

"Simulating The Performance of Fixed-Bed Granular Activated Carbon Adsorbers:  
Removal of Synthetic Organic Chemicals in the  
Presence of Background Organic Matter"

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## **ABSTRACT**

Granular Activated Carbon (GAC) adsorption is an effective treatment technology for the removal of Synthetic Organic Chemicals (SOCs) from drinking water supplies. This treatment process can be expensive if not properly designed. Application of mathematical models is an attractive method to evaluate the impact of process variables on process design and performance. Practical guidelines were developed to select an appropriate model framework and to estimate site-specific model parameters to predict GAC adsorber performance. Pilot plant and field scale data from 11 different studies were utilized to investigate the effectiveness of this approach in predicting adsorber performance in the presence of background organic matter (BOM). These data represent surface and ground water sources from four different countries. The modeling approach was able to adequately describe fixed-bed adsorber performance for the purpose of determining the carbon usage rate and process design variables. This approach is more accurate at predicting bed life in the presence of BOM than the current methods commonly used by practicing engineers.

## INTRODUCTION

Granular activated carbon (GAC) adsorption is an effective treatment technique for removing synthetic organic chemicals (SOCs) from surface and groundwaters, but GAC may be an expensive process if not properly designed. The design of GAC adsorbers requires the proper selection of the following variables: type of adsorbent, empty bed contact time (EBCT), and bed configuration (e.g., beds in series or parallel operation). Present design information is obtained from rapid small scale columns (RSSCTs), vendor experience and pilot plant studies. RSSCTs and pilot investigations can be time consuming and expensive, especially if they are not properly planned. An additional or complementary approach involves the use of mathematical models to predict process performance and select the optimum process design. Mathematical models can be used to: (1) assess the preliminary design and economic feasibility of using adsorption processes by estimating GAC usage rates, (2) plan the scope of RSSCT and pilot plant studies, and (3) interpret RSSCT and pilot plant results.

The main obstacle in using mathematical models is that they require site-specific parameters that can only be obtained through a number of bench-scale experiments. Furthermore, sufficient knowledge of various adsorption model options is required for a designer to select appropriate adsorption models and the sequence of the model application to predict the adsorber performance in removing SOCs under field conditions. Hence, this paper presents an approach that will: 1) estimate site-specific adsorption

model parameters; and 2) select appropriate models to predict the adsorber performance in removing SOC<sub>s</sub> under specific field conditions.

### **Background Organic Matter (BOM) Effects on SOC Adsorption**

Factors that influence the effect of BOM on SOC adsorption include BOM preloading time, adsorbent type, background water constituents and physical properties, and solute type, each of which will be discussed in this section.

#### **BOM Preloading Time**

The solid-phase solute concentration (amount of solute adsorbed onto the adsorbent) is assumed to be in equilibrium with the liquid-phase solute concentration at the adsorbent surface. The Freundlich single solute isotherm is used to estimate this equilibrium:

$$q_e = KC_e^{1/n} \tag{1}$$

Where:

$C_e$  = the equilibrium concentration of the solute in the liquid at the particle interface  
( $\mu\text{mole/L}$ )

$q_e$  = the equilibrium solid-phase mass of solute per mass of adsorbent ( $\mu\text{mole/g}$ )

$K$  = Freundlich coefficient ( $\mu\text{mole/g}[\text{L}/\mu\text{mole}]^{1/n}$ )

$1/n$  = Freundlich exponent accounting for adsorption site energy distribution  
(dimensionless)

It is important to note that the values for the experimentally determined Freundlich parameters  $K$  and  $1/n$  are solute and adsorbent specific.

Adsorbed mass ( $q_e$ ) versus aqueous phase concentration ( $C_e$ ) can be plotted on a log-log scale in linear form, on which the y-intercept equals the Freundlich  $K$ , and the slope is equal to the Freundlich  $1/n$ . As seen in Figure 1, the Freundlich  $K$  value decreases with increasing BOM preloading time for the adsorption of trichloroethylene (TCE) onto preloaded GAC (Zimmer et al, 1988). Results from other research demonstrate that adsorption isotherms of other SOCs on preloaded GAC produce parallel lines to the original single solute isotherm (Sontheimer et al, 1988, Benz 1989, Summers et al 1989, Hand et al 1989, Munz et al 1990, Crittenden et al 1991, Haist 1991, Ulmer 1998).

Kilduff (1998) confirmed the reduction in Freundlich  $K$  over time and also noted the phenomenon of an initial increase in Freundlich  $1/n$  during adsorption at low loadings of the preloading compound, explained by high energy sites being filled preferentially by BOM. However, at higher levels of preloading, site energy distribution shifted even more to lower energy sites, reducing average site energy and adsorption capacity. At this point, Freundlich  $1/n$  becomes constant and  $K$  is reduced with increased loading. More research should be performed to understand the early stage of preloading. However, because BOM is available in such high quantities in surface and ground waters (as

compared to the concentrations of micropollutants for GAC removal), BOM preloading results in an isotherm that is parallel to the original single solute isotherm, but lower on the y-axis, or with a decreased Freundlich K value. Thus, this model accounts for BOM preloading by reducing the Freundlich K of the adsorbate.

### **Influence of Adsorbent Type**

Zimmer et al (1988) compared the effect of BOM preloading time on three different carbon types and found that, for a specific BOM and SOC the effect of preloading time varied between adsorbents.

Carter et al (1992) examined the adsorption of TCE preloaded GAC of different mesh sizes, which are a function of the particle diameter. Initially, mesh size mattered over a period of less than 4 weeks. However, carbon adsorbers used in drinking water treatment typically operate for much longer periods of time, on a scale of months to years, where different mesh carbons begin to approach the same behavior. Due to the relative magnitude of internal surface area as compared to external surface area on GAC particles, it is expected that mesh size will not affect adsorption unless it does so by greatly reducing the intraparticle diffusion path in cases where diffusion is the dominant adsorption mechanism.

Li et al (2003) examined influence of PAC pore size distribution and BOM molecular weight on the pore blockage effects of BOM on atrazine adsorption. Comparing the adsorption behavior of atrazine onto BOM preloaded PACs, the authors found that PAC

with larger fractions of mesopores (20-500 Å) and secondary micropores (8-20 Å) displayed less pore blocking effects from BOM than compared with PAC that had a smaller fraction of such pores.

### **Influence of Water Type and Solution Chemistry**

To understand how BOM effects SOC adsorption, it is important to first understand the adsorption behavior of BOM. Kilduff, Karanfil, and Weber (1996) observed that increases in ionic strength (IS) cause a reduction in the molecular size of humic molecules in solution by causing the macromolecules to coil, allowing them to enter smaller pores than they would have access to at their greater sizes. Further research by Kilduff and Karanfil (2002) examined the question of how solution chemistry effects SOC uptake. GAC uptake of TCE was found to decrease with increasing ionic strength (IS) due to an increased adsorption of dissolved organic matter (DOM) during the preloading at higher IS, resulting in less sites available for the subsequent TCE adsorption. An important conclusion here is that the chemistry of a solution can influence the physical characteristics of the adsorbates.

Molecular weight of BOM also influences its adsorption behavior. Fettig (1985) showed that when the adsorption behavior of BOM fractions of molecular weight less than 600, from 600 to 3000, and greater than 3000 were compared; the lowest molecular weight BOM fraction adsorbed the strongest, displaying the steepest isotherm, and the largest molecular weight fraction displayed the most shallow isotherm slope.

Kilduff, Karanfil, and Weber (1998) showed that GAC loaded with humic substances of molecular weight greater than 3,000 adsorbed similar TCE amounts as virgin GAC; while GAC preloaded with humic substances of molecular weight less than 3,000 adsorbed less TCE than the virgin GAC. As an explanation for the different effects of the two molecular weight classes of BOM, the authors suggested that lower molecular weight BOM could occupy the portion of the GAC that contained smaller pores, of diameter less than 10 Å, which the larger molecular weight BOM could not reach. Additionally, when mixed fractions of low and high molecular weight BOM were exposed to the GAC, those mixtures with a greater fraction of BOM of molecular weight less than 3,000 influenced TCE adsorption the greatest.

Research by Li et al, (2003) examined the molecular weight distribution of BOM adsorbed onto PAC, and found that (on a scale of molecular weights from zero to 2000) BOM within the molecular weight range of 200-700 Daltons was responsible for most of the pore blocking that caused the subsequent reduction in adsorbent capacity for SOCs.

Solution chemistry, including the effects of ionic strength, dissolved oxygen concentration, and BOM molecular weight fractionation, influences how BOM preloading impacts subsequent SOC adsorption. Thus, on similar adsorbents, the same SOC may show different adsorption behavior in the presence of different background waters. Figure 2 shows how the Freundlich K of TCE varies with preloading time in the



presence of the five different background waters (three surface and two ground water) included in the model.

### **Influence of Solute Type**

Matsui et al (2002) examined the adsorption of a hydrophobic pesticide (simazine) and a hydrophilic pesticide (asulum) onto GAC preloaded with BOM. It was shown that lower molecular weight BOM (of a size to pass through an ultra filtration membrane) had a greater impact on simazine (hydrophobic pesticide) adsorption than high molecular weight BOM. However, whether BOM could pass through UF did not affect asulum (hydrophilic pesticide) adsorption. That is, asulum adsorption was reduced regardless of the molecular weight of BOM. Thus, the impact of BOM preloading on subsequent pesticide adsorption varied between chemicals of different hydrophobicities. The model accounts for the effects of BOM preloading by chemicals as a class. Nine classes of chemicals are provided for in the model, as discussed later in the paper.

## **MATERIALS AND METHODS: MODELING APPROACH AND PARAMETER**

### **ESTIMATION METHODS**

A modeling approach was developed to predict the effluent concentration profiles for SOCs leaving a fixed-bed adsorber. The ultimate goal is to predict the removal of SOCs from a variety of water matrices containing both SOCs and background organic matter (BOM). To date, SOC and BOM interactions in fixed beds have been found to be site-specific and impact adsorber performance (Sontheimer et al, 1988). The development of the approach will continue as additional information on SOC and BOM interactions

provides better insight into model parameter selection. Accordingly, the practical guidelines described herein may be considered a work in progress, which can easily be updated as new information on SOC and BOM interactions becomes available. The approach described herein brings together a collection of models that describe adsorption equilibrium (thermodynamic models) and the transport of SOCs in a fixed-bed (column models) in a logical fashion.

### **Fixed Bed Models**

The pore and surface diffusion model (PSDM) is a comprehensive mass transfer model that includes the mass transfer mechanisms shown in Figure 3. The pore diffusion model (PDM) includes only the contribution of pore diffusion to the intraparticle mass flux, and is the actual model utilized when BOM is present. Mass balances for the mobile fluid and stationary adsorbent phases for the models results in two partial differential (PDEs), one for the liquid-phase mass balance and the other for the intraparticle phase. The development and solution of the equations for the PSDM, PDM, and surface diffusion model (SDM), are given by Friedman (1985), Crittenden et al (1986), Sontheimer et al (1988), and Hand et al (1984).

### **Fixed-Bed Model Parameter Estimation**

The following recommendations are in no way the last word on fixed bed model parameter estimation. One inherent problem with the mass transfer models is that diffusion interactions are described without cross diffusion coefficients. Obtaining a complete set of diffusion coefficients including diffusion interaction is a formidable task.

Moreover, when BOM interactions are considered, it may be impossible to predict diffusion and equilibrium interactions. Accordingly, diffusion and equilibrium interactions are considered in an empirical fashion as described below. They are based on several hundred model-data comparisons; and, as more experience is obtained in determining model parameters, improvements may be expected.

### **Equilibrium parameters for mass transfer models.**

The solid-phase solute concentration (amount of solute adsorbed onto the adsorbent) is assumed to be in equilibrium with the liquid-phase solute concentration at the adsorbent surface. The Freundlich single solute isotherm is used to estimate this equilibrium, given previously (as Equation 1).

Unidentified background organic matter (BOM) present in surface and ground waters reduces the GAC capacity for SOCs (Sontheimer et al, 1988, Zimmer et al 1988, Haist 1991, Benz 1989, Summers et al 1989, Hand et al 1989, Munz et al 1990, Crittenden et al 1991). These results and others demonstrate that parallel lines to the original isotherm description are obtained for surface and ground waters, as discussed previously.

Accordingly, the reduction in column capacity for individual SOCs can be represented as a reduction of the Freundlich capacity parameter,  $K$  (Zimmer et al, 1988) in fixed bed calculations, with no change modeled in the Freundlich  $1/n$  value for a given solute. The following empirical equation is used to obtain the Freundlich capacity parameter that describes the column capacity for SOCs in the presence of BOM (Sontheimer et al, 1988):

$$\frac{K(t)}{K} = 0.01 * [A1 - A2 * t + A3 * \exp(-A4 * t)] \quad (2)$$

Where:

$K(t)$  = the Freundlich coefficient ( $\mu\text{mole/g}[\text{L}/\mu\text{mole}]^{1/n}$ ) of a solute within a specific water matrix containing BOM, at time (t) of exposure to the BOM

t = the adsorber operation time (days)

A1, A2, A3, A4 = empirical kinetic constants specific to a given SOC, water matrix, and GAC type.

Table 1 summarizes the empirical constants (Equation 2) for trichloroethene (TCE), for the five different water matrices and two GAC types available within the current model. The five water choices consist of two surface waters, Portage Lake (Houghton, MI, DOC=1.6mg/L) and Rhine River (where the Rhine water represents a surface water with significant anthropogenic inputs, DOC=2.25mg/L), and three ground waters (Houghton, MI, DOC=1.5mg/L; Wausau, WI, DOC=8.1mg/L; and Karlsruhe, Germany, DOC=0.7mg/L). Figure 2 shows a graph of the reduction in Freundlich K for TCE with time in each of the five background water matrices.

A general relationship between column capacity reduction and the K and 1/n values of single solute isotherms for a variety of SOCs has yet to be developed (Zimmer et al 1988, Sontheimer et al, 1988, Benz et al 1989). However, once a background water matrix is chosen from the five available, the reduction in Freundlich K for TCE in that water can be estimated. The model includes Freundlich K reduction factors for nine chemical groups,

including halogenated alkanes, halogenated alkenes, trihalomethanes, aromatics, nitro compounds, chlorinated hydrocarbons, phenols, polynuclear-aromatics and pesticides, as shown in Table 2, and applied in the equation below (Bhuvendralingam, 1992).

$$\frac{K(t)}{K} = B_1 \times \left[ \frac{K(t)}{K} \right]_{\text{TCE}} + B_2 \quad (3)$$

The parameters in Table 2 were determined from isotherms conducted on Calgon F-100 GAC pre-exposed to Karlsruhe (Germany) groundwater, and strictly speaking they are only valid for that water. Thus, it is assumed that relative reductions observed between the various classes of SOCs and TCE are similar for other waters. Accordingly, the impact of BOM on column capacity can be determined from Tables 1 and 2 for a variety of compounds and waters by applying first equation 2 and then equation 3. This approach for determining the impact of BOM on column capacity has resulted in reasonable predictions of breakthrough curves (Zimmer et al, 1988; Bhuvendralingam 1992, Alben et al, 1992).

Concentration of the micropollutant is known to have very little impact on the reduction in carbon capacity for the SOC due to the presence of BOM. It can be calculated from the data shown in Figure 3 that for TCE adsorbed onto F-400 carbon in the presence of groundwater, at 10 µg/L there is a 99% reduction in carbon capacity and at 1000 µg/L there is a 97.6% reduction on carbon capacity (Baldauf and Zimmer, 1986). In this case, over the range of SOC concentrations of concern in drinking water treatment, there was a less than 2% difference in the reduction of carbon capacity due to the presence of background NOM. Thus, the concentration of the micropollutant in the presence of BOM is not treated as a factor which influences the Freundlich K values.

### External mass transfer coefficients for mass transfer models.

External mass transfer coefficients are estimated from this correlation (Gnielinski 1978):

$$k_f = \frac{(1 + 1.5(1 - \varepsilon))\phi D_\ell}{2R} \left[ 2 + 0.644 Re^{1/2} Sc^{1/3} \right] \quad (4)$$

in which,

$$D_\ell = \frac{13.26 * 10^{-5}}{\left[ \frac{1}{d} \right]^{1.4} V_b^{0.589}} \quad (5)$$

$$Re = \frac{2 r_\ell R V}{e \eta} \quad (6)$$

$$Sc = \frac{\eta}{r_\ell D_\ell} \quad (7)$$

in which,  $k_f$  is the liquid phase mass transfer coefficient (cm/sec);  $\varepsilon$  is the fixed-bed void fraction,  $R$  is the adsorbent particle radius (cm);  $\phi$  is the adsorbent particle shape correction factor (Sontheimer et al, 1988);  $D_\ell$  is the liquid diffusivity of the SOC (cm<sup>2</sup>/sec);  $\eta$  is the viscosity of water (centipoise);  $\rho_w$  is the density of water (g/cm<sup>3</sup>);  $V$  is the superficial loading velocity (cm/sec); and  $V_b$  is the molar volume of the SOC at the boiling point temperature (cm<sup>3</sup>/mol). The value of  $\phi$  depends on how  $R$  is determined. If the average value of  $R$  is determined by spatial analysis the value of  $\phi$  is between 1.1 and 1.4 for GACs (Sontheimer et al, 1988). If  $R$  is obtained from a sieve analysis, no shape factor (sphericity) is required because most GAC particles tend to be cylindrical and small values of  $R$  will be obtained. In most cases, intraparticle diffusion controls the adsorption

rate and  $\phi$  will be set at a value of 1. The model allows differing values of  $\phi$  to be used. However, for all model runs presented herein, a value of 1 was used.

### **Intraparticle mass transfer coefficients for mass transfer models.**

Figure 4 shows that intraparticle mass transfer can occur by either surface or pore diffusion. Surface diffusion coefficients are calculated from the following equation, which is obtained by relating the surface diffusion flux to the pore diffusion flux (Crittenden et al 1987).

$$D_s = SPDFR * \left[ \frac{D_\ell \varepsilon_p C_o}{\varepsilon_p K C_o^{1/n} \rho_a} \right] \quad (8)$$

in which, SPDFR is the surface to pore diffusion flux ratio,  $C_o$  is the average influent liquid phase concentration ( $\mu\text{mole/L}$ ),  $\rho_a$  is the apparent adsorbent particle density including pore volume ( $\text{g/cm}^3$ ),  $\tau_p$  is the tortuosity of the diffusion path length within the adsorbent particle, and  $\varepsilon_p$  is the adsorbent particle void fraction.

Pore diffusion coefficients are calculated from the following equation which relates the liquid phase diffusivity and intraparticle physical properties (Zimmer et al, 1988).

$$D_p = \frac{D_\ell}{\tau_p} \quad (9)$$

Intraparticle pore and surface diffusion mechanisms are influenced by diffusion interactions, and it is only possible to provide the following general guidelines to estimate diffusion coefficients.

A method for calculating the impact of BOM fouling on the intraparticle diffusion rate was proposed by Sontheimer et al (1988), and presents the data and methodology for a correlation to account for the impact of BOM fouling on the intraparticle diffusion rate.

When the adsorption process is controlled by the competitive interactions between SOCs and BOM, pore diffusion is the dominate intraparticle mass transfer mechanism and Equation 9 is used. (The SPDFR in Equation 8 is set equal to zero in this case, and the PSDM becomes a PDM.) Experience has shown that when the adsorber operation time is less than about 70 days,  $\tau_p$  is equal to 1.0 (Sontheimer et al, 1988). After 70 days of adsorber operation,  $\tau_p$  is assumed to increase linearly with time and the following equation is used (Sontheimer, et al, 1988).

$$\tau_p = 0.334 + 6.61 \times 10^{-6} * t \quad (10)$$

in which, time is expressed in minutes.

### **Approximating GAC Use Rate with Hand Calculations**

Engineers often require quick, back of the envelope calculations to approximate GAC use rates. The current method used by engineers, and taught in most engineering curriculum is based on a steady state mass balance around the carbon reactor (Metcalf & Eddy 2002, Qasim et al 2000, Faust & Aly 1998).



$$\frac{m_{GAC}}{Qt} = \frac{C_0 - C_e}{q_e} \quad (11)$$

Where  $m_{GAC}$  is the mass of carbon in grams,  $Q$  is the volumetric water flow rate in liters/time,  $t$  is time,  $C_0$  is the influent liquid concentration of the pollutant in micrograms/liter,  $C_e$  is the effluent liquid concentration of the pollutant in micrograms/liter, and  $q_e$  is the concentration of pollutant on the adsorbent in micrograms/gram of GAC, which is calculated using the Freundlich isotherm (equation 1) in the appropriate units. Equation 11 calculates the carbon use rate in grams/liter. To compare these use rates with those provided in the model results for GAC, which are presented in units of liters of water treated per gram of GAC used, the reciprocal of the results if Equation 11 was taken. This provided results of comparable units.

## RESULTS AND DISCUSSION

Figure 1 displays the reduction in capacity of the GAC as a function of exposure time of the GAC to BOM for TCE. As shown in Figure 2 and Tables 1 & 2, the reduction in  $K$  depends on the water source and the type of compound. For fixed bed calculations, Equation 2 and Table 1 are used to account for the influence of BOM on TCE adsorption due to varying background water matrices; then Equation 3 and Table 2 are used to relate the effect of BOM on TCE to the effect of BOM on various chemical groups. Table 3 describes the studies that were used to determine the heuristics for model parameter estimation. In all, fixed bed data from 15 studies on 11 different water sources, 10 different compounds and 50 different EBCTs were compared to the PSDM. As shown in Table 3, it appears at this point that two  $K$  reduction correlations with time describe most

of the data: (1) Rhine river water, and (2) Karlsruhe ground water. The Rhine correlation tends to give the greatest impact as a function of time initially and the Karlsruhe correlation gives the lowest initial impact as a function of time. The Karlsruhe correlation is remarkably similar to the reductions which were observed with the Wausau water matrix. Consequently, these correlations tend to span the expected impact of BOM based on the data that is available to date.

Figure 5 shows the model predictions for the removal of chloroform ( $C_0 = 930.4 \mu\text{g/L}$ , EBCT = 9.8 min,  $v = 5.19 \text{ m/hr}$ , data source Alben et al, 1992) from Hudson River water using the two surface water choices provided in the model (Rhine River and Keweenaw Waterway) and organic free water (OFW). The Environmental Protection Agency (EPA) maximum contaminant level (MCL) for total trihalomethanes (TTHMs) is 0.1 mg/L or 100  $\mu\text{g/L}$ . Thus, the carbon use rates for each of the models was compared at the MCL. Table 4 shows the volume of water treated per mass of GAC (VTM) as predicted by the hand calculations (Equation 11) and for each of the Freundlich K reduction correlations in addition to the standard deviation between a regression of the effluent data and the model effluent predictions up to the effluent concentration specified on the table.

As shown in Table 4, the Equation 11 estimates the largest VTM (13.03 L/g), which is approximately three and a half times the actual VTM (3.73 L/g), and results in the largest standard deviation between this model and the regressed data. The PDM using

the Rhine River Water predicts the VTM (4.13 L/g) closest to the actual data, as evidenced by the smallest standard deviation between this model and the regressed effluent data.

Figure 6 shows the model predictions for the removal of 1,2-dichloropropane ( $C_0 = 0.5 \mu\text{g/L}$ , EBCT = 14.3 min,  $v = 7.23 \text{ m/hr}$ , Data source Kruithoff et al 1989) from Dutch ground water using the three ground water choices provided in the model (Karlsruhe, Wausau, and Houghton). The EPA MCL for 1,2-dichloropropane is 0.005 mg/L or 5  $\mu\text{g/L}$ . However, the data for this model included an average influent concentration of 0.5  $\mu\text{g/L}$ . Thus, the carbon use rates for each of the models could not be compared at the MCL, and were instead compared at  $C/C_0$  of fifty percent, or an effluent concentration of 0.25  $\mu\text{g/L}$ .

Table Table 5 shows the volume of water treated per mass of GAC (VTM) for each of these models in addition to the PSDM using organic free water, including the standard deviation between a regression of the effluent data and each of the model effluent predictions at the effluent concentration specified within the table. Once again, the equation 12 VTM (427 L/g) is much higher than the PDM using Karlsruhe (65.8 L/g) or Wausau (72.4 L/g) ground water, or the PSDM in OFW (215 L/g). Thus, the model, using the Karlsruhe groundwater matrix, provides a much smaller standard deviation from the data VTM (52.3 L/g) than the PSDM in organic free water or Equation 11 (see Table 5).

Figure 7 shows the model predictions for the removal of TCE ( $C_0 = 90 \mu\text{g/L}$  EBCT = 4.8 min,  $v = 10 \text{ m/hr}$ , Data source Bhuvendralingam 1992) from Manheim ground water using the three ground water choices provided in the model. The EPA MCL for TCE is  $5 \mu\text{g/L}$ . Table 6 shows the accompanying VTMs for these models and the PSDM using OFW; including the standard deviation between a regression of the effluent data and each of the model effluent predictions. Once again, Equation 11 provides the highest VTM predictions, while the PSDM using OFW VTM predictions provide predictions much higher than the PDM using surrogate surface waters.

Figure 8 shows the model predictions for the removal of PCE ( $C_0 = 26 \mu\text{g/L}$  EBCT = 4.8 min,  $v = 10 \text{ m/hr}$ , Data source Bhuvendralingam 1992) from Manheim ground water using the three ground water choices provided in the model. The EPA MCL for PCE is  $5 \mu\text{g/L}$ . Table 7 shows the accompanying VTMs for these models and the PSDM using OFW; including the standard deviation between a regression of the effluent data and each of the model effluent predictions. Once again, Equation 11 provides the highest VTM predictions (2243 L/g), while the PSDM using OFW VTM predictions (994 L/g) are much higher than the PDM using surrogate surface waters (ranging from 119.5 L/g to 145 L/g). Thus, the model provides a much smaller standard deviation from the data than the PSDM in organic free water (see Table 7 and Figure 8) or Equation 11.

Although there is some variation in model results based on surrogate water matrix choice, regardless of matrix used, the standard deviation between the model and data was significantly less for this model than for a PSDM not accounting for organic matter, and exceptionally smaller than that of Equation 11.

## **CONCLUSIONS**

Equilibrium and kinetic studies have shown that background organic matter (expressed in terms of DOC) which are present in ground and surface waters can significantly reduce both adsorption capacity and kinetics for SOCs on GAC. Currently, there are no mass transfer models which have been developed to predict diffusion and equilibrium interactions that occur in fixed-beds. However, some trends in the manner in which the effective surface and pore diffusivities change with time and bed-length can be observed from comparisons of the models with field data. Models that account for the dependence of adsorption capacity and kinetics upon time and bed-length can be used to estimate effective diffusivities with enough precision to make crude design calculations. Equation 3 is used to predict the reduction in Freundlich K by chemical class. As more data becomes available for the adsorption of different compounds in the presence of NOM, the correlations can be refined for each chemical class. Accordingly, the practical guidelines described herein may be considered a work in progress, and more model data comparisons are needed to develop some confidence in the model's ability to describe GAC performance in the field.

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Table 1: Empirical Kinetic Constants Describing the Reduction in the Freundlich Isotherm Capacity Parameter for TCE in the Presence of Various Background Water Matrices, for use with Equation 2 (Sontheimer et al, 1988)

Background Water Matrix	DOC <sup>3</sup> (mg/L)	Empirical Kinetic Constants			
		A1	A2	A3	A4
		(-)	(day <sup>-1</sup> )	(-)	(day <sup>-1</sup> )
Surface water with significant anthropogenic input. (Rhine River, Germany) <sup>1</sup>	2.25	35.0	8.86x10 <sup>-4</sup>	65.0	1.29x10 <sup>-1</sup>
Surface water with a small amount of anthropogenic input. (Portage Lake, Michigan) <sup>2</sup>	1.6	51.0	1.33x10 <sup>-1</sup>	49.0	4.03x10 <sup>-2</sup>
Ground water in Germany that caused reduction in capacity similar to six other German ground waters. (Karlsruhe, Germany) <sup>1</sup>	0.7	65.0	9.66x10 <sup>-2</sup>	35.0	1.44x10 <sup>-1</sup>
Rural Midwestern ground water (Wausau, Wisconsin) <sup>2</sup>	8.1	83.0	1.31x10 <sup>-1</sup>	17.0	3.82x10 <sup>-1</sup>
Rural Northern ground water (Houghton, Michigan) <sup>2</sup>	1.5	66.0	2.23x10 <sup>-2</sup>	34.0	1.05x10 <sup>-1</sup>

<sup>1</sup>Calgon F100 GAC

<sup>2</sup>Calgon F400 GAC

<sup>3</sup>Dissolved Organic Carbon (DOC), (El-Behlil, 1990)

Table 2: Correction Factors for the Reduction in the Freundlich Isotherm Capacity Parameter for Different Classes of Compounds, for use with Equation 3 (Bhuvendralingam, 1992).

Group	Surrogate Compound	Equation Relative to the Reference Compound - TCE
Halogenated Alkanes	1,1,1-Trichloroethane	$\frac{K(t)}{K} = 1.2 \left[ \frac{K(t)}{K} \right]_{TCE} - 0.2$
Halogenated Alkenes	Trichloroethene	$\frac{K(t)}{K} = \left[ \frac{K(t)}{K} \right]_{TCE}$
Trihalo-methanes	Chloroform	$\frac{K(t)}{K} = \left[ \frac{K(t)}{K} \right]_{TCE}$
Aromatics	Toluene	$\frac{K(t)}{K} = 0.9 \left[ \frac{K(t)}{K} \right]_{TCE} + 0.1$
Nitro Compounds	3,4-Dinitrotoluene	$\frac{K(t)}{K} = 0.75 \left[ \frac{K(t)}{K} \right]_{TCE} + 0.25$
Chlorinated Hydrocarbons	1,4-Dichlorobenzene	$\frac{K(t)}{K} = 0.59 \left[ \frac{K(t)}{K} \right]_{TCE} + 0.41$
Phenols	2,4-Dichlorophenol	$\frac{K(t)}{K} = 0.65 \left[ \frac{K(t)}{K} \right]_{TCE} + 0.35$
Polynuclear-Aromatics (PNAs)	Methylene Blue	$\frac{K(t)}{K} = 0.32 \left[ \frac{K(t)}{K} \right]_{TCE} + 0.68$
Pesticides	Atrazine	$\frac{K(t)}{K} = 0.05$

Table 3: Summary of pilot plant and full-scale studies used to evaluate the empirical model correlations.

Water Source	Organic Compounds Present in ( $\mu\text{g/L}$ ), and DOC Concentration (mg/L)	GAC Type/ No. of Studies/ Scale	EBCT (minutes)	Surrogate Water Source Used in PSDM
Groundwater, Wausau, WI USA	cis-1,2-Dichloroethene, 70.9 Trichloroethene, 47.9 Tetrachloroethene, 37.6 1,1,1-Trichloroethane, 0.90 Xylenes, 19.0; Toluene, 19.3 Ethylbenzene, 4.50 DOC, 8.35	F-400 (12x40 mesh)  2 studies, Pilot and Full Scale	Pilot 1.01, 3.09, 5.08, 10.4, 21.2, 32.3 Full Scale 12.7	Groundwater Karlsruhe, Germany
Portage Lake Water Houghton, MI USA	Chloroform, 930.4 Bromoform, 1,838.4 Dibromochloromethane, 1,618.5 1,2-Dibromomethane, 1,418.6 Trichloroethene, 878.2 Tetrachloroethene, 1,023.6 DOC, 1.5 - 6.5	F-400 (12x40 mesh)  Pilot Study	Pilot 2.37, 4.73 9.77	Portage Lake Water Houghton, MI USE
Groundwater, Lahnstein, Germany	Trichloroethene, 53.0 Tetrachloroethene, 16.0 DOC, 1.3	H71 (12x30 mesh)  Pilot Study	Pilot 2.41, 6.29 9.67, 13.06	Groundwater Karlsruhe, Germany
Groundwater, Pforzheim, Germany	1,1,1-Trichloroethane, 1.0 Trichloroethene, 32.0 Tetrachloroethene, 12.0 DOC, 1.4	H71 (12x30 mesh)  Pilot Study	Pilot 2.1,4,7,7.3, 11.5, 14.1	Groundwater Karlsruhe, Germany
Groundwater, Isolohn, Germany	1,1,1-Trichloroethane, 37.0 Trichloroethene, 250.0 Tetrachloroethene, 48.0 DOC, 0.8	F100 (12x40 mesh)  H71 (12x30 mesh)	Pilot 1.0, 3.5, 6.0, 8.5, 10.0  Pilot 1.0, 3.5, 6.0, 8.5, 10.0	Groundwater Karlsruhe, Germany
Groundwater, Mannheim, Germany	Trichloroethene, 90.0 Tetrachloroethene, 26.0 DOC, 0.6	F100 (12x40 mesh)	Full Scale 4.8, 7.8, 15.6	Groundwater Karlsruhe, Germany
Hudson River Water Waterford, NY USA	Chloroform, 2.4 Trichloroethene, 97.0 Atrazine, 7.8 (2,4-Dichlorophenoxy)acetic acid, 18.0 DOC, 2.2	F300 (12x30 mesh)	Pilot 16.0	Rhine River Water Speyer, Germany
Dutch Groundwater, Netherlands	1,2-Dichloropropane Bentazone	F400 (12x30 mesh)	Pilot 10.2, 14.3	Groundwater Karlsruhe, Germany
Rhine River Water Speyer, Germany	Trichloroethene	F100 (12x40 mesh)		Rhine River Water Speyer, Germany
Greater Miami Aquifer Ohio, USA	cis-1,2-Dichloroethene	F400 (12x40 mesh)	Pilot 1.8, 4.54, 7.95	Rhine River Water Speyer, Germany
Spring Water Porrentruy, Switzerland	Trichloroethene	F100 (12x40 mesh)	Pilot 6.6, 9.0, 12.0	Rhine River Water Speyer, Germany



Table 4 compares the results of various model predictions for the removal of Chloroform (  $C_0 = 930.4 \mu\text{g/L}$ ) from Hudson River water using various surrogate background waters. EBCT = 9.8 min,  $v = 5.19 \text{ m/hr}$ . Data source Alben et al (1992).

	water treated (l/g) at 0.1 mg/l TTHM*	Standard Deviation** $SD = \sqrt{\frac{1}{(n-1)} \sum_{i=1}^{n-1} \left( \frac{X_{data} - X_{model}}{X_{data}} \right)^2}$
Effluent Data	3.73	
PDM using Rhine River water as a surrogate	4.13	0.2762
PDM using Keweenaw waterway water as a surrogate	6.14	0.5210
PSDM using Organic Free Water	8.34	1.022
Equation 11	13.03	2.493

\*0.1 mg/l is the MCL for Total Trihalomethanes.

\*\*SD between regression of effluent data ( $y = 9\text{E-}09x^3 - 2\text{E-}05x^2 + 0.0198x + 1.9474$ , where the y-axis represents liters of water treated per gram of GAC, and the x-axis represents the liquid concentration of chloroform in  $\mu\text{g/l}$ ,  $R^2 = 0.9196$ ) and model prediction for liters of water treated per gram of GAC.

Table 5. compares the results of the model prediction for the removal of 1,2-dichloropropane ( $C_0 = 0.5 \mu\text{g/L}$ , EBCT = 14.3 min,  $v = 7.23 \text{ m/hr}$ , adsorbed on Calgon F-400 GAC. Data Source Kruithoff et al, 1989) from Dutch ground water using varying background water matrices, with that of actual adsorber effluent data, and the ECM model for the removal of 1,2-dichloropropane from Dutch ground water.

	water treated (l/g) at $0.25 \mu\text{g/l}$ of DCP*	Standard Deviation** $SD = \sqrt{\frac{1}{(n-1)} \sum_{i=1}^{n-1} \left( \frac{X_{data} - X_{model}}{X_{data}} \right)^2}$
Effluent Data	52.3	
PDM using Karlsruhe ground water as a surrogate	65.8	0.4532
PDM Wausau ground water as a surrogate	72.4	0.6020
PDM using Houghton ground water	92.6	0.9551
PSDM using OFW	215	3.112
Equation 11	427	7.164

\* $5 \mu\text{g/l}$  is the MCL for 1,2-dichloropropane, but the data from this adsorber has a  $C_0$  of  $0.5 \mu\text{g/l}$ . Thus,  $0.25 \mu\text{g/l}$  is  $C/C_0 = 0.5$ .

\*\*SD between regression of effluent data ( $y = -511.49x^3 + 436.44x^2 + 33.783x + 24.59$ , where the y-axis represents liters of water treated per gram of GAC, and the x-axis represents the liquid concentration of DCP in  $\mu\text{g/l}$ ,  $R^2 = 0.9185$ ) and model prediction for liters of water treated per gram of GAC.

Table 6 compares the results of the model for the adsorption of Trichloroethene (Co = 90 µg/L, adsorbed on Calgon F-100, EBCT=4.8min, v=10m/h, T= 12°C, Data Source: Bhuvendralingam 1992) using varying background water matrices with that of adsorption data from Manheim ground water, Germany, and the PSDM using OFW and ECM models.

	water treated (l/g) at 5 µg/l of TCE*	Standard Deviation** $SD = \sqrt{\frac{1}{(n-1)} \sum_{i=1}^{n-1} \left( \frac{X_{data} - X_{model}}{X_{data}} \right)^2}$
Effluent Data	28.8	
PDM using Karlsruhe ground water as a surrogate	11.8	0.4136
PDM Wausau ground water as a surrogate	14.4	0.3658
PDM using Houghton ground water	12	0.4495
PSDM using OFW	95	2.010
Equation 11	200	5.944

\*5 µg/l is MCL for TCE.

\*\*SD between regression of effluent data ( $y = 0.0006x^3 - 0.0798x^2 + 3.7463x + 11.992$ , where the y-axis represents liters of water treated per gram of GAC, and the x-axis represents the liquid concentration of TCE in µg/l,  $R^2 = 0.9703$ ) and model prediction for liters of water treated per gram of GAC.

Table 7 compares the results of the model for the adsorption of Tetrachloroethene ( $C_0 = 26 \mu\text{g/L}$ , adsorbed on Calgon F-100, EBCT=4.8 min  $v=10\text{m/h}$   $T=12\text{C}$ , Data Source Bhuvendralingam 1992) using varying background water matrices, with that of actual adsorber effluent data, and the ECM model for the removal of tetrachloroethene from Manheim (Germany) groundwater.

	water treated (l/g) at $5 \mu\text{g/l}$ of PCE*	Standard Deviation** $SD = \sqrt{\frac{1}{(n-1)} \sum_{i=1}^{n-1} \left( \frac{X_{data} - X_{model}}{X_{data}} \right)^2}$
Effluent Data	96	
PDM using Karlsruhe ground water as a surrogate	119.5	0.2030
PDM Wausau ground water as a surrogate	130.5	0.3164
PDM using Houghton ground water	145	0.4936
PSDM using OFW	994	9.354
Equation 11	2243	22.36

\* $5 \mu\text{g/l}$  is MCL for PCE.

\*\*SD between regression of effluent data ( $y = -0.0078x^3 + 0.2305x^2 + 5.6178x + 62.666$ , where the y-axis represents liters of water treated per gram of GAC, and the x-axis represents the liquid concentration of PCE in  $\mu\text{g/l}$ ,  $R^2 = 0.996$ ) and model prediction for liters of water treated per gram of GAC.

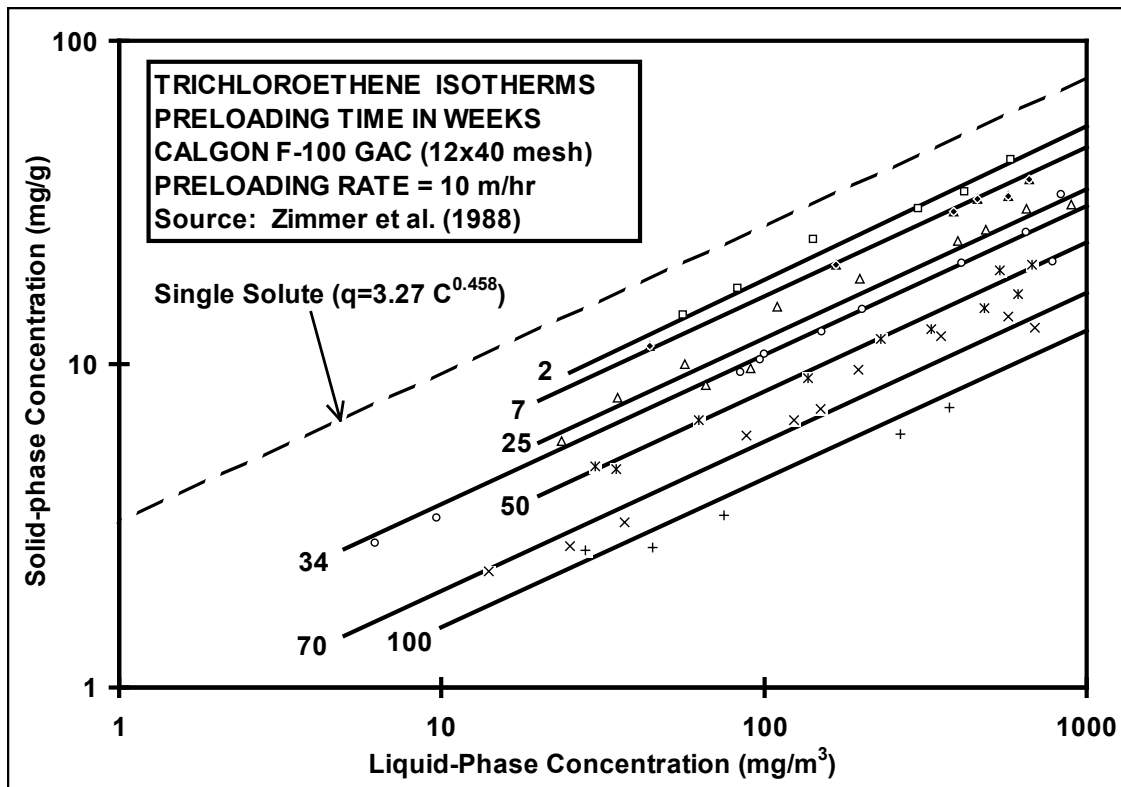


Figure 1. Adsorption Equilibrium Isotherm for TCE as a Function of Exposure Time to Karlsruhe Tap Water (After Zimmer et al. 1988)

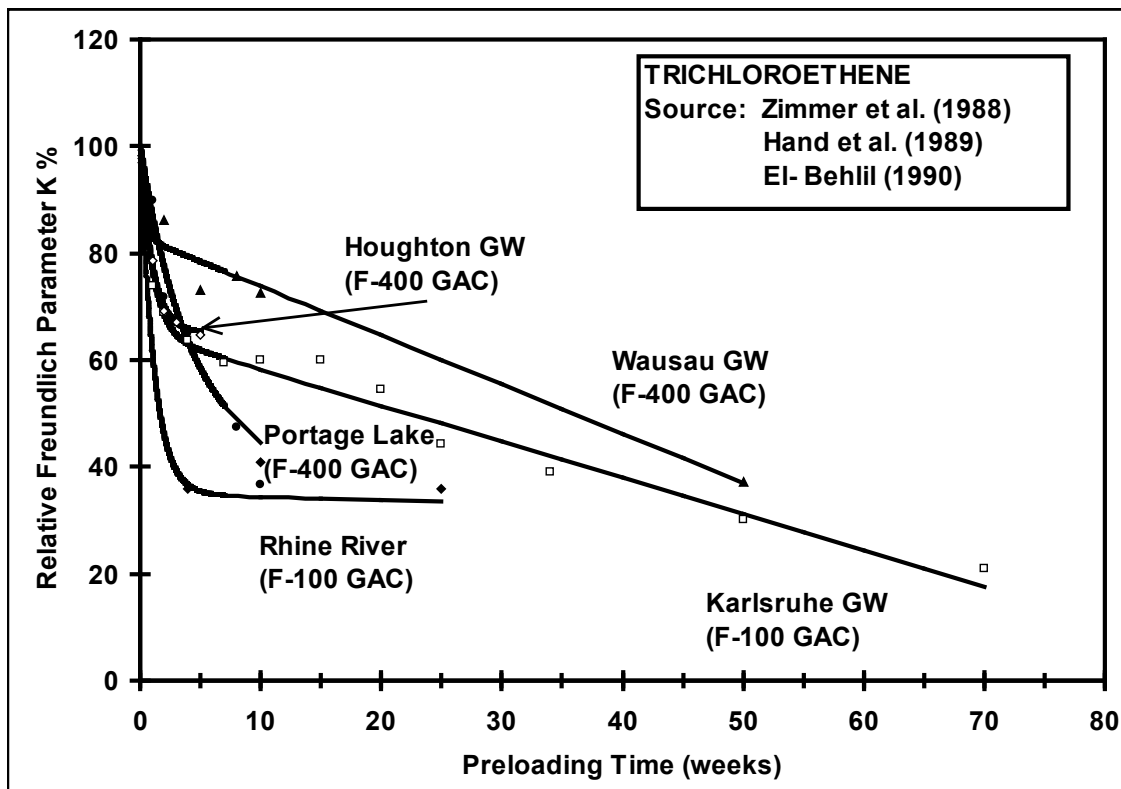


Figure 2. Freundlich K reductions for TCE as a function of time for various background waters.

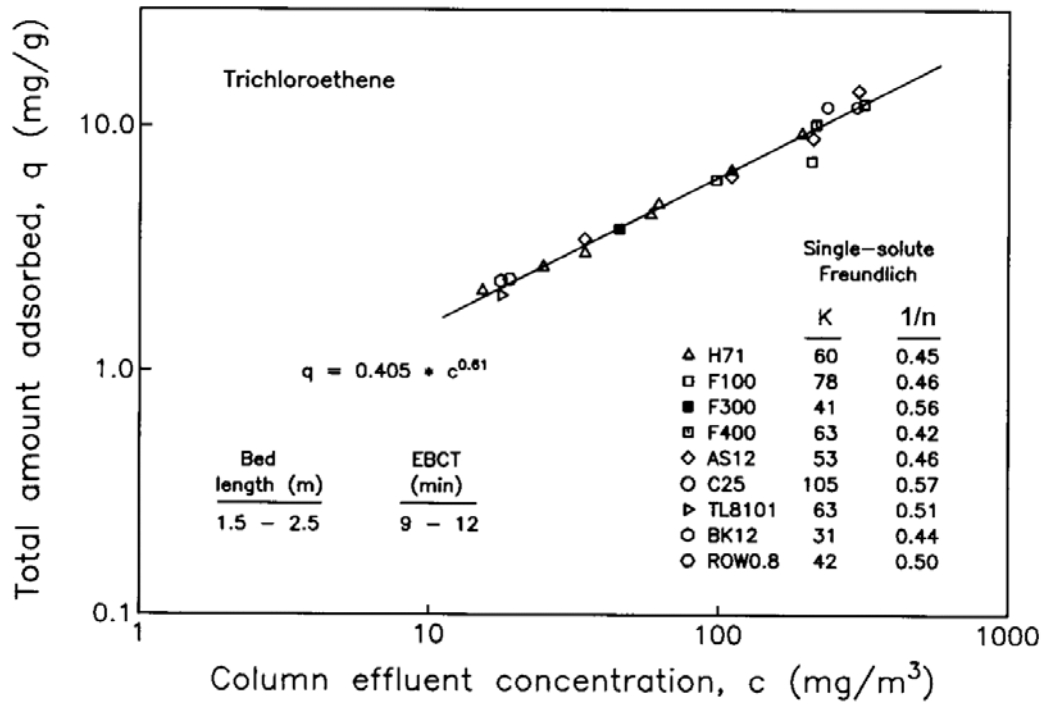


Figure 3. The solid-phase concentration, at complete breakthrough, as a function of aqueous concentration for several groundwater sources and nine activated carbons (Baldauf and Zimmer, 1986).

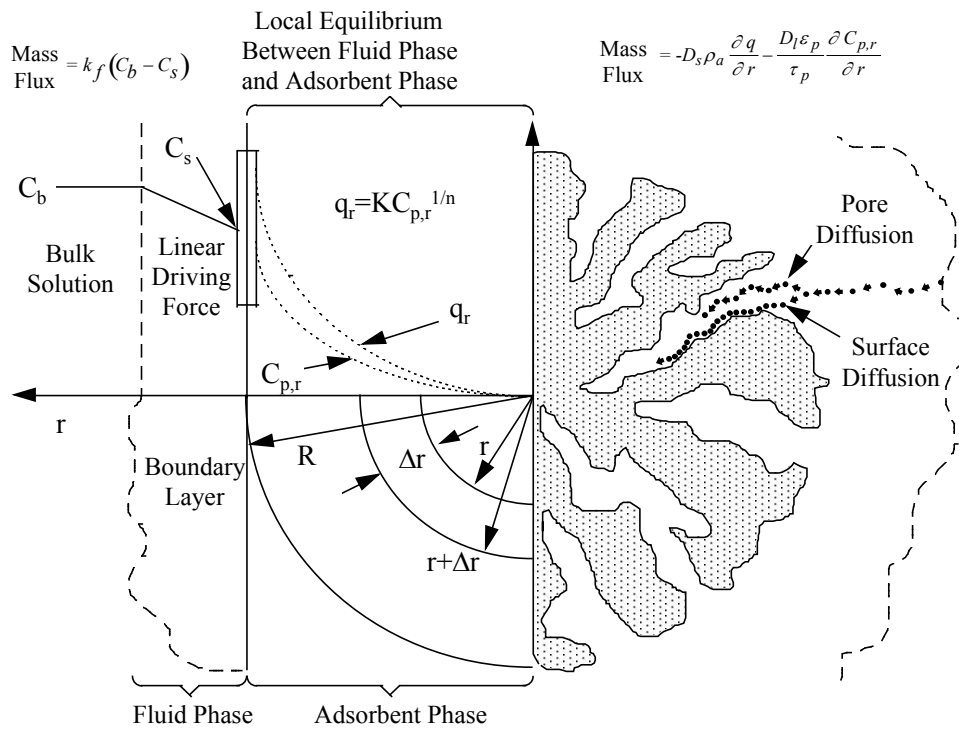


Figure 4. Mechanisms which are included in partial differential equations that describe the pore surface diffusion model (PSDM).



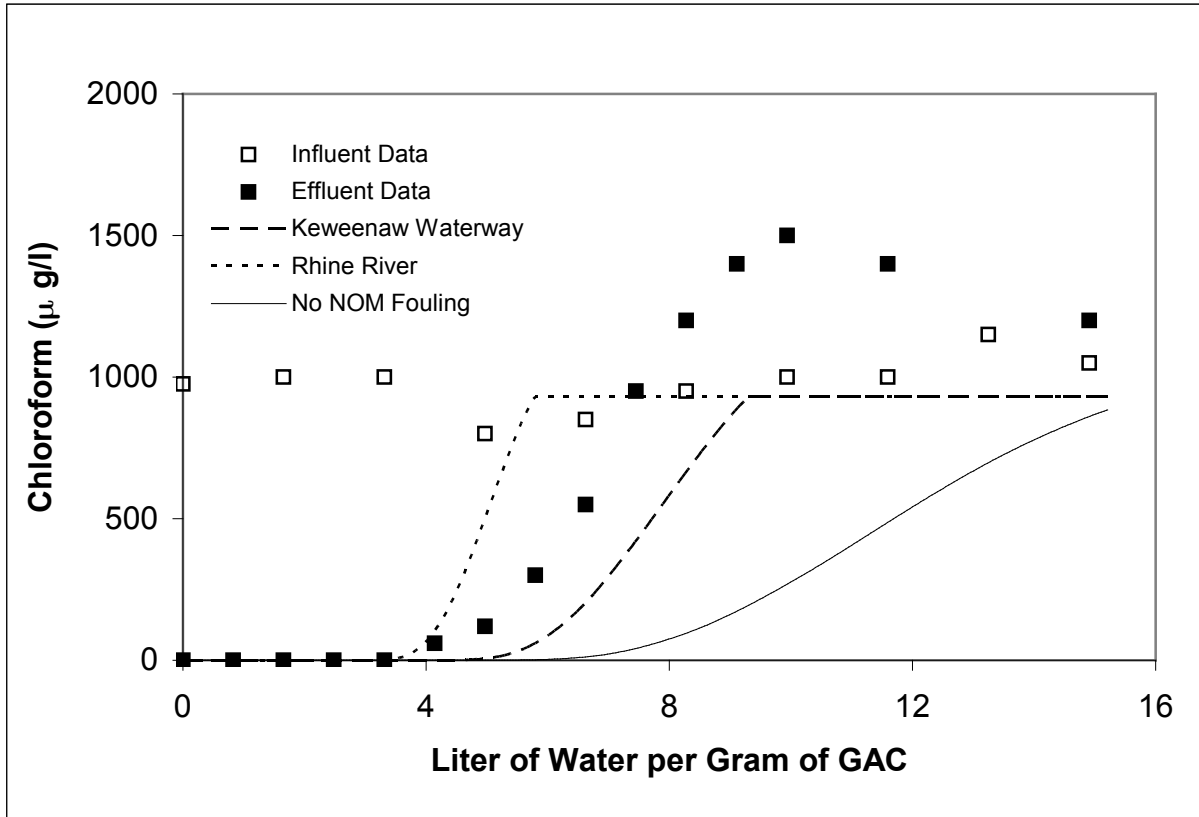


Figure 5. PDM prediction for the removal of Chloroform ( $C_0 = 930.4 \mu\text{g/L}$ ) from Hudson River water using various surrogate background waters. EBCT = 9.8 min,  $v = 5.19 \text{ m/hr}$ . Data source Alben et al (1992). Table 5 shows a comparison of the volume of water treated per mass of GAC for each of the model predictions, and compares the standard deviation between the effluent data and model predictions.

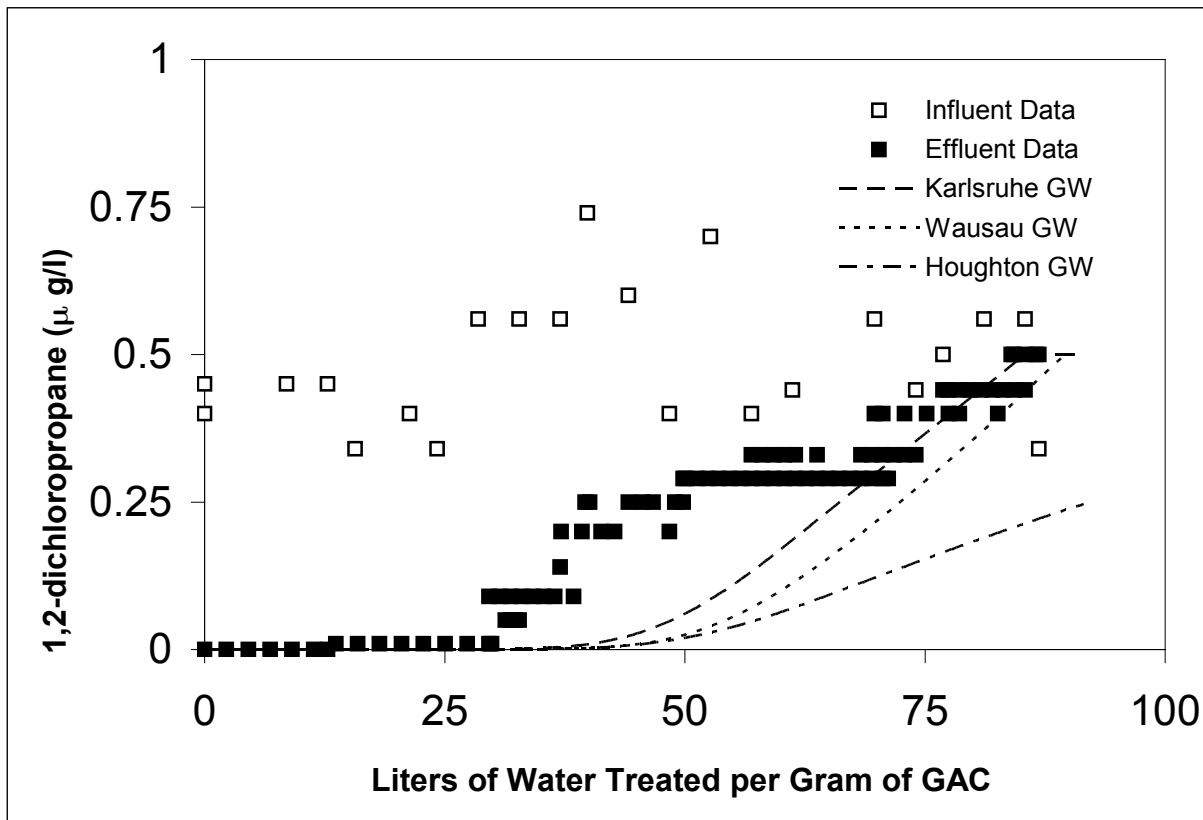


Figure 6. PDM prediction for the removal of 1,2-dichloropropane ( $C_0 = 0.5 \mu\text{g/L}$ ) from Dutch ground water using Karlsruhe ground water as a surrogate. EBCT = 14.3 min,  $v = 7.23 \text{ m/hr}$ , adsorbed on Calgon F-400 GAC. Data Source Kruithoff et. al. (1989).

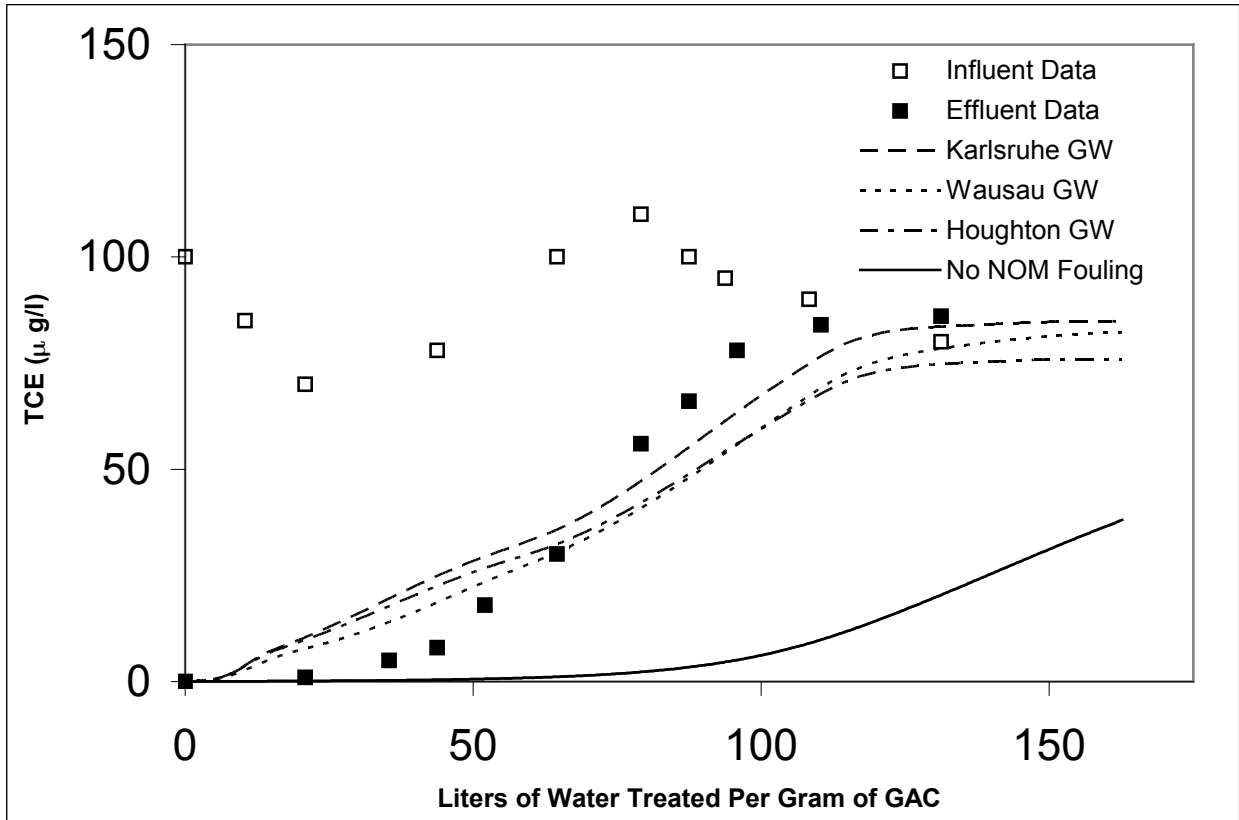


Figure 7 Trichloroethene ( $C_0 = 90 \mu\text{g/L}$ ) adsorption data from Manheim ground water, Germany, adsorbed on Calgon F-100, EBCT=4.8min,  $v=10\text{m/h}$ ,  $T= 12^\circ\text{C}$ , Data Source: Bhuvendralingam 1992.

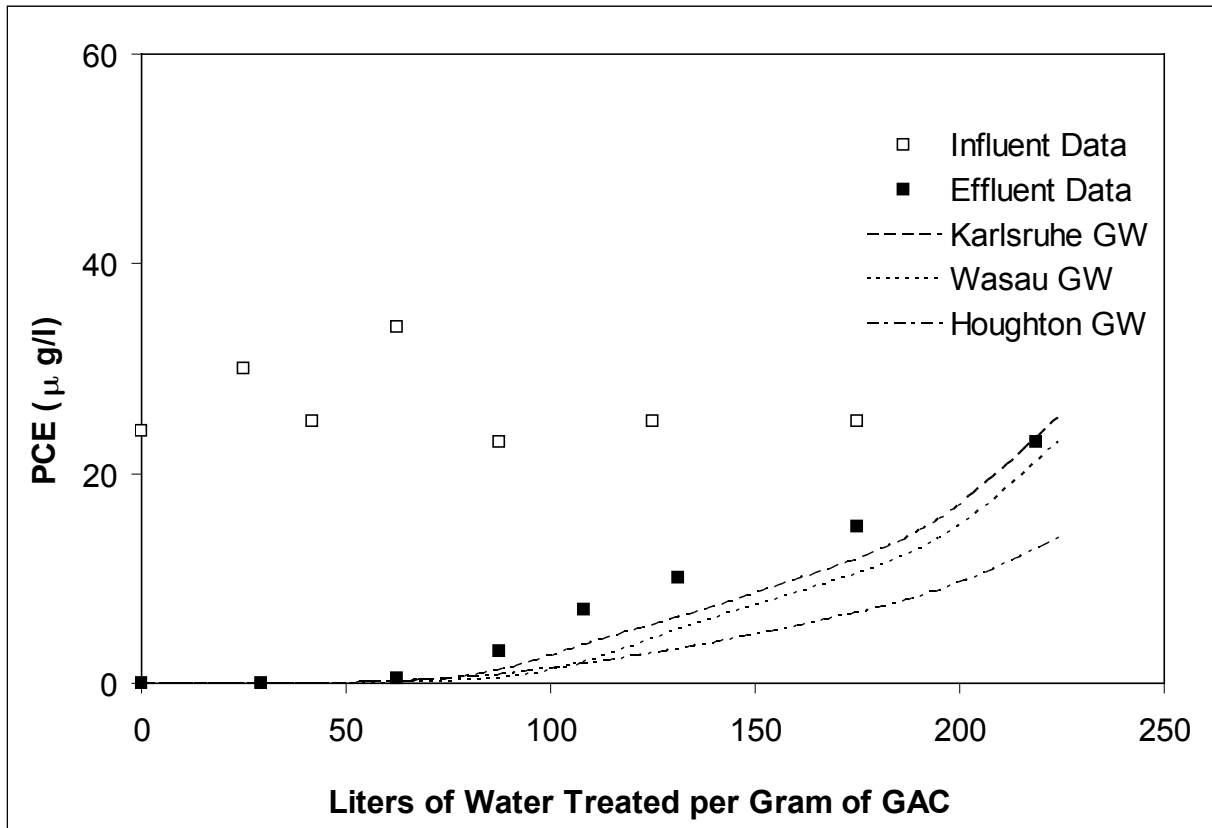


Figure 8 Tetrachloroethene ( $C_0 = 26 \mu\text{g/L}$ ) adsorption data from Manheim Ground Water, Germany, adsorbed on Calgon F-100, EBCT=4.8 min  $v=10\text{m/h}$   $T=12\text{C}$ , Data Source Bhuvendralingam 1992.