems*. Wiley-Interscience, New York.

Weber, W. J. Jr & Liu, K. T. 1980 Determination of mass transport parameters for fixed-bed adsorbers. *Chem. Engng Communs* **6**, 49–60.

Weber, W. J. Jr, Katz, L. A. & McGinley, P. A. 1992 A distributed reactivity model for sorption by soils and sediments: 1. Conceptual basis and equilibrium assessments. *Environ. Sci. Technol.* **26**(10), 1955–1962.