# PREDICTING ADSORPTION ISOTHERMS IN NATURAL WATER USING POLYPARAMETER LINEAR FREE ENERGY RELATIONSHIPS

BY

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DISSERTATION

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# Abstract

Activated carbon is widely used in drinking water treatment to remove both natural organic matter (NOM) and trace organic contaminants. Adsorption isotherms for trace contaminants in the presence of NOM are needed to predict the performance of activated carbon for removing these compounds, but such data are not available for most of these contaminants and it would be expensive to carry out isotherm tests for all compounds of interest. This research was conducted to reduce the effort required to determine needed isotherm data by using molecular parameters to predict these data. Polyparameter linear free energy relationships (pp-LFER) for trace contaminants adsorbed on activated carbon from organic-free water have been well developed, and this research was carried out to extend the method to predict the adsorption capacity of activated carbon in natural water. Literature values of molecular descriptors of pharmaceuticals, endocrine disrupting compounds and some industrial solvents were used to predict natural water isotherms. Suwannee River NOM was used to represent natural water organic matter.

The first part of this study used oxidized graphite to represent a typical activated carbon surface. Oxidized graphite was used to eliminate the effect of pores on adsorption capacity so that surface chemical interactions can be better understood. pp-LFERs for trace contaminants adsorbed on oxidized graphite (OG) from organic-free water and water containing Suwannee River natural organic matter (SRNOM) were developed. The pp-LFERs were developed for measured partitioning coefficients $K_d$ (i.e. the ratios of adsorption uptake $q_e$ over the equilibrium concentration $C_e$). The best-fit pp-LFER correlation for predicting single solute $log\ K_d$ was

determined to depend on solute activity a (i.e. the ratio of equilibrium concentration of a specific solute over its water solubility):

$$log\ K_{d,i} = [(13.30 \pm 5.83) + (1.96 \pm 1.22) log\ a_i]V + [(-9.97 \pm 5.37) - (1.16 \pm 1.11) log\ a_i]B + [(1.02 \pm 3.10) - (0.16 \pm 0.64) log\ a_i]S + [(0.24 \pm 2.41) + (0.08 \pm 0.51) log\ a_i]E + [(-4.12 \pm 3.87) - (0.66 \pm 0.81) log\ a_i]A + [(-11.87 \pm 5.20) - (2.34 \pm 1.08) log\ a_i]$$ .

The best-fit pp-LFER correlation for adsorption from water containing SRNOM was determined to depend on solute equilibrium concentration:

$$log\ K_{d,i} = [(1.57 \pm 0.63) + (0.36 \pm 0.26) log\ C_{e,i}]V + [(-2.49 \pm 0.57) - (0.66 \pm 0.25) log\ C_{e,i}]B + [(2.11 \pm 0.25) + (0.30 \pm 0.15) log\ C_{e,i}]S + [(0.03 \pm 0.23) + (0.36 \pm 0.10) log\ C_{e,i}]E + [(-0.51 \pm 0.25) + (0.04 \pm 0.14) log\ C_{e,i}]A + [(-1.27 \pm 0.42) - (1.60 \pm 0.23) log\ C_{e,i}]$$ .

The results showed that predictions by the pp-LFER model for adsorption by oxidized graphite are within a factor of two from the experimental values.

In the second part of this study, a pp-LFER was developed to predict activated carbon adsorption isotherms of trace organic contaminants in the presence of Suwannee River natural organic matter (SRNOM) using molecular descriptors of the trace organic contaminants. The trace organic contaminants used to develop the pp-LFER include pesticides, pharmaceuticals, endocrine disrupting compounds and some industrial solvents and the molecular descriptors (*V*, *A*, *B*, *S*, *E*) can be found in the literature.

The best-fit pp-LFER equation was determined to be:

$$\log K_{d,i} = [(-6.79 \pm 3.06) + (-0.71 \pm 0.77)\log C_{e,i}]V + [(7.84 \pm 2.27) + (1.63 \pm 0.64)\log C_{e,i}]B + [(1.08 \pm 0.48) + (-0.14 \pm 0.15)\log C_{e,i}]S + [(-1.26 \pm 0.74) + (-0.83 \pm 0.19)\log C_{e,i}]E + [(0.52 \pm 2.57) + (0.20 \pm 0.62)\log C_{e,i}]A + [(8.54 \pm 1.68) + (0.67 \pm 0.45)\log C_{e,i}].$$

This pp-LFER equation was able to predict activated carbon adsorption isotherms that are within a factor of 1.81 from the experimental values. The equation was also able to predict atrazine adsorption isotherms in two other natural waters that are within a factor of 3 from the experimental values.

To Father and Mother

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# Chapter 1: Introduction

## 1.1 Applications of Activated Carbon

Activated carbon has been used for water treatment since the 1920s for taste and odor control (Sontheimer et al., 1988). Today, activated carbon is listed as the best available technology for removal of many target organic contaminants (Pontius, 2003). Both powdered activated carbon (PAC) and granular activated carbon (GAC) are widely used in the water treatment industry. PAC is added in powdered form at different points in the water treatment system. GAC is usually packed into a column and used as a filtration step in the water treatment system. The low capital cost and the ease of changing carbon dosage according to water quality changes make the addition of PAC very desirable for controlling taste and odor compounds. However, a GAC column would be more cost effective if the taste and odor problem exists throughout the year.

## 1.2 Characteristics of Activated Carbon

Both surface chemistry and pore size distribution (PSD) will affect the ability of activated carbon to adsorb. The type of surface chemical functional groups will determine the interactions of the adsorbate with the activated carbon surface. PSD, on the other hand, will determine how much adsorbate of certain size and shape can access the pore surface.

Extensive studies have been done to determine the effects of pore size distribution on adsorption. The pore with the highest adsorption energy is one that has multiple contact points with the

adsorbate, and this adsorbate will have a size that is close to the pore size (Sontheimer et al., 1988). It is important that the activated carbon used for water treatment has large amounts of suitable pores for target contaminants.

The International Union of Pure and Applied Chemistry (IUPAC) categorized the size of pores using four different pore widths. Primary micropores have width less than 8 Å, secondary micropores have width of 8-20 Å, mesopores have width of 20-500 Å and macropores have width larger than 500 Å (Lastoskie et al., 1993). Most of the surface area available for adsorption is in the micropore size (Sontheimer et al., 1988). Ebie et al. did isotherm experiments with single organic compounds and demonstrated that small halogenated organic compounds adsorbed primarily in pores smaller than 15 Å (Ebie et al., 1995). They also did experiments with one type of natural organic matter (NOM) and found that NOM adsorbed in the pore size range of 30-100 Å.

Many studies were also done to better understand the effects of surface chemistry of activated carbon on adsorption. The activated carbon surface is heterogeneous and has several chemical functional groups, most of which contain oxygen. The oxygen functional groups commonly present on the activated carbon surface are carboxylic acid groups, phenolic hydroxyl groups and quinone carboxyl groups (Boehm, 2002). The presence of these oxygen functional groups increases the surface acidity. The increased acidity causes the surface to become more hydrophilic and to decrease adsorption of hydrophobic organic compounds (Karanfil and Kilduff, 1999). This decrease in adsorption was accounted by Li et al. in their study by the

enhanced water adsorption due to the increase in hydrophilicity of the activated carbon surface (Li et al., 2002).

Besides surface acidity, other surface interactions were also studied. Electrostatic and dispersive interactions on the activated carbon surface were looked at in the work by Radovic et al. who showed that modification of the carbon surface will affect adsorption of aromatic compounds (Radovic et al., 1997). Franz et al. showed the major mechanisms through which oxygen functional groups affect adsorption are hydrogen bonding, dispersive/repulsive interactions and water adsorption (Franz et al., 2000). They also showed that the functional groups of aromatic compounds will affect how target molecules interact with the carbon surface. Details on the different types of surface interactions will be further discussed in Chapter 2.

### 1.3 Taste and Odor Compounds

The presence of taste and odor compounds has been a difficult aesthetic issue for the drinking water industry and GAC and PAC have been successful in removing them. Two common taste and odor compounds are 2-methylisoborneol (MIB) and geosmin (Gillogly et al., 1998); (Gillogly et al., 1999a); (Gillogly et al., 1999b). They are metabolites of algae and actinomycetes and consumers can detect the musty odor of both of these compounds at levels as low as 5-10 ng/L (Young et al., 1996); (Cook et al., 2001). The size of MIB and geosmin is 0.6-0.8 nm and it can be expected that they will adsorb on the smaller pores of activated carbon (Newcombe et al., 1997); (Newcombe, 2008). The presence of other constituents in the water will also affect the effectiveness of the activated carbon (Newcombe et al., 2002); (Newcombe et al., 2002);

(Hepplewhite et al., 2004). Thus, a careful selection of the right type of activated carbon for this application is important

### 1.4 Synthetic Organic Contaminants

Activated carbon is not only effective in removing taste and odor compounds, but also can remove synthetic organic contaminants. Synthetic organic chemicals (SOCs) are defined as man made organic compounds that are created by industrial synthesis. Some examples are industrial solvents, pesticides and polyaromatic hydrocarbons (PAHs). Trichloroethylene (TCE) is a common industrial solvent and it is widely used in activated carbon studies (Karanfil and Kilduff, 1999); (Kilduff and Wigton, 1999); (Kilduff and Karanfil, 2002); (Guo et al., 2007). Quinlivan et al. showed that the effective pores for TCE removal should be 1.5 times the kinetic diameter of TCE (Quinlivan et al., 2005).

Atrazine is a pesticide widely used in agriculture and commonly found in drinking water sources. There are a lot of studies in the literature which use atrazine as the target contaminant (Qi et al., 1994); (Pelekani and Snoeyink, 1999); (Pelekani and Snoeyink, 2001); (Pelekani and Snoeyink, 2000). It has been shown that both pore size distribution and surface chemistry affect how atrazine is removed by activated carbon.

## 1.5 Emerging Organic Contaminants

In recent years, the presence of pharmaceuticals and endocrine disrupting compounds in our drinking water has become of great concern to the public (Richardson, 2007). The presence of these compounds in our surface waters was evaluated by some researchers (Falconer et al., 2006); (Snyder et al., 2003). Since the compounds are present, it is important to evaluate current drinking water treatment systems to determine whether they can be removed. Many studies have been performed to evaluate our current drinking water treatment systems to determine if they are effective in reducing these emerging contaminants to an acceptable level (Westerhoff et al., 2005); (Snyder et al., 2007); (Chang et al., 2004).

Removal of some emerging organic contaminants by activated carbon was evaluated in several studies and it was shown that activated carbon is generally effective (Zhang and Zhou, 2005); (Yu et al., 2008); (Yoon et al., 2005); (Fukuhara et al., 2006). The removal of a mixture of endocrine disrupting compounds, pharmaceuticals, personal care products and flame retardants by several adsorbents was studied by Rossner et al. (Rossner et al., 2009) and they showed that activated carbon was the most effective adsorbent as compared to a carbonaceous resin and two high-silica zeolites. Fukuhara et al. showed that the amount of estrone and 17 β-estradiol removed by activated carbon depended on the pore diameter, specific surface area, the hydrophobicity of the target chemicals and the type and concentration of other water constituents (Fukuhara et al., 2006).

## 1.6 Natural Organic Matter

Natural organic matter (NOM) exists ubiquitously in the environment and in most of our water sources. NOM results from degrading plants and animals and consists of humic acids, carboxylic acids, proteins, lipids and amino acids. PAC and GAC are both effective in removing NOM. Under the Stage 2 Disinfection Byproduct Rule (DBPR), utilities are required to reduce the concentration of disinfection byproducts found in the distribution system. NOM is one of the major disinfection byproduct (DBP) precursors; by removing NOM, DBP formation can be reduced. The Stage 2 DBPR will drive utilities to consider using GAC for removing NOM.

The wide molecular weight distribution of NOM affects how it adsorbs on activated carbon. Studies showed that capacity of activated carbon for NOM increases as NOM size decreases (Kilduff et al., 1996); (McCreary and Snoeyink, 1980). The chemistry of NOM adsorption on activated carbon was studied by Karanfil et al. (Karanfil et al., 1996). They showed that NOM adsorption capacity increased as the amount of acidic functional groups increased, as long as the increase in functional groups did not increase NOM solubility.

Although activated carbon has been effective in removing trace organic contaminants, the presence of NOM in water sources has been a great challenge. The presence of NOM greatly reduces the capacity of activated carbon for trace organic contaminants. Many studies have been done to understand the competitive mechanism of NOM on the adsorption of trace organic contaminants. Qi et al. (Qi et al., 1994) found that NOM, present at a much higher concentration

in mg/L levels, will compete strongly with trace organic contaminants, which are present at µg/L levels, for adsorption sites on activated carbon.

Many studies have been done to understand the mechanism of the competitive effects of NOM on the removal of trace organic contaminants. NOM competes with trace organic compounds for adsorption sites via two major mechanisms: direct site competition and pore blockage. Smaller molecular weight NOM that is of similar size and weight as the target compounds competes with trace compounds for the same sites. Larger molecular weight NOM adsorbs in larger pores and blocks the smaller molecular weight trace compounds from reaching the inner pores; thus, the rate of adsorption of trace compounds is reduced (Carter et al., 1992).

Li et al. used model compounds, p-dichlorobenzene and polystyrene sulfonates to mimic small molecular size and large molecular size NOM respectively (Li et al., 2003). They showed that NOM of small molecular size greatly reduced the capacity of activated carbon for trace organic compounds but did not significantly affect adsorption kinetics, whereas large molecules reduced adsorption kinetics without significantly affecting adsorption capacity.

Ding et al. (Ding et al., 2008) determined that the pore size distribution of activated carbon would determine the adsorption capacity for trace organic compounds. Several mechanisms of NOM competition were analyzed and it was determined that NOM that adsorbed in the 15-50 Å pore size range was the most effective at blocking pores. NOM that adsorbs in the pores reduces the rate of diffusion of organic compounds being adsorbed onto activated carbon. Thus, they

recommended that the volume of pores of this size range be increased to decrease pore blockage effects.

### 1.7 Motivation for Predicting Adsorption Isotherms for Activated Carbon

To predict the performance of activated carbon in a particular system, both the adsorption rate and capacity of the carbon have to be either experimentally determined or systematically estimated. The adsorption capacity of activated carbon generally shows which type of activated carbon is the most effective for the target purpose and can be used to estimate the performance of activated carbon in a treatment process. Adsorption capacity can be determined by conducting isotherm tests. However, since there are more than 100,000 chemicals and mixtures presently produced and used in the world and adsorption isotherm data are only readily available for a few of these, collecting isotherm data for all chemicals and mixtures will be expensive and unrealistic (Schwarzenbach et al., 2006).

As analytical techniques become more sophisticated and the detection limits of chemicals are lowered, it is expected that more stringent regulations will be set for water utilities. Being able to predict adsorption isotherms will be very valuable in determining the effectiveness of activated carbon for removal of target chemicals. The capacity of activated carbon in a natural water can be estimated with the equivalent background compound model using single solute isotherm data (Graham et al., 2000). However, if the adsorption isotherm data in natural water can be predicted without the need to determine isotherms, performance estimation can be done more easily and cheaply.

Several theories have been proposed to predict single solute adsorption isotherms of organic compounds on activated carbon. Crittenden et al. (Crittenden et al., 1999) integrated linear solvation energy relationship (LSER) parameters into Polanyi potential theory and correlated the adsorption isotherms of compounds with 4 LSER parameters. The Polanyi Potential equation was normalized by LSER parameters to achieve the correlation. The LSER parameters represent different types of interactions between organic compounds and activated carbon. These researchers used single solute isotherm data from the literature that included data for 4 different groups of adsorbents with a total of 8 adsorbents, and 4 different groups of adsorbates with a total of 56 organic compounds. Correlation curves were developed for compounds with specific functional groups for each adsorbent but an overall correlation curve for the adsorption isotherms of all organic compounds was not determined. The correlations of the adsorption isotherms for halogenated aliphatic organic compounds, halogenated aromatic organic compounds and aromatic organic compounds on F-400 carbon and LSER parameters were well developed, but correlations of adsorption isotherms for polyfunctional organic compounds and aromatic organic compounds and sulfonated aromatic organic compounds were not.

Li et al. (Li et al., 2005) developed another method to predict single solute isotherms using Polanyi-Dubinin-Manes (PDM) model. They developed a good correlation between the oxygen content of the activated carbons and the water affinity coefficients. This correlation integrated into the PDM model was successful in predicting single solute isotherms for three adsorbents and two adsorbates. The predictions agreed well with the experimental data.

A recent study by de Ridder et al. used quantitative structure activity relationships (QSARs) to develop a model to predict carbon loading ($q_e$).on F400 activated carbon in ultrapure water (de Ridder et al., 2010). Organic compounds were organized into four groups for good predictions of $q_{e.}$ Polarizability of the solute, hydrophobic partitioning of the solute and the log of the equilibrium aqueous concentration, log $C_e$, were found to be linearly correlated to log $q_e$. The log $q_e$ values of most solutes were predicted within 0.5 log units from the experimental values.

Another approach to predict the adsorption coefficients of several organic compounds on activated carbon was to develop a Linear Solvation Energy Relationship using the chemical activities of adsorbates. An adsorption coefficient is the ratio of equilibrium concentrations of an organic compound on activated carbon to that in the aqueous phase. The chemical activity of an adsorbate is the ratio of the concentration in the aqueous phase at equilibrium to that at saturation. Shih and Gschwend (Shih and Gschwend, 2009) directly fitted experimental adsorption coefficients and chemical activities of 14 organic compounds with the corresponding LSER parameters of the compounds. They were successful in correlating the experimental single solute adsorption coefficients with the LSER parameters.

Shih and Gschwend (Shih and Gschwend, 2009) demonstrated that polyparameter linear free energy relationships (LFERs) can be used to predict single solute isotherms on activated carbon. It is reasonable to hypothesize that polyparameter LFERs can be used to predict adsorption isotherms in the presence of one type of NOM.

## 1.8 Research Objectives

There are many studies that adsorption isotherms of organic compounds in pure water can be predicted. However in reality, there will always be NOM in drinking water sources and that will change how organic compounds interact with the surface of carbon. It will be very useful if adsorption isotherms in the presence of NOM can be predicted directly.

The objective of this research was to develop a correlative equation that can predict the adsorption capacity of activated carbon in natural water using molecular descriptors of trace organic contaminants. Surface chemistry and pore size distribution of activated carbon, molecular properties of the adsorbate, and the type of natural organic matter (NOM) can influence the capacity of activated carbon. In order to determine the role of NOM, it was decided to first determine the effect of one type of NOM on trace compound adsorption on a non-porous carbon, and then to determine the effect on porous activated carbon Specific objectives of this research were:

1. Determine the influence of only surface chemistry on adsorption capacity for non-porous graphite. Without the presence of pores the chemistry of the surface adsorption can be specifically quantified. The highly hydrophobic surface of graphite can be oxidized before use to make its surface similar to that of a typical activated carbon;
2. Develop pp-LFER equations to predict the partitioning coefficient ($Log\ K_d$) of trace organic compounds on oxidized graphite in the absence and presence of one type of NOM;

3. Validate the above two equations. Adsorption isotherms for compounds not used to develop the correlations will be predicted and compared to experimental data;
4. Develop a pp-LFER equation to predict the partitioning coefficient ($Log\ K_d$) of trace compounds on activated carbon in the presence of one type of NOM;
5. Validate the activated carbon pp-LFER equation. Adsorption isotherms for compounds not used to develop the correlation will be predicted and compared to experimental data;
6. Apply the activated carbon pp-LFER equation to predict adsorption isotherms of atrazine in other natural waters with the same carbon;
7. Evaluate the critical number of trace compounds isotherms needed to develop a pp-LFER equation;
8. Compare the oxidized graphite equations and activated carbon equation to evaluate how the tendency of solute partitioning change with the presence of pore size distribution.

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# Chapter 2: Theory and Applications of Polyparameter Linear Free Energy Relationship

## 2.1 Theory

Linear free energy relationships (LFERs) are extrathermodynamic correlations used to understand the characteristics of equilibrium and kinetic processes from the perspective of molecular structural contributions. LFERs are empirically determined and can be used to predict partition coefficients of organic compounds. Free energy change for the transfer of one mole of organic compound from the aqueous phase to activated carbon is related to the partition coefficient of the activated carbon as follows:

$$\Delta G_{overall} = -RT\ln(K_{eq}) \quad (2.1)$$

where $\Delta G_{overall}$ = Overall free energy change of the chemical equilibrium

$R$ = Gas constant

$T$ = Temperature

$K_{eq}$ = Partitioning coefficient

LFERs have been commonly used in a form where the logarithm of reaction rate or equilibrium constants of one series of reactions is correlated linearly with the logarithm of reaction rate or equilibrium constants of another associated series of reactions. The Brønsted equation, developed in 1924 by Brønsted and Pederson, correlates the catalysis reaction rate with the ionization constant of acids was the first LFER that is recognized widely (Wells, 1968).

LFERs are used in the environmental engineering field to understand the equilibrium partitioning of organic compounds in several natural phases. The fate and transport of organic contaminants in the environment can then be better understood (Nguyen et al., 2005). LFERs have also been used in understanding the equilibrium partitioning of organic compounds on activated carbon. Free energy change for the transfer of one mole of organic compound from the aqueous phase to activated carbon is related to the adsorption capacity of activated carbon (Abe et al., 1983).

The type of LFER described above is known as a one-parameter LFER and it is mainly used to correlate a well-known parameter to unknown parameter. For example, in the following equation, the unknown natural organic carbon-water partition coefficient $K_{i,oc}$ is correlated with the well-known octanol-water partition coefficient $K_{i,ow}$. Coefficients $a$ and $b$ represent the differential interactions of the solute in the two phases (Schwarzenbach et al., 2003).

$$\log K_{i,oc} = a \log K_{i,ow} + b \qquad (2.2)$$

A one-parameter LFER predicts well within one class of compounds. Although there are many one-parameter LFERs developed for different systems, the applicability of one-parameter linear free energy relationships have been very limited. It is often observed that the one-parameter LFER is unable to predict for compounds that are not in the same class. That is mainly because one particular parameter is picked to represent all the interactions between the solute and the natural phases of concern. However equilibrium partitioning coefficients are often governed by several different types of molecular interactions between a solute molecule and the aqueous and solid phase.

Unlike one-parameter LFERs, a polyparameter LFER is able to take into account the different molecular interactions between the solute and the natural phases. There are multiple kinds of molecular interactions between an organic compound and activated carbon. Thus, the polyparameter LFER can be useful in predicting the adsorption capacity of the activated carbon for different trace organic contaminants.

The types of interactions that affect adsorption capacity of activated carbon are dependent on the following:

1. Molecular properties of the organic compound
2. Type of NOM existing in the natural water
3. Surface chemistry of the activated carbon
4. Pore size distribution of the activated carbon

The overall free energy equation for polyparameter LFER can be represented as follows:

$$-\Delta G_{overall} = \Delta G_{solute-solvent} + \Delta G_{solvent-adsorbent} - \Delta G_{solute-adsorbent} \quad \text{.....(2.3)}$$

From the much-simplified equation, energy is needed to break the bond between the solvent and adsorbent and also the bond between the solute and solvent, in this case, the solvent being water.

$$\Delta G_{solute-solvent} = vV \quad \text{.....(2.4)}$$

The free energy of the interaction between the solute and water is proportional to molecule size, which can be represented by the McGowan's characteristic molecular volume ($V$) (McGowan and Mellors, 1986). The coefficient $v$ would characterize the difference in the cohesive forces of the solute molecules in water and on carbon.

$$\Delta G_{solvent-adsorbent} - \Delta G_{solute-adsorbent} = eE + sS + aA + bB \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.5)$$

The differential free energy change of the interaction between solute and adsorbent and the interaction between solvent and adsorbent is correlated to four parameters: *E, S, A* and *B*. Parameter *E* being the excess molar refraction of the solute and it accounts for the induction of dipoles within the solute molecule and that correspond to the nonspecific interactions. Parameter *S* describes the polarity and polarizability of the solute. Parameter *A* is the overall hydrogen-bond acidity of the solute and that represent the solute's ability to accept electrons. Parameter *B* is the overall hydrogen-bond basicity and it represents the solute's ability to donate electrons. All parameters can be obtained from the literature. This nomenclature was introduced by Abraham et al (Abraham et al., 2004).

The values of the coefficients in front of the parameters, i.e. the small letters, will be determined by the chemical properties of both water and carbon. The coefficient *e* is determined by the differential non specific interactions of the solute and the two phases. The non specific interactions are caused by both induced dipole-induced dipole interactions and also dipole-induced dipole interactions. The coefficient *s* is determined by the differential dipole-dipole interactions of the solute in water and on carbon. It represents the electrostatic interactions determined by dipole-dipole interactions. The coefficient *a* is determined by the differential amount of H-bond acceptor sites in water and on carbon. The coefficient *b* is determined by the differential amount of H-bond donating sites in water and on carbon.

Combining all above the equations we obtain the pp-LFER for the partitioning coefficient $log\ K_d$:

$$\log K_d = eE + sS + aA + bB + vV + c \text{ .....(2.6)}$$

The constant *c* is determined by the volume entropy effects and it is free energy contribution that is specific to the two phases.

Partitioning coefficients *log* $K_d$ only represent the adsorption phenomena at infinite-dilution conditions. However, amount of organic compound adsorbed on carbon varies with the aqueous concentration of the organic compound. Experimental adsorption isotherms are non-linear because of this aqueous concentration dependence. Linear isotherms are only observed for a very narrow range of aqueous concentrations. Therefore, to be able to predict *log* $K_d$ that is representative of environmental conditions, it will be important to include the concentration dependence into the predictive equation:

$$\log K_{d,i} = (e_1 + e_2 \log(a_{e,i}))E + (s_1 + s_2 \log(a_{e,i}))S + (a_1 + a_2 \log(a_{e,i}))A + (b_1 + b_2 \log(a_{e,i}))B + (v_1 + v_2 \log(a_{e,i}))V_x + c_1 + c_2 \log(a_{e,i}) \text{ ....(2.7)}$$

where $C_e$, (µg/L) = Concentration of adsorbate *i* in solution at equilibrium

$q_{e,i}$ (µg/ mg carbon) = Concentration of adsorbate *i* on carbon at equilibrium

$S_w$ (µg/L) = Solubility of adsorbate

$a_{e,i} = C_{e,i} / S_w$

$K_{d,i} = q_{e,i} / C_{e,i}$

The above equation includes the chemical activities of the adsorbates and represents the intermolecular interactions of compounds at varying concentration that will affect adsorption onto activated carbon.

## 2.2 Applications

Although the one-parameter LFER has very limited applications, it is useful for compounds that have similar functional groups. The one-parameter LFER can either account for van der Waals interactions or H-bond interactions because there is only one molecular parameter in the predictive equation. Better predictions will be obtained for a series of partitioning coefficients which vary only in one type of molecular interactions. For example, the application of the one-parameter LFER to predict reactions of a homologous series of chemicals usually is successful because H-bond interactions would either be unavailable or they would be a constant for each compound in the group (Goss and Schwarzenbach, 2001).

For predicting a wider range of chemical compounds, pp-LFERs are generally more successful, but the data set required for reliable predictions will be much larger as compared to one-parameter LFERs. The best results are obtained with a data set consisting of a huge array of neutral chemical compounds. For any given partitioning coefficient, the wider the range of functional groups included in the development of the polyparameter LFER, the better the predictions.

Polyparameter LFERs have been successful in predicting equilibrium partition coefficients of organic compounds between water and NOM in soils and sediments (Nguyen et al., 2005). Polyparameter LFERs have also been successful in predicting the equilibrium partition coefficient of organic compounds in NOM-free water onto activated carbon (Shih and Gschwend, 2009).

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# Chapter 3: Linear Free Energy Relationship for Predicting Adsorption of Trace Organic Pollutants from Natural Water onto Oxidized Graphite

## 3.1 Introduction

There have been several approaches employed to predict single solute adsorption isotherms from NOM-free water. Crittenden et al. (Crittenden et al., 1999) integrated linear solvation energy relationship (LSER) parameters into the Polanyi potential theory and correlated the adsorption isotherms of compounds with 4 LSER parameters. A second method for NOM-free water using the Polanyi-Dubinin-Manes (PDM) model was developed by Li et al. (Li et al., 2005) to predict single solute activated carbon isotherms. They developed a good correlation between the oxygen content of the adsorbents and the water affinity coefficients. This correlation was then integrated into the PDM and they were successful in using it to predict single solute isotherms for three adsorbents and two adsorbates. A third approach was to develop a Linear Solvation Energy Relationship for $log\ K_d$ using the chemical activities of adsorbates. (Shih and Gschwend, 2009) The adsorption coefficient, $K_d$, is the ratio of the adsorbed concentration of an organic compound to the aqueous phase concentration at equilibrium. Shih and Gschwend successfully fitted the experimental adsorption coefficients and chemical activities (the ratio of the equilibrium solution concentration to the saturation concentration) of 14 organic compounds with the corresponding LSER parameters of the compounds.

Natural organic matter (NOM) is ubiquitous in our water sources. It greatly reduces the capacity of activated carbon for trace organic contaminants via competition for adsorption sites because

NOM is present at mg/L levels while trace compounds are present at µg/L levels and below. Therefore, it will be useful to have an equation that is able to predict adsorption isotherms in the presence of NOM for utilities to use directly.

The objective of this chapter was to develop pp-LFER correlative equations that can predict the adsorption capacity of organic contaminants on oxidized graphite in pure water and natural water using molecular descriptors of the trace compounds. Oxidized graphite was used as a non-porous adsorbent representative of the activated carbon surface. The effect of activated carbon pore size distribution on adsorption capacity will be evaluated in chapter 5 and a pp-LFER correlative equation will be developed for activated carbon.

## 3.2 Materials and Methods

### 3.2.1 Water

Single solute isotherm experiments were performed in NOM-free water. Organic free water (OFW) was generated by passing de-ionized water through a NANOpure ultrapure water system (Barnstead, Dubuque, Iowa).The dissolved organic carbon (DOC) concentration of the organic-free water was lower than 0.3 mg/L.

Suwannee River NOM (International Humic Substances Society, St. Paul, Minnesota, USA), isolated by reverse osmosis, was received in dry form. The SRNOM was dissolved in OFW and filtered with a 0.45µm nylon membrane filter to remove suspended solids. The stock concentration of 200 mg/L was subsequently diluted to prepare the solution used to perform natural water isotherm experiments. The final solution TOC concentration was measured as 4 mg/L and the pH was 7.0.

### 3.2.2 Adsorbents

To understand the influence of surface chemistry on activated carbon adsorption, graphite, a non-porous adsorbent was selected. However, unlike activated carbon, the surface of graphite does not have oxygen functional groups. Thus graphite was oxidized to make an activated carbon-like surface before it was used for isotherm tests. Graphite powder (Sigma, St. Louis, Missouri, USA) was suspended in OFW, and ozone gas was bubbled through the suspension for 5 hrs to oxidize the graphite. (PCI Model GL-1, PCI Ozone & Control Systems, W. Caldwell, NJ) The oxidized graphite was filtered and then washed with 3 L of OFW. After this treatment, the oxidized

graphite was dried at 60$^{o}$C for 24 hrs. The dried, oxidized graphite was then kept in a bottle in a desiccator for later use. The graphite was analyzed using X-ray-Photoelectron Spectroscopy (XPS) for its carbon and oxygen contents. XPS spectra were acquired from a Physical Electronics PHI 5400 (Perkin-Elmer, MN). The element peak areas were normalized using atomic sensitivity factors to obtain the carbon to oxygen ratios.

### 3.2.3 Adsorbates

Ten compounds were selected as the target trace organic contaminants, including organic solvents (trichloroethylene, 1-heptanol, nitrobenzene), endocrine disrupting compounds (estradiol, bisphenol A), an explosive (2, 4-dinitrotoluene), an insecticide (lindane), an herbicide (atrazine), a polycylic aromatic hydrocarbon (naphthalene) and a pharmaceutical (diazepam). The 10 compounds have a range of molecular descriptors that covers the characteristics of most chemical contaminants. $^{14}$C-labeled forms of the 10 compounds were used (American Radiolabeled Chemicals, Inc). See Table 1 for structure and properties of the selected adsorbates.

### 3.2.4 Isotherm experiments with oxidized graphite

Single solute isotherms and competitive adsorption isotherms of 10 compounds were determined using traditional bottle-point isotherm tests. (Randtke and Snoeyink, 1983) The concentration of stock solution used for each compound was $10^{-3}$ of its solubility. A different amount of oxidized carbon was used for each compound to give a $10^{-4}$ to $10^{-6}$ of aqueous solubility range of final aqueous equilibrium concentration ($C_e$). Bottles were sealed with aluminum foil and mixed using a rotating tumbler. Seven days equilibrium time was used for all isotherms. All isotherm

experiments of volatile compounds were carried out in isotherm bottles with no headspace and sealed with aluminum foil and crimp top caps with a Teflon/silica septum.

After 7 days of equilibration, the aqueous phase concentration of the solute was sampled and the solid phase concentration was calculated a using mass balance. Two blanks were included for each set of isotherm experiments to monitor the amount of solute lost besides adsorption. Less than 10% loss was observed for the 7 days equilibration time.

### 3.2.5 Analytical Methods

Samples were analyzed at the end of 7 days. All samples were taken using a 5 ml glass syringe. For non-volatile and low solubility compounds (estradiol, lindane, naphthalene, diazepam), the bottles were settled for 8 hrs before samples were taken. For non-volatile and high solubility compounds (atrazine, 2,4-dinitrotoluene, bisphenol A), aqueous samples were taken and filtered with a 0.45 µm nylon membrane filter. For volatile and high solubility compounds (trichloroethylene, 1-heptanol, nitrobenzene), the bottles were settled for 8 hrs before samples were taken.

The 2.5 mL of aqueous sample was then mixed with 18 mL of scintillation cocktail in a 20 mL scintillation vial and analyzed using a liquid scintillation analyzer (TriCarb Model 1600A, Packard Instrument Co. Downers Grove, IL). Each analysis session included 2 blanks.

### 3.2.6 Development of Predictive Polyparameter Linear Free Energy Relationship (pp-LFER)

$K_d$ values were calculated using the following equation:

$$K_d = q_e / Ce \quad \text{.....} (3.1)$$

where $q_e$ = adsorbed concentration at equilibrium and

$C_e$ = aqueous concentration at equilibrium

These *log* $K_d$ values of 9 compounds were then used to fit the adsorbate molecular properties using equation 2.7 described above. Multiple linear regressions were applied to the experimental *log* $K_d$ data using Sigma Plot 2000 (SPSS, Chicago, IL) to obtain the coefficients. The partitioning of the aqueous solute to oxidized graphite will determine coefficients $e_1$, $e_2$, $s_1$, $s_2$, $a_1$, $a_2$, $b_1$, $b_2$, $v_1$, $v_2$, $c_1$, $c_2$.

### 3.2.7 Validation of the pp-LFER model

The fitted equations were used to predict *log* $K_d$ values for the 10$^{th}$ compound that was not used for fitting. The predicted *log* $K_d$ values were then compared with experimental *log* $K_d$ values to determine if the fitted equations were applicable to other compounds.

## 3.3 Results and Discussion

### 3.3.1 Characterization of oxidized graphite

After ozonation, the oxygen concentration (mass percentage) of graphite was increased from 1.22% to 4.52%. This oxygen concentration was similar to the 7.21% of a commercial activated carbon SA-UF. Langley and Fairbrother (2007) showed that ozone increased the surface oxygen concentration of base char from 12% to 28%. The same study also showed that ozone increased the concentration of most surface oxygen functional groups (hydroxyl, carbonyl, carboxylic acid, lactone, pyrone and esters) thus increasing the surface chemical heterogeneity. (Langley and Fairbrother, 2007)

### 3.3.2 Oxidized graphite isotherms

To determine the effects of surface oxygen functional groups, adsorption isotherms were determined for atrazine on graphite and oxidized graphite. As expected the atrazine capacity on oxidized graphite was 3 times lower than on graphite because the surface of oxidized graphite was more hydrophilic. The Freundlich parameters $K_f$ = 0.0148 [(mg/g)/ (µg/L)$^{1/n}$] and $1/n$ = 0.63 for graphite decreased to $K_f$ = 0.0051 [(mg/g)/ (µg/L)$^{1/n}$] and $1/n$ = 0.45 for oxidized graphite.

Isotherm data were collected for 10 organic compounds (trichloroethylene, 1-heptanol, nitrobenzene, estradiol, 2, 4-dinitrotoluene, lindane, atrazine, naphthalene, diazepam, bisphenol A) in both OFW and dissolved SRNOM water. (OFW= Organic free water, SRNOM =

Suwannee river natural organic matter) The Freundlich parameters of 10 compounds in OFW and dissolved SRNOM water were tabulated in Table 2.

The capacity of oxidized graphite decreased in the presence of NOM for most compounds except nitrobenzene. Specifically, for atrazine the Freundlich parameters $K_f$ = 0.0085 [(mg/g)/ (μg/L)$^{1/n}$] and 1/n = 0.74 for adsorption from pure water decreased to $K_f$ = 0.0044 [(mg/g)/ (μg/L)$^{1/n}$] and 1/n = 0.58 for adsorption from SRNOM- containing water. The reduction in capacity was also observed by many studies. (Pelekani and Snoeyink, 1999); (Li, 2002); (Knappe et al., 1998); (Ding et al., 2006)

### 3.3.3 Single solute isotherm fitted pp-LFER

The best-fit pp-LFER equation for predicting single solute *log* $K_d$ was determined to be:

$$\log K_{d,i} = [(13.30 \pm 5.83) + (1.96 \pm 1.22)\log a_i]V + [(-9.97 \pm 5.37) - (1.16 \pm 1.11)\log a_i]B +$$
$$[(1.02 \pm 3.10) - (0.16 \pm 0.64)\log a_i]S + [(0.24 \pm 2.41) + (0.08 \pm 0.51)\log a_i]E +$$
$$[(-4.12 \pm 3.87) - (0.66 \pm 0.81)\log a_i]A + [(-11.87 \pm 5.20) - (2.34 \pm 1.08)\log a_i] \quad (3.2)$$

Figure 3.1 showed that the predicted single solute *log* $K_d$ values were well correlated with the experimental data ($R^2$ = 0.97). The best-fit pp-LFER equation showed that the coefficients of parameter *S* and parameter *E* were determined to be negligible. Thus, the amount of solute adsorbed onto oxidized graphite is indirectly proportional to the H-bond accepting nature of the solute (parameter *B*), directly proportional to the solute's dispersion interactions (parameter *V*) and slightly proportional to the solute's ability to donate an H-bond. The constant (coefficient *C*)

of the best-fit pp-LFER equation was significantly different from zero thus showing that the entropy interactions will affect how solutes adsorb on oxidized graphite.

Similar trends were observed by Shih and Gschwend in their work on developing LSERs for activated carbon. (Shih and Gschwend, 2009) They showed that both solute's dispersion interactions (parameter *V*) and the H-bond accepting nature of the solute (parameter *B*) were the major factors controlling adsorption of organic chemicals onto activated carbon. This comparison showed that with the presence of pores did not significantly affect the chemical interactions between solutes and the surface of carbon.

The best fit pp-LFER equation for predicting single solute *log* $K_d$ was used to predict the single solute *log* $K_d$ of the 10$^{th}$ compound that was not used in fitting procedure. Figure 3.1 shows the comparison of the predicted *log* $K_d$ values of single soute Bisphenol A and experimental single solute *log* $K_d$ values. The predicted single solute *log* $K_d$ values for Bisphenol A agree well with the experimental single solute *log* $K_d$ values. The best-fit pp-LFER equation predicted $K_d$ values that are about 2 times higher than the experimental $K_d$.

### 3.3.4 Natural water isotherm fitted pp-LFER

The best-fit pp-LFER equation for predicting *log* $K_d$ in the presence of NOM was determined to be:

$$\log K_d = [(-3.72 \pm 5.86) - (1.39 \pm 1.35)\log a_i]V + [(4.16 \pm 5.21) + (1.63 \pm 1.17)\log a_i]B + [(-10.45 \pm 3.04) - (2.70 \pm 0.68)\log a_i]S + [(6.21 \pm 2.47) + (1.39 \pm 0.58)\log a_i]E + [(8.65 \pm 4.15) + (2.10 \pm 0.99)\log a_i]A + [(6.52 \pm 5.18) + (1.45 \pm 1.17)\log a_i] \quad (3.3)$$

Figure 3.2 showed that the predicted *log* $K_d$ values were well correlated with the experimental data with $R^2 = 0.92$.

The best-fit pp-LFER equation for predicting *log* $K_d$ in the presence of NOM was used to predict the *log* $K_d$ of Bisphenol A in the presence of NOM. The predicted *log* $K_d$ values of Bisphenol A were plotted against the experimental *log* $K_d$ values in Figure 3.2. Equation 3.3 predicted larger *log* $K_d$ values as compared to the experimental *log* $K_d$ values. The difference between the predicted *log* $K_d$ values and experimental *log* $K_d$ increased with increasing *log* $a_i$ (activity). Unlike single solute isotherms, activity of trace compounds may not be a good parameter to relate to the amount of solute adsorbed when natural organic matter is present. NOM may increase in the solubility of trace organic compounds when it is present. Some studies demonstrated that in the presence of dissolved organic matter, solubility of hydrophobic organic compounds is enhanced, (Chiou et al., 1987); (Chiou et al., 1986); (Hassett and Anderson, 1979) and it is reasonable that enhanced solubility of some compounds caused the poor correlation.

Since *log* $a_i$ was not a good representation of the surface saturation of adsorbates in the presence of NOM, *log* $C_e$ values were used instead to get the following best-fit pp-LFER equation for predicting isotherms in the presence of NOM:

$$\log K_{d,i} = [(1.57 \pm 0.63) + (0.36 \pm 0.26)\log C_{e,i}]V + [(-2.49 \pm 0.57) - (0.66 \pm 0.25)\log C_{e,i}]B + [(2.11 \pm 0.25) + (0.30 \pm 0.15)\log C_{e,i}]S + [(0.03 \pm 0.23) + (0.36 \pm 0.10)\log C_{e,i}]E + [(-0.51 \pm 0.25) + (0.04 \pm 0.14)\log C_{e,i}]A + [(-1.27 \pm 0.42) - (1.60 \pm 0.23)\log C_{e,i}] \quad (3.4)$$

Figure 3.3 shows that the predicted *log* $K_d$ values were well correlated with the experimental data with $R^2 = 0.99$. The best-fit pp-LFER equation showed that all coefficients were not negligible. Nguyen et al (Nguyen et al., 2005) obtained pp-LFERs for the equilibrium partition of organic

compounds between water and natural organic matter in soils and sediments. Their pp-LFERs also showed that coefficients of the best fit equation were all statistically significant. Thus in the presence of natural organic matter, the chemical interactions of organic contaminants and carbon surface is affected by all molecular parameters.

The experimental isotherm in the presence of NOM of the 10$^{th}$ compound was used to validate the best-fit pp-LFER equation. The best-fit pp-LFER equation for predicting $log\ K_d$ using $log\ C_e$ was used to predict the $log\ K_d$ of lindane, and these values are compared to the experimental values in Figure 3.3. Equation 3.4 predicted $K_d$ values that are lower than the experimental $K_d$ values by a factor of 1.17. $log\ C_e$ values can better represent the solute concentration effects on adsorption because the equilibrium concentration already included the enhanced solubility effect of the trace compounds in the presence of NOM.

The validity of this approach was tested by withholding 1 out of 10 compounds for the pp-LFER fitting procedure for all 10 compounds. The predicted $K_d$ values of the 10$^{th}$ compound were compared with experimental values and the difference was summarized in Table 3. Among the 10 compounds, prediction for lindane and trichloroethylene is the best with the ratios between predicted and experimental values being 1.17 and 1.16, respectively. The prediction for bisphenol A and estradiol were worse. For estradiol and bisphenol A the best-fit equation predicted NOM $K_d$ values that are about 3.84 and 3.77 times lower than the experimental NOM $K_d$. Figure 3.4 shows the predicted NOM $log\ K_d$ value for bisphenol A.

The correlation results showed that it is important to select a set of compounds that cover a wide range of molecular parameters to allow the predictive equation to be more robust. As shown in Table 1, the ranges represented are E from 0.21 to 2.08, S from 0.37 to 1.77, A from 0 to 0.99, B from 0.03 to 1.25, V from 0.71 to 2.19 and aqueous solubility from 0.26 to 1949 mg/L. But the fitted equation will not be able to make good predictions of compounds that have *log* $K_d$ values that are beyond the fitting set. Examples were bisphenol A and estradiol where the experimental $K_d$ values were beyond those used in the fitting set and the difference between predicted values and experimental values is about factor of 3.

### 3.3.5 Freundlich parameters from $K_d$ values

Freundlich parameters are commonly used in models that predict performance of activated carbon in water treatment systems. Adsorption isotherms are usually fitted with the Freundlich equation as follows:

$$q_e = K_f C_e^{\frac{1}{n}} \quad \text{.....(3.5)}$$

The Freundlich equation can also be log-transformed to give the following equation:

$$\log q_{e,i} = \log K_{f,i} + \frac{1}{n}\log C_{e,i} \quad \text{.....(3.6)}$$

For single solute isotherms:

$$\log a_i = \frac{\log C_{e,i}}{\log S_{w,i}} \quad \text{.....(3.7)}$$

$$\log K_{d,i} = \frac{\log q_{e,i}}{\log C_{e,i}} \quad \text{.....(3.8)}$$

Using equations 3.2, 3.6, 3.7 and 3.8, we can attain single solute $K_f$ and *1/n* values using the molecular descriptors and solubility concentration of each compound:

$$\log K_{f,i} = (13.30V - 9.97B + 1.02S + 0.24E - 4.12A - 11.87)-$$

$$(1.96V - 1.16B - 0.16S + 0.08E - 0.66A - 2.34)\log S_{w,i} \quad \text{.....(3.9)}$$

$$\frac{1}{n} = 1.96V - 1.16B - 0.16S + 0.08E - 0.66A - 1.34 \quad \text{.....(3.10)}$$

For NOM isotherms:

Using equations 3.4, 3.6 and 3.8, we can obtain the NOM $K_f$ and *1/n* using the molecular descriptors of each compound:

$$Log K_{f,i} = 1.57V - 2.49B + 2.11S + 0.03E - 0.51A - 1.27 \quad \text{.....(3.11)}$$

$$\frac{1}{n} = 0.36V - 0.66B + 0.30S + 0.36E + 0.04A - 0.60 \quad \text{.....(3.12)}$$

Thus, a correlation for $K_d$ can be used to estimate Freundlich parameters ($K_f$ and *1/n*).

## 3.4 Conclusion

- A pp-LFER equation has been developed for trace organic compounds adsorption on oxidized graphite in pure water and its able to predict $K_d$ values that were about a factor of 2 different from the experimental $K_d$ values.
- A pp-LFER equation has been developed for trace organic compounds adsorption on oxidized graphite in water containing NOM and its able to predict $K_d$ values that were about a factor of 1.17 different from the experimental $K_d$ values.

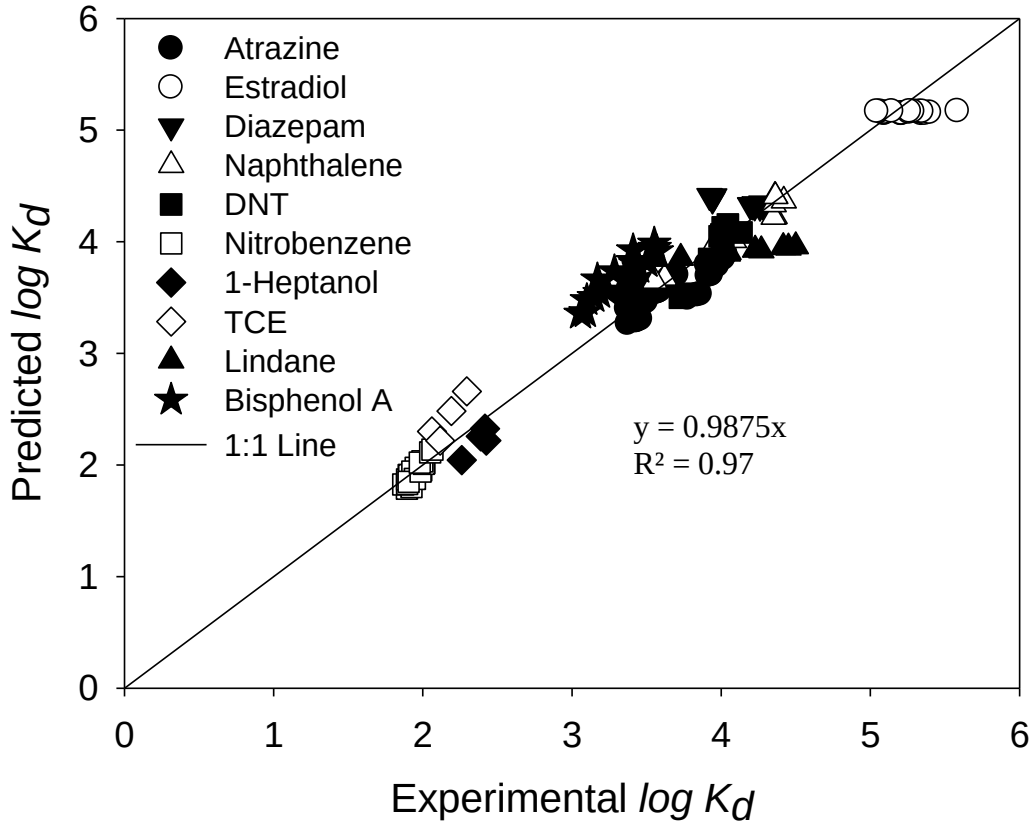


**Figure 3.1: Plot of fitted *log $K_d$* from the correlation developed for single solute isotherm data against the experimental *log $K_d$* of 9 organic compounds. Single solute bisphenol A *log $K_d$* values were predicted and compared with the experimental *log $K_d$* on this plot marked as stars.**

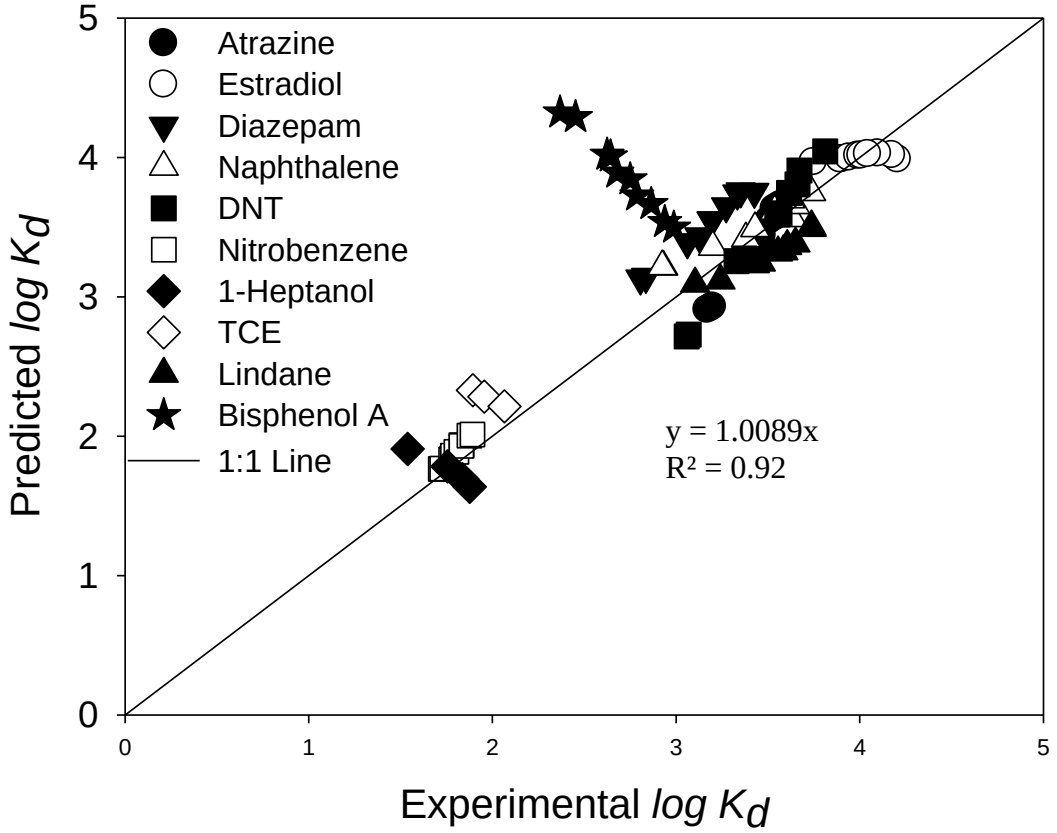


**Figure 3.2: Plot of fitted *log $K_d$* from the correlation developed for NOM isotherm data against the experimental *log $K_d$* of 9 organic compounds using *log a* values. NOM bisphenol A *log $K_d$* values were predicted and compared with the experimental *log $K_d$* on this plot marked as stars.**

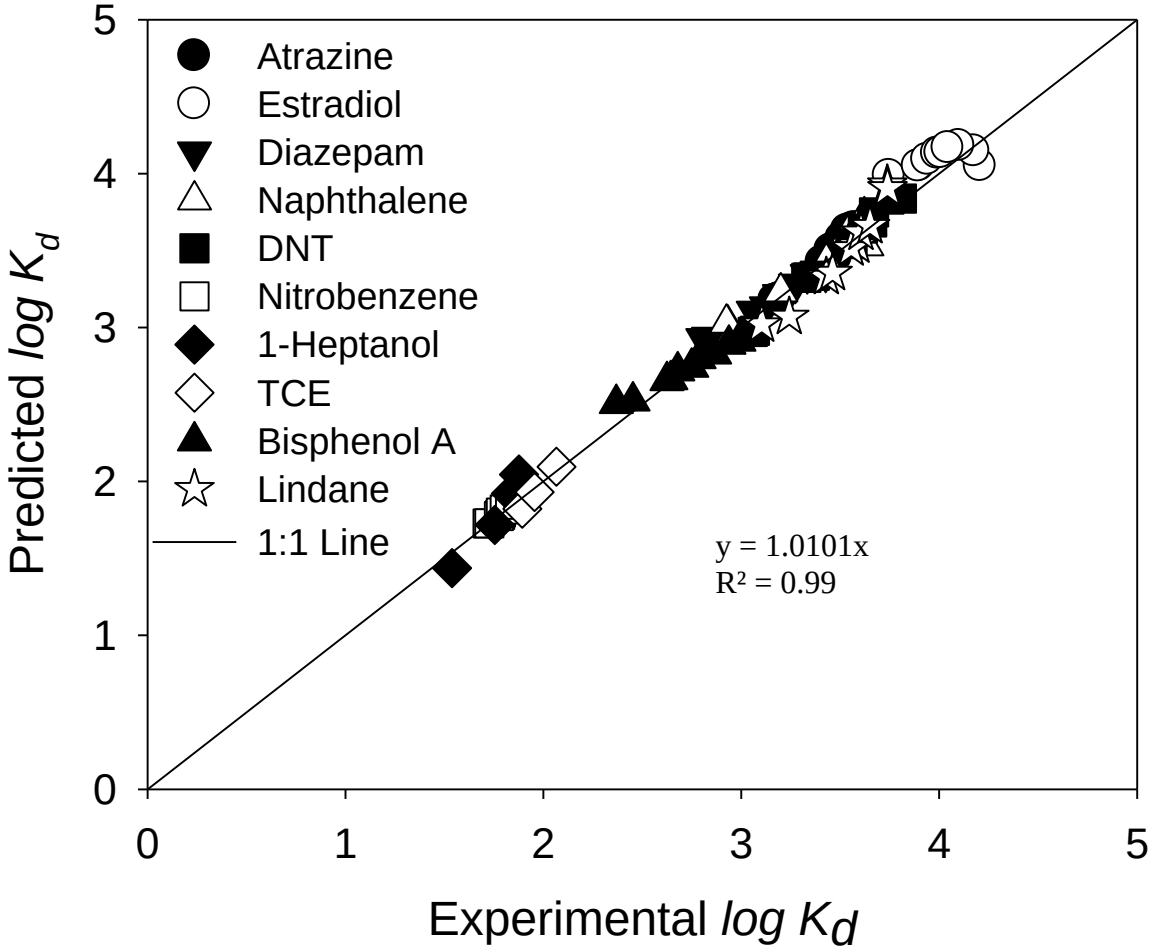


**Figure 3.3: Plot of fitted *log $K_d$* from the correlation developed for NOM isotherm data against the experimental *log $K_d$* of 9 organic compounds using *log $C_e$* values. NOM lindane *log $K_d$* values were predicted and compared with the experimental *log $K_d$* on this plot marked as stars.**

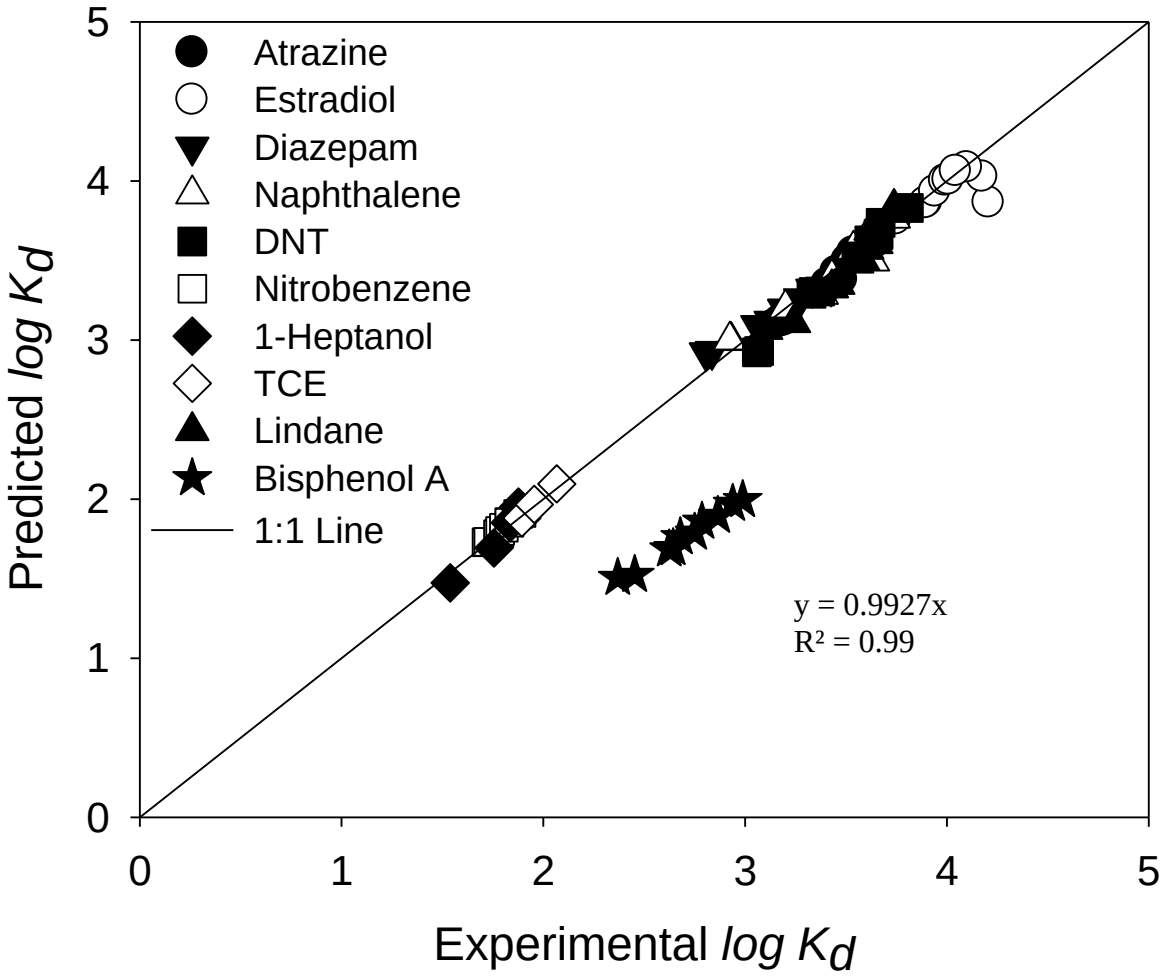


**Figure 3.4: Plot of fitted *log $K_d$* from the correlation developed for NOM isotherm data against the experimental *log $K_d$* of 9 organic compounds using *log $C_e$* values. NOM bisphenol A *log $K_d$* values were predicted and compared with the experimental *log $K_d$* on this plot marked as stars.**

# Tables:

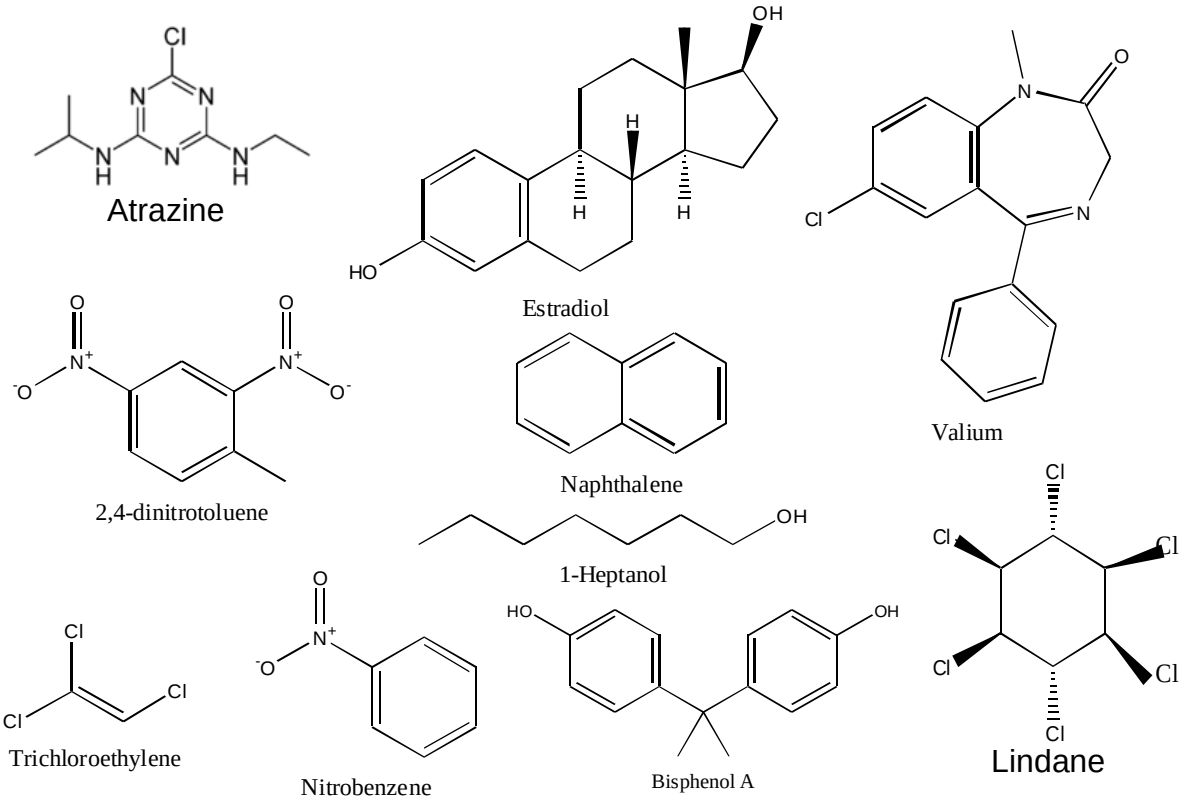


**Table 3.1: Aqueous solubility (Yaw, 1999); (ADME/ Tox WEB) and molecular properties (Abraham et al., 1994a); (Abraham et al., 1994b) (ADME/ Tox WEB) of compounds used for fitting of both single solute and *log* $K_d$ in the presence of NOM predictive equations**

| No | Compound | E | S | A | B | $V_x$ | Aq. Solubility (mg/L) |
|---|---|---|---|---|---|---|---|
| 1 | Atrazine | 1.95 | 1.64 | 0 | 1.04 | 1.61 | 70 |
| 2 | Estradiol | 1.80 | 1.77 | 0.86 | 1.10 | 2.19 | 0.26 |
| 3 | Diazepam | 2.08 | 1.55 | 0.09 | 1.25 | 2.07 | 50 |
| 4 | Naphthalene | 1.34 | 0.92 | 0 | 0.20 | 1.08 | 30 |
| 5 | 2,4-dinitrotoluene | 1.17 | 1.27 | 0.07 | 0.51 | 1.20 | 270 |
| 6 | Lindane | 1.45 | 0.91 | 0 | 0.68 | 1.57 | 7.31 |
| 7 | Nitrobenzene | 0.87 | 1.11 | 0 | 0.28 | 0.89 | 1949 |
| 8 | Trichloroethylene | 0.52 | 0.37 | 0.08 | 0.03 | 0.71 | 1100 |
| 9 | 1-Heptanol | 0.21 | 0.42 | 0.37 | 0.48 | 1.15 | 1740 |
| 10 | Bisphenol A | 1.61 | 1.56 | 0.99 | 0.94 | 1.86 | 300 |

**Table 3.2: Experimental Freundlich isotherm parameters of 10 compounds**

| Compound | Single solute $K_f$ | Single solute *1/n* | NOM $K_f$ | NOM *1/n* |
|---|---|---|---|---|
| Atrazine | 1416 | 0.74 | 250 | 0.58 |
| Estradiol | 101434 | 0.95 | 177 | 0.56 |
| Diazepam | 820 | 0.60 | 67 | 0.40 |
| Naphthalene | 245 | 0.45 | 70 | 0.40 |
| 2,4 dinitrotoluene | 1170 | 0.63 | 185 | 0.41 |
| Nitrobenzene | 87 | 0.47 | 62 | 0.28 |
| 1-Heptanol | 32 | 0.48 | 6 | 0.28 |
| Trichloroethylene | 25 | 0.52 | 12 | 0.32 |
| Lindane | 107 | 0.33 | 64 | 0.41 |
| Bisphenol A | 442 | 0.58 | 80 | 0.34 |

**Table 3.3: Ratio of predicted $K_d$ values and experimental $K_d$ values of the 10th compound (not used in the fitting procedure)**

| Compounds | SS Predicted/ Experimental $K_d$ | NOM Predicted $K_d$/ Experimental $K_d$ |
|---|---|---|
| Atrazine | 8.42 | 1.33 |
| Estradiol | 4.33 | 3.84 |
| Diazepam | 12.60 | 1.50 |
| Naphthalene | 2.83 | 2.12 |
| 2,4-DNT | 4.30 | 2.81 |
| Lindane | 5.02 | 1.17 |
| Nitrobenzene | 11.43 | 2.58 |
| Trichloroethylene | 1.84 | 1.16 |
| 1-Heptanol | 4.25 | 1.54 |
| Bisphenol A | 2.50 | 3.77 |

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# Chapter 4: Application of Oxidized Graphite Predictive Equations

## 4.1 pp-LFER Equation Development

In Chapter 3, nine compounds were chosen to represent several different intermolecular interactions with oxidized graphite. The LFER parameters and aqueous solubilities of these 9 compounds covered a wide range of values as shown in Table 1 of Chapter 3; the ranges represented for *E* are from 0.21 to 2.08, for *S* from 0.37 to 1.77, for *A* from 0 to 0.86, for *B* from 0.03 to 1.25 and for *V* from 0.71 to 2.19.

However, in order to efficiently develop pp-LFERs that are able to predict good isotherms, careful selection of organic compounds is essential. The linear free energy parameters values for atrazine, estradiol, diazepam, nitrobenzene, trichloroethylene and 1-heptanol cover the ranges of all the parameters for the 9 compounds in this study. Estradiol was the compound with the highest $V = 2.19$, $S = 1.77$ and $A = 0.86$. Diazepam was the compound with the highest $E = 2.08$ and $B = 1.25$. Trichloroethylene was the compound with the lowest $V = 0.71$, $B = 0.03$ and $S = 0.37$. 1-Heptanol was the compound with the lowest $E = 0.21$ and atrazine was the compound with the lowest $A = 0$. Estradiol had the lowest aqueous solubility = 0.26 mg/L and nitrobenzene had the highest solubility = 1949 mg/L. In Figure 4.1, it was observed that by choosing these 6 compounds, the predicted $K_d$ values for single solute isotherms agree well with the experimental data with $R^2 = 0.99$. The equation for predicting single solute isotherms on oxidized graphite using only 6 compounds is:

$$\log K_{d,i} = [(-4.68 \pm 3.79) + (-1.00 \pm 0.88)\log a_i]V + [(2.88 \pm 5.00) + (0.66 \pm 1.10)\log a_i]B + [(-0.49 \pm 2.51) + (-0.20 \pm 0.62)\log a_i]S + [(3.66 \pm 3.15) + (0.55 \pm 0.71)\log a_i]E + [(6.41 \pm 2.63 + (1.00 \pm 0.64)\log a_i]A + [(0.92 \pm 2.91) + (-0.07 \pm 0.64)\log a_i] \quad (4.1)$$

However, when the single solute pp-LFER equation was used to predict adsorption isotherms of naphthalene, 2, 4-dinitrotoluene, bisphenol A and lindane, the $K_d$ predictions were within a factor of 120, or within a 2 log *factor*, different from the experimental values. Although the parameters of these 4 compounds were within the ranges covered by the 6 compounds, the types of chemical interactions that determine single solute isotherms apparently are more complex than what these 6 compounds can represent. One factor contributing to the complexity of the system is oxidative coupling of organic compounds on the surface of activated carbon. Vidic et al. showed that in the presence of oxygen, adsorption of phenolic compounds on activated carbon surface was higher than what was observed when oxygen is absence in the system (Vidic et al., 1997); (Vidic and Suidan, 1991); (Tessmer et al., 1997). They determined that this phenomenon was caused by polymerization of trace organic compounds on the activated carbon surface. Thus in the case of single solute isotherm predictions, the chemical interactions were more complex than what the range of molecular parameters can represent.

For isotherms in the presence of NOM, using the same 6 compounds, Figure 4.2 showed that the predicted $K_d$ values agree well with the experimental data with $R^2 = 0.99$. When the pp-LFER equation was used to predict $K_d$ values of naphthalene, 2,4-dinitrotoluene and lindane, the predictions were within a factor of 2, or within 0.3 log factor, of the experimental values. The equation for predicting isotherms in the presence of NOM using only 6 compounds is:

$$\log K_{d,i} = [(-2.02 \pm 0.91) + (-1.24 \pm 0.78)\log C_{e,i}]V + [(1.05 \pm 0.90) + (0.96 \pm 0.82)\log C_{e,i}]B + [(0.85 \pm 0.68) + (-0.25 \pm 0.73)\log C_{e,i}]S + [(0.76 \pm 0.81) + (0.56 \pm 0.74)\log C_{e,i}]E + [(1.11 \pm 0.82) + (0.88 \pm 0.69)\log C_{e,i}]A + [(1.67 \pm 0.68) + (-0.08 \pm 0.55)\log C_{e,i}] \quad (4.2)$$

To test whether all the range of molecular parameters are needed to predict isotherms in the presence of NOM; one more compound was left out for pp-LFER equation fitting. In Figure 4.3 it was shown that when estradiol was left out, the $K_d$ predictions for naphthalene, 2, 4-dinitrotoluene, bisphenol A, lindane and estradiol were factors of 1.05 to 49.96 different from the experimental values. Estradiol is the largest compound in our data set; it also has the lowest solubility and the highest $K_d$ value. So without it in the data set, certain chemical interactions will not be well represented and thus the big discrepancies between the predicted values and the experimental values. Therefore we can conclude that to develop good pp-LFERs for isotherms in the presence of NOM, 6 compounds with values of LFER parameters and solubility that cover a range that includes the parameters of the compounds for which isotherms are to be predicted is required.

### 4.2 Prediction of Isotherm Data on Activated Carbon Using the Correlation Developed for Oxidized Graphite

In Chapter 4 we determined the effects of chemical interactions on adsorption of trace compounds on oxidized graphite in the presence and absence of natural organic matter. However, to be able to predict activated carbon adsorption isotherms using the oxidized graphite equations, we will need to consider the higher surface area and pore size distribution of activated carbon.

Activated carbon being very porous has a higher surface area compared to oxidized graphite. It can be expected that activated carbon with a larger surface area will have a higher adsorption

capacity compared to oxidized graphite. Most activated carbons also have a range of pore sizes and this can affect the way trace organic contaminants adsorb. The effects of pore size distribution on the adsorption of trace compounds on activated carbon were well documented in the literature (Ebie et al., 2001); (Pelekani and Snoeyink, 1999); (Pelekani and Snoeyink, 2000); (Ding et al., 2008).

A preliminary evaluation of the application of the oxidized graphite pp-LFER equation for activated carbon predictions was carried out using activated carbon isotherms found in literature. These isotherms were compared to the predictions made using the oxidized graphite pp-LFER equation for the same compound. The difference in surface area of the activated carbon in comparison to that of the activated carbon was taken into account but the pore size distribution difference was not.

Atrazine in the absence and presence of NOM isotherm data can be found in work by To et al. and Ding et al. (To et al., 2008); (Ding et al., 2006). Both To et al. and Ding et al. used a commercial PAC, Norit SA-UF (NORIT France, S.a.r.l., Le Blanc Mesnil Cedex, France) with a nitrogen BET surface area of 1112 $m^2/g$ (Li et al., 2003) and an oxygen content that was measured to be 7.21mass percent. To et al. also made used of SRNOM, which was obtained from the same source as the material used in this study and thus is thought to be similar to what was used in this study. Ding et al. used two different sources of natural water, one being the groundwater from Clinton Water Works (CWW), Clinton, IL and the other being the groundwater from a well located next to Newmark Civil Engineering Laboratory (NCEL) at the

University of Illinois. Relevant properties of the NOM in these waters can be found in the respective papers.

Trichloroethylene activated carbon isotherm data in the absence and presence of NOM can be found in work by Kilduff and Karanfil (Kilduff and Karanfil, 2002). Kilduff and Karanfil used a microporous coal base activated carbon, F400 from Calgon, Pittsburg, PA. The surface area of F400 was 948 $m^2/g$ and the oxygen content was 7.3% mass concentration (Karanfil and Kilduff, 1999); (Yue et al., 2006). Kilduff and Karanfil used a poly(maleic acid) (PMA) and the properties of this NOM component can be found elsewhere (Carter et al., 1992). The isotherm data for the two compounds were used to compare to the predicted values from the pp-LFER oxidized graphite equations.

2-Methylisoborneol (MIB) isotherm data in the absence and presence of NOM can be found in work by Newcombe et al. (Newcombe et al., 2002); (Newcombe et al., 2002). This study used several commercially available activated carbons, one of which was F400, which is the same as what was used in the TCE study. Newcombe et al. used Myponga reservoir water and the NOM was isolated into several different groups based on molecular weight. Extensive characterization of the raw water and groups of NOM isolates were carried out. MIB in the presence of NOM isotherm data can also be found in work by Cook et al. (Cook et al., 2001). Their study used a coconut based, steam activated carbon, Picactif 1100 PAC (PICA) with a surface area of 1241 $m^2/g$. Cook et al. used four different sources of natural water and the NOM was well characterized.

Figure 4.4 shows that by normalizing the $K_d$ values of single solute activated carbon atrazine isotherm data with the surface area of the carbon, the experimental $K_d$ values are within a factor of 3 compared to the predicted $K_d$ values obtained from the oxidized graphite (OG) single solute predictive equation, which are also normalized with the surface area of oxidized graphite. Figure 4.4 also shows that the normalized experimental single solute activated carbon trichloroethylene $K_d$ values are within a factor of 2 to 5 compared to the normalized $K_d$ values predicted by the OG single solute predictive equation. It is also shown in Figure 4.4 that the normalized $K_d$ values predicted by the OG single solute predictive equation of MIB are within an average factor of 2.5 compared with the normalized experimental $K_d$ values.

These good predictions may be due to the similarities in the chemical interactions on oxidized graphite and activated carbon. Both SA-UF and F400 carbons have oxygen concentration of about 7% mass concentration and oxidized graphite has oxygen concentration of about 5%. This oxygen level is comparable to the oxygen concentration level on the oxidized graphite used in this study; thus this might be the reason why normalized predictions of adsorption isotherms agree well with the experimental isotherms. However, for carbons with higher oxygen concentration levels, the predictions might not agree as well because the chemical interactions of compounds with a highly oxidized surface may be very different compared to the oxidized graphite used in this study.

Pore size distribution data of SA-UF and F400 can be found in work of Ding et al. and Karanfil and Kilduff (Ding, 2010); (Karanfil and Kilduff, 1999). The surface areas and pore sizes of activated carbon were measured by nitrogen adsorption isotherms. The molecular size of

nitrogen was reported by Quirke et al. to be 3.5-3.7 Å (Quirke and Tennison, 1996). The molecular sizes of atrazine and trichloroethylene were reported by Guo et al. to be 8-20 Å and 5-8 Å (Guo et al., 2007). The smallest molecular size cutoff for pore size distribution measurements was 15-20 Å; the smallest pores that nitrogen, atrazine and trichloroethylene can adsorb on cannot be differentiated by current pore size measurements.

Since the pore size distribution cannot be further differentiated for the three compounds that was used in this study, future work will have to be done in order to determine if the good predictions are due to the similarities in chemical interactions between oxidized graphite and activated carbon or it is a compensating effects of chemical interactions and pore size distribution effects. One important issue to note is the predictions have worked well for compounds that are slightly larger than nitrogen. For compounds that are much larger than nitrogen, the pp-LFER equation of oxidized graphite might predict $K_d$ values that are much greater than the experimental $K_d$. That is because some of the surface area accessible to nitrogen might not be accessible to the larger target organic contaminants.

Figure 4.5 shows that the predictive equation for isotherms in the presence of NOM determined for oxidized graphite could be used to predict atrazine, trichloroethylene and MIB isotherms of activated carbon in the presence of NOM by dividing $K_d$ values with the surface area of the carbon. The normalized $K_d$ values of the activated carbon atrazine isotherm in the presence of NOM are within a factor of 2 compared to the normalized $K_d$ values predicted by the OG pp-LFER equation. For trichloroethylene, the adsorption isotherms predicted by the OG pp-LFER

equation were within a factor of 3 as compared to the experimental adsorption isotherms of activated carbon in the presence of NOM.

However for MIB, in the presence of NOM, the normalized $K_d$ values predicted by the OG pp-LFER were about 1268 times higher than the normalized experimental $K_d$ values. The type of NOM used in the MIB studies may explain these big discrepancies. The NOM used in the MIB studies consist of a substantial percentage of small molecular weight NOM that is similar in size as MIB. Thus, there might be greater competition from the NOM for the same pores and thus caused less adsorption of MIB as compared to what was predicted by the OG pp-LFER equation. These discrepancies demonstrate that the type of pores available for adsorption and the type of NOM present in the water are important variables. By considering just the surface area difference between oxidized graphite and activated carbon is insufficient to predict for a different carbon and a different natural water source.

From what was observed for atrazine, trichloroethylene and 2-methylisoborneol, it can be concluded that pore size distribution of activated carbon and type of NOM are important factors to consider for predicting good isotherm data with the pp-LFER approach. Therefore, a pp-LFER for one activated carbon and one type of NOM will be developed in the next chapter.

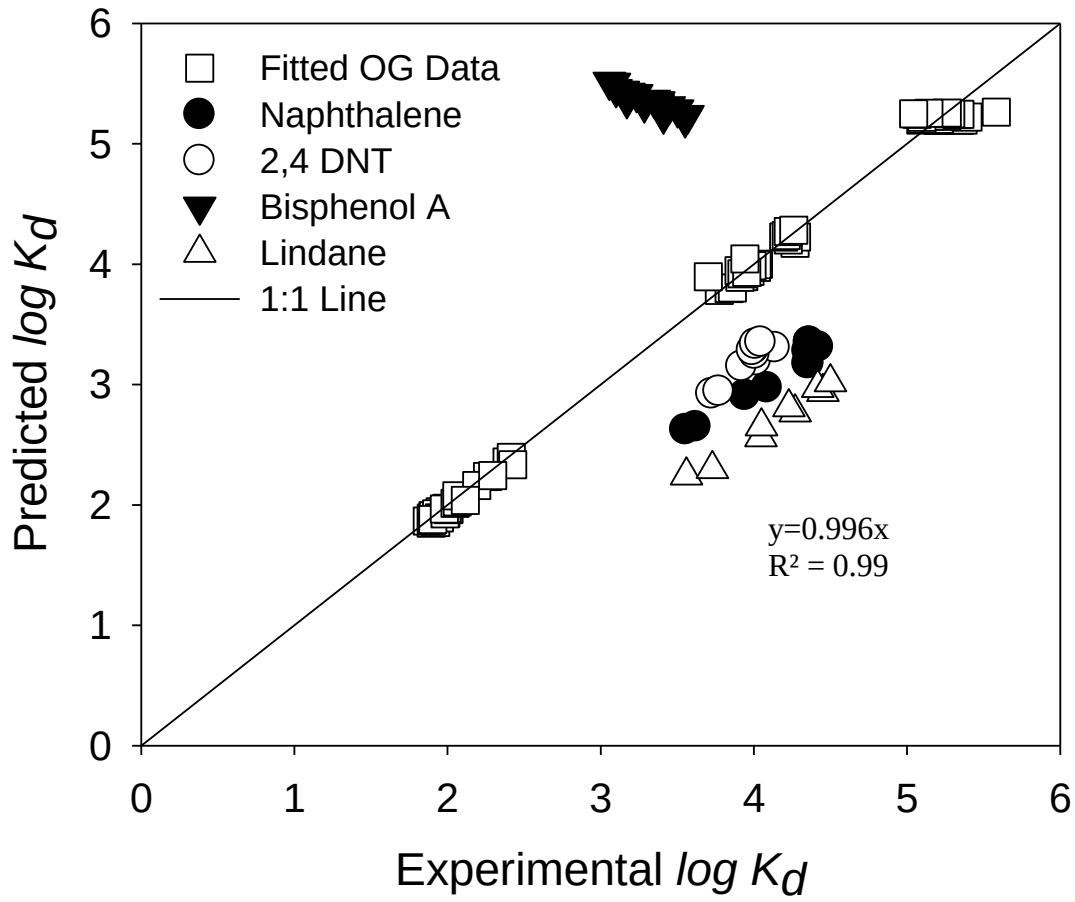


**Figure 4.1: Plot of fitted *log $K_d$* from the correlation developed for single solute isotherm data against the experimental *log $K_d$* of 6 organic compounds. Single solute Naphthalene, 2, 4 DNT, Bisphenol A and Lindane *log $K_d$* values were predicted and compared with the experimental *log $K_d$* on this plot.**

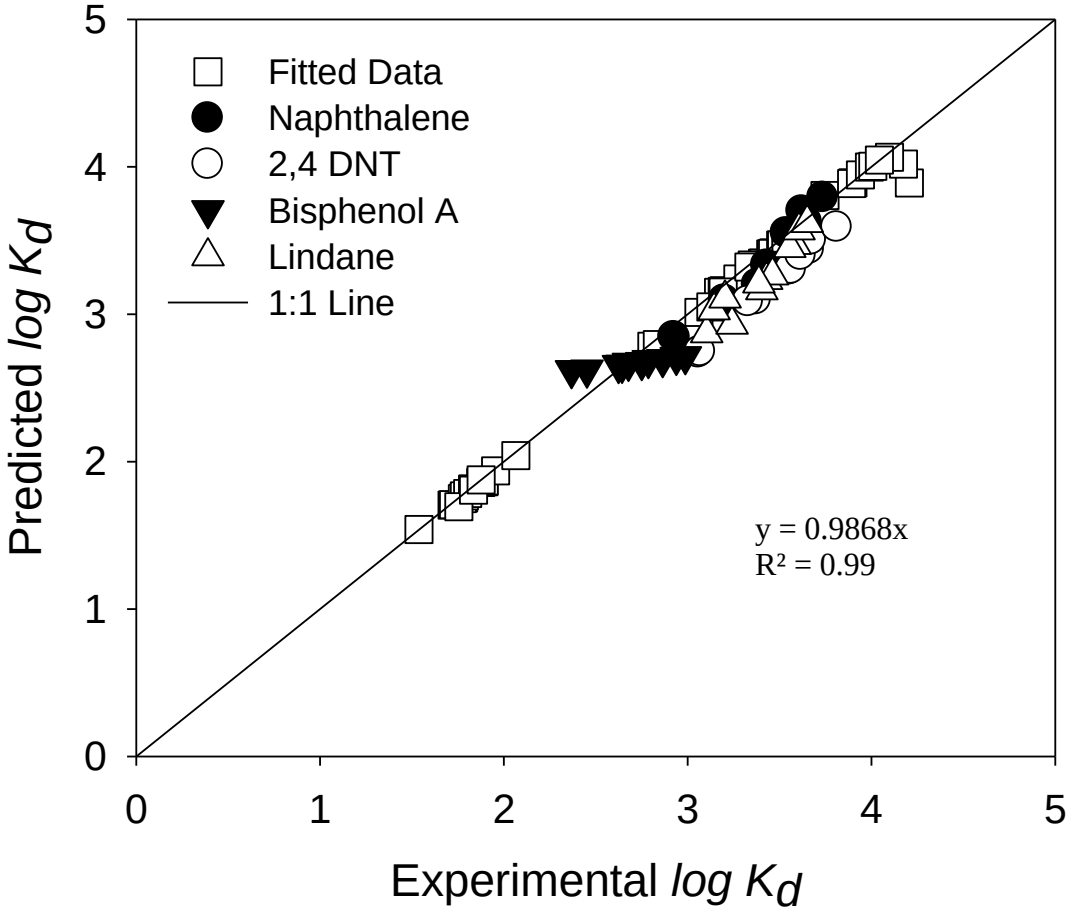


**Figure 4.2: Plot of fitted *log $K_d$* from the correlation developed for isotherms in the presence of NOM against the experimental *log $K_d$* of 6 organic compounds. Naphthalene, 2, 4 DNT, Bisphenol A and Lindane *log $K_d$* values in the presence of NOM were predicted and compared with the experimental *log $K_d$* on this plot.**

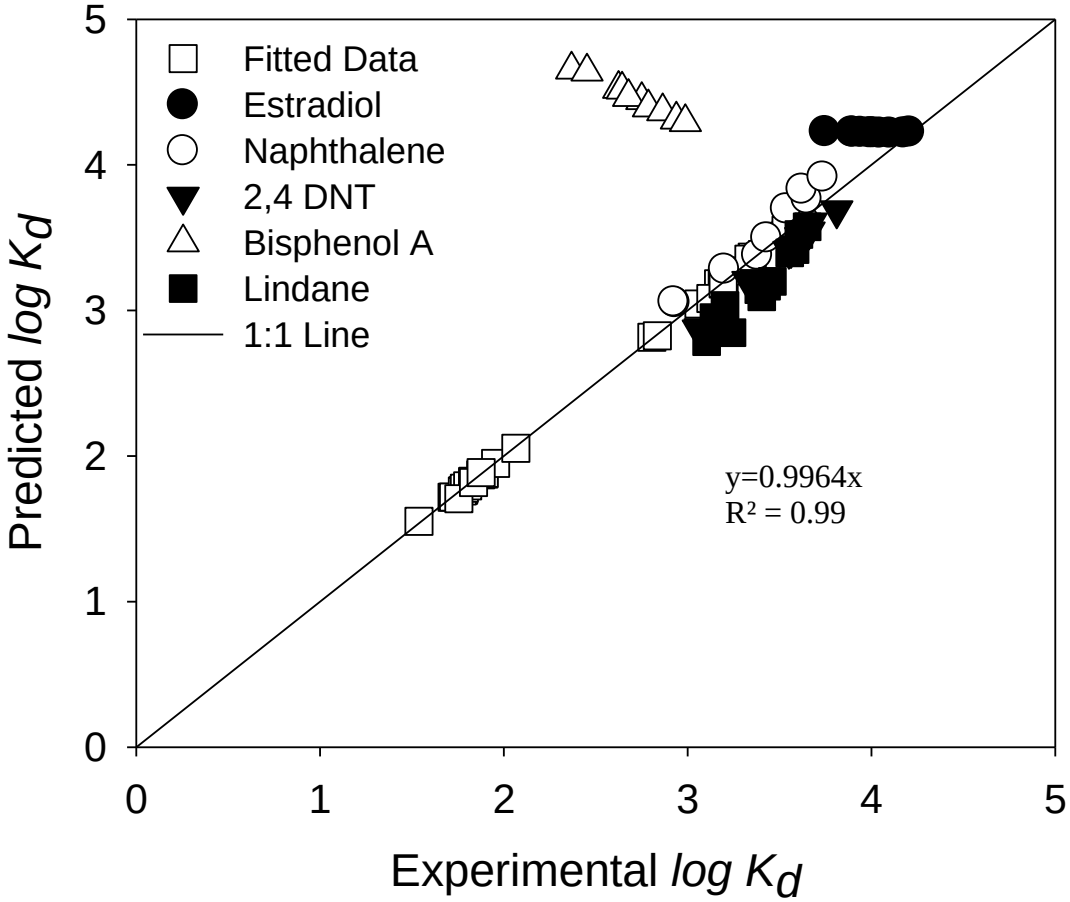


**Figure 4.3: Plot of fitted *log $K_d$* from the correlation developed for isotherms in the presence of NOM against the experimental *log $K_d$* of 5 organic compounds. Estradiol, naphthalene, 2, 4 DNT, bisphenol A and lindane *log $K_d$* values in the presence of NOM were predicted and compared with the experimental *log $K_d$* on this plot.**

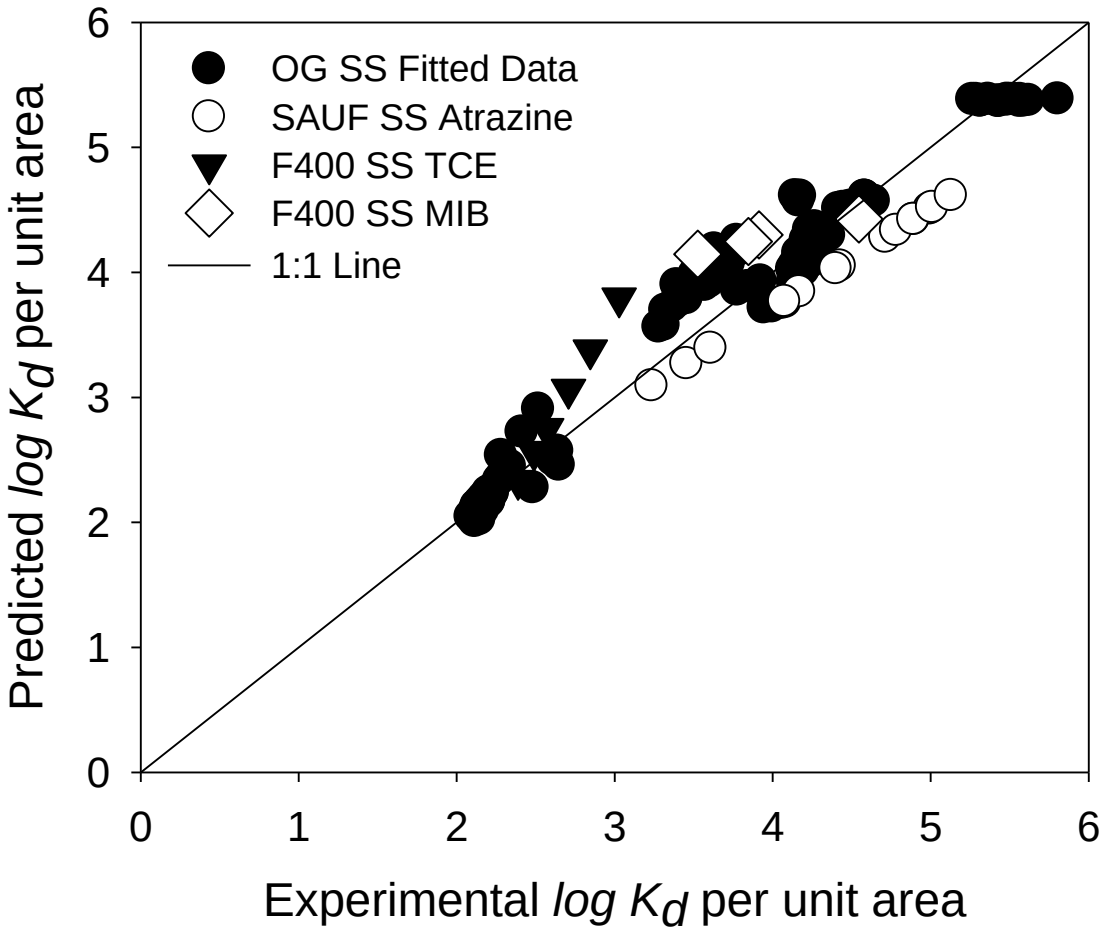


**Figure 4.4: Plot of predicted single solute (SS) *log $K_d$* values (per unit area) using the determined equation for oxidized graphite (OG) vs experimental SS *log $K_d$* values (per unit area) of atrazine on SA-UF activated carbon (SAUF), trichloroethylene on F400 activated carbon and MIB on F400 activated carbon. The predicted SS *log $K_d$* values were normalized with the surface area of OG (0.6m$^2$/g) while the experimental SS *log $K_d$* values were normalized with the surface area of SAUF carbon (1112 m$^2$/g) and F400 carbon (948 m$^2$/g) (To et al., 2008); (Ding et al., 2006); (Newcombe et al., 2002); (Newcombe et al., 2002).**

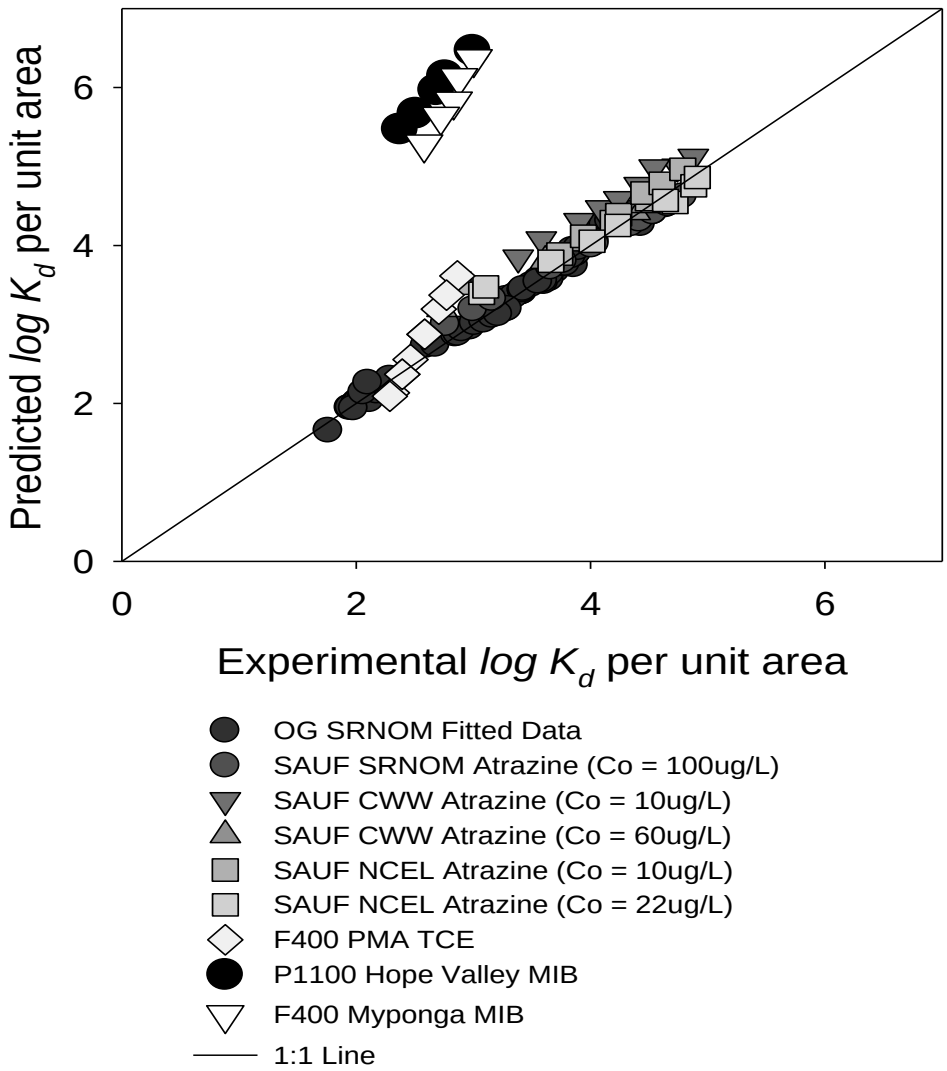


**Figure 4.5: Plot of predicted Suwannee River NOM (SRNOM), Clinton Water Works NOM (CWW) and Newmark Groundwater NOM (NCEL) *log $K_d$* values (per unit area) using the determined equation for OG vs experimental SRNOM, CWW and NCEL *log $K_d$* values (per unit area) of atrazine on SA-UF. The plot also include predicted poly(maleic acid) (PMA) *log $K_d$* values (per unit area) using the OG equation vs experimental PMA *log $K_d$* values (per unit area) of TCE on F400. The plot also include predicted Hope Valley NOM (HV) and Myponga reservoir NOM (MRNOM) *log $K_d$* values (per unit area) using the OG equation vs experimental HV and MRNOM *log $K_d$* values (per unit area) of MIB on PICA and F400. The predicted *log $K_d$* values were normalized with the surface area of OG (0.6m$^2$/g) while the experimental SRNOM, CWW and NCEL *log $K_d$* values were normalized with the surface area of SAUF AC (1112 m$^2$/g), the experimental PMA *log $K_d$* values and HV *log $K_d$* values were normalized with the surface area of F400 (948 m$^2$/g) and the experimental MRNOM *log $K_d$* values were normalized with the surface area of PICA (1241m$^2$/g) (To et al., 2008); (Ding et al., 2006); (Cook et al., 2001) (Newcombe et al., 2002); (Newcombe et al., 2002).**

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# Chapter 5: Linear Free Energy Relationship for Predicting Adsorption of Trace Organic Pollutants from Natural Water onto Activated Carbon

## 5.1 Introduction

Both pore size distribution (PSD) and surface chemistry of activated carbon will affect how organic compounds adsorb. Adsorbates of a particular shape and size can only access some portions of the pore surface, which are determined by the pore size distribution of the activated carbon. The types of chemical functional groups on the activated carbon surface determine interactions between adsorbates and the activated carbon surface.

In chapter 3, the effects of surface chemistry on adsorption isotherm prediction in the absence and presence of natural organic matter (NOM) were determined on non-porous oxidized graphite. It was shown that a polyparameter linear free energy relationship (pp-LFER) is able to predict oxidized graphite adsorption isotherms for both cases successfully. The pp-LFER approach correlated 5 molecular descriptors of organic compounds and the aqueous equilibrium concentration with the adsorption partition coefficient on oxidized graphite. The pp-LFER theory was introduced and developed by Abraham et al. (Abraham et al., 2004). It has been used to predict several partition coefficients in different environmental systems (Nguyen et al., 2005); (Goss, 1997)). A detailed explanation of pp-LFERs can be found in chapter 2.

The equation that was developed to predict isotherms in natural water is as follows:

$$\log K_{d,i} = (e_1 + e_2 \log(C_{e,i}))E + (s_1 + s_2 \log(C_{e,i}))S + (a_1 + a_2 \log(C_{e,i}))A + (b_1 + b_2 \log(C_{e,i}))B + (v_1 + v_2 \log(C_{e,i}))V_x + c_1 + c_2 \log(C_{e,i}) \quad \text{…...(5.1)}$$

where $K_{d,i} = q_{e,i} / C_{e,i}$; $C_{e,i}$ (µg/L) is the concentration of adsorbate i in solution at equilibrium and $q_{e,i}$ (µg/ mg carbon) is the concentration of adsorbate i on carbon at equilibrium

Besides the surface chemistry of activated carbon, the pore size distribution of activated carbon will also affect trace organic compounds and NOM adsorption. Based on the knowledge from the oxidized graphite study, the objective of this chapter was to develop pp-LFER for activated carbon adsorption capacity of trace organic compounds in the presence of NOM using molecular descriptors of the trace compounds.

## 5.2 Materials and Methods

### 5.2.1 Water

De-ionized water was passed through a NANOpure ultrapure water system (Barnstead, Dubuque, Iowa) to produce distilled deionized (DDI) water. The simulated natural water was prepared by dissolving dry form Suwannee River NOM (International Humic Substances Society, St. Paul, Minnesota, USA), isolated by reverse osmosis, in DDI water. The total organic concentration (TOC) of the stock concentration was measured to be 200 mg/L. The stock was then diluted to prepare the solution used to perform isotherm experiments and the final TOC concentration was measured as 4 mg/L and the pH was 7.0.

### 5.2.2 Adsorbent

A commercially available activated carbon, Norit SA-UF powered activated carbon (Norit France, S.a.r.l., Le Blanc Mesnil Cedex, France) was chosen. The SA-UF PAC was dried at 105$^{o}$C overnight, and cooled in a desiccator before weighing. The surface area of SA-UF was determined to be 1112 $m^2/g$ and the majority of the pores are in the micropores and primary mesopores size range (Li et al., 2003). The surface oxygen content of SA-UF carbon was found to be 7.21 mass percent (Chapter 3).

### 5.2.3 Adsorbates

$^{14}$C-labeled target trace organic contaminants were used (American Radiolabeled Chemicals, Inc): four organic solvents (trichloroethylene, 1-heptanol, nitrobenzene, benzene), two endocrine

disrupting compounds (estradiol, bisphenol A), one explosive (2, 4-dinitrotoluene), one herbicide (atrazine), one polycylic aromatic hydrocarbon (naphthalene) and a pharmaceutical (diazepam). The molecular descriptors of the 10 target organic contaminants are listed in Table 1. The molecular descriptors have a range of values that are broad enough to cover a wide range of organic contaminants.

### 5.2.4 Isotherm Tests

Bottle-point isotherm tests were determined for each compound for 7 days (Randtke and Snoeyink, 1983). The initial concentration used for each compound was $10^{-3}$ to $10^{-5}$ of its solubility. For each compound, a different amount of activated carbon was used to achieve an aqueous equilibrium concentration ($C_e$) of $10^{-4}$ to $10^{-8}$ of its solubility. The isotherm bottles were prepared with no headspace, sealed with aluminum foil and mixed for seven days. Isotherms of non-volatile compounds were done using screw top caps with Teflon septa while isotherms of volatile compounds were done with crimp top caps with Teflon/silica septa.

After 7 days, aqueous samples were taken from the isotherm bottles and analyzed. The solid phase concentration was computed using a mass balance. Each set of isotherm experiments had two blanks to determine loss due to factors other than adsorption. Less than 10% loss was found after 7 days.

### 5.2.5 Analytical Methods

The isotherms samples were taken with a 5 ml glass syringe. Samples of estradiol, naphthalene and bisphenol A solution were filtered with 0.45 µm glass fiber membrane filters. Samples of atrazine, 2, 4-dinitrotoluene and diazepam were filtered with 0.45 µm nylon membrane filters. Samples of the solutions with volatile and high solubility compounds (trichloroethylene, 1-heptanol, nitrobenzene, benzene) were taken after the carbon in the bottles was allowed to settle for 8 hours.

Eighteen mL of scintillation cocktail was mixed with 2.5 mL of aqueous sample in a 20 mL scintillation vial. The mixture was then analyzed using a liquid scintillation analyzer (TriCarb Model 1600A, Packard Instrument Co. Downers Grove, IL).

### 5.2.6 Development of Predictive Polyparameter Linear Free Energy Relationship (pp-LFER)

$K_d$ values of isotherms in natural water were calculated for 10 compounds as follow:

$$K_d = q_e / C_e \quad \text{.....(5.2)}$$

where $q_e$ = adsorbed concentration at equilibrium and

$C_e$ = aqueous concentration at equilibrium

The experimental *log* $K_d$ values, *log* $C_e$ values and 5 molecular descriptors of 9 compounds were tabulated and fitted with multiple linear regression using equation 5.1 (Sigma Plot 2000, SPSS, Chicago, IL) to obtain the coefficients. The coefficients $e_1$, $e_2$, $s_1$, $s_2$, $a_1$, $a_2$, $b_1$, $b_2$, $v_1$, $v_2$, $c_1$, $c_2$ determine the tendency of how trace organic compounds partition onto activated carbon in the presence of NOM.

### 5.2.7 Validation of the pp-LFER model

After the pp-LFER equation was determined, it was used to predict *log* $K_d$ values for the 10$^{th}$ compound, the compound that was not used for fitting. The predicted *log* $K_d$ values were compared to experimental *log* $K_d$ values to determine whether the fitted pp-LFER equation could be used to predict isotherms.

## 5.3 Results and Discussion

### 5.3.1 Activated carbon isotherms

Freundlich isotherm parameters for the 10 target organic contaminants in water containing Suwannee river natural organic matter (SRNOM) on activated carbon are reported in Table 2. The *1/n* of heptanol and bisphenol A were observed to be greater than 1. That can be due to the hydroxyl functional group of one molecule interacting with another hydroxyl functional group of another molecule or the hydroxyl functional groups of NOM thus causing more molecules to adsorb beyond the activated carbon surface.

Freundlich isotherm parameters for the 10 target organic contaminants in water containing SRNOM on oxidized graphite are reported in Table 3. In the presence of pores, the order of $K_d$ describing adsorption on activated carbon is different from what was observed on oxidized graphite. Thus, it was shown that the pore size distribution of activated carbon strongly affects the interactions of compounds and NOM with the activated carbon surface.

### 5.3.2 Natural water isotherm fitted pp-LFER

Adsorption data for 9 compounds (atrazine, estradiol, diazepam, 1-heptanol, trichloroethylene, nitrobenzene, benzene, 2, 4- dinitrotoluene, naphthalene) were used to fit the pp-LFER equation and thus determine the coefficients of the parameters in the equation. In Figure 5.1 it is shown that the predicted $log\ K_d$ values were well correlated with experimental $log\ K_d$ ($R^2 = 0.98$).

The best fit pp-LFER equation was established to be:

$$\log K_d = [(-6.79 \pm 3.06) + (-0.71 \pm 0.77)\log C_{e,i}]V + [(7.84 \pm 2.27) + (1.63 \pm 0.64)\log C_{e,i}]B + [(1.08 \pm 0.48) + (-0.14 \pm 0.15)\log C_{e,i}]S + [(-1.26 \pm 0.74) + (-0.83 \pm 0.19)\log C_{e,i}]E \; [(0.52 \pm 2.57) + (0.20 \pm 0.62)\log C_{e,i}]A + [(8.54 \pm 1.68) + (0.67 \pm 0.45)\log C_{e,i}] \quad (5.3)$$

The best-fit equation showed that coefficients $v_2$, $s_2$, $a_1$ and $a_2$ were statistically negligible. The two most important parameters that affect the adsorption were *V* and *B*. This was similar to what Shih and Gschwend observed in their work with single solute isotherm predictions (Shih and Gschwend, 2009).

### 5.3.3 Validation of pp-LFER equation

To determine if the pp-LFER equation, equation 5.3, is able to predict isotherms for other compounds not used in the fitting, the isotherm of bisphenol A was predicted and compared with its experimental isotherm. The data in Figure 5.1 show that the predicted *log* $K_d$ values of bisphenol A, were well correlated with its experimental *log* $K_d$ values. The predicted $K_d$ values are within a factor of 1.81 from the experimental $K_d$ values.

Further validation of the pp-LFER approach was done by withholding 1 out of 10 compounds for the fitting procedure, for all 10 compounds. Table 4 is a tabulation of the average difference between the predicted $K_d$ value of the $10^{th}$ compound and its experimental $K_d$ values. Predictions of $K_d$ values for most compounds were within a factor of 2 with the exceptions of heptanol, atrazine and nitrobenzene. Heptanol has the lowest $K_d$ values and atrazine has the highest $K_d$ values among all 10 compounds. Thus, when either heptanol or atrazine was not used in the fitting process, the predictions of the $K_d$ values were not as good because the predictions will be

an extrapolation of the $K_d$ range used in the fitting. But the extrapolation still yields predicted values that were within a factor of 10 of the experimental values. Nitrobenzene is the compound with the highest aqueous solubility and when it is not used in the fitting, the predictions were an average factor of 6.23 from the experimental values. This indicates that aqueous solubility is an important factor to consider during the selection of compounds to use for fitting.

### 5.3.4 Comparison of the pp-LFER equations for oxidized graphite and activated carbon

The pp-LFER equation for prediction of isotherms in natural water on oxidized graphite was:

$$\log K_{d,i} = [(1.57 \pm 0.63) + (0.36 \pm 0.26)\log C_{e,i}]V + [(-2.49 \pm 0.57) - (0.66 \pm 0.25)\log C_{e,i}]B + [(2.11 \pm 0.25) + (0.30 \pm 0.15)\log C_{e,i}]S + [(0.03 \pm 0.23) + (0.36 \pm 0.10)\log C_{e,i}]E + [(-0.51 \pm 0.25) + (0.04 \pm 0.14)\log C_{e,i}]A + [(-1.27 \pm 0.42) - (1.60 \pm 0.23)\log C_{e,i}] \quad (3.4)$$

In the presence of pore size distribution effects, the signs of $v_1$ and $v_2$ of the activated carbon pp-LFER equation changed from positive values to negative values. The signs of $b_1$ and $b_2$ also changed from negative values to positive values. In terms of chemical interactions, these changes imply that the chemical interactions of target organic compound with the activated carbon surface in the presence of NOM changed in the presence of pores.

The negative sign of coefficients $v_1$ and $v_2$ indicates that the smaller the compound, the higher the $K_d$ and thus more adsorption on activated carbon in the presence of NOM. One good comparison is between estradiol and atrazine. Atrazine is smaller than estradiol with all other parameters to be close with the exception of parameter $A$ but coefficient $a_1$ and $a_2$ have been shown to be negligible. The $K_d$ of atrazine is higher than that of estradiol; and thus more atrazine is removed by activated carbon in the presence of NOM than estradiol. The signs of coefficients

$v_1$ and $v_2$ in this study was also opposite to what was observed in work by Shih and Gschwend on activated carbon adsorption in pure water (Shih and Gschwend, 2009). The signs of coefficients $v_1$ and $v_2$ were positive, meaning that larger target organic compounds will adsorb more onto activated carbon. This difference indicates that the accessibility of larger target organic contaminants to the pores of activated carbon will be hindered more as compared to smaller target organic contaminants in the presence of NOM.

The positive signs of coefficients $b_1$ and $b_2$ indicate that the higher the tendency of the target organic compound towards accepting a hydrogen bond, the more it will adsorb onto activated carbon in the presence of NOM. This trend is again opposite to what was observed for oxidized graphite and for what was observed for activated carbon adsorption in pure water. But it can be observed that the coefficient $b_1$ gradually increased from -9.97 (oxidized graphite in pure water) to -4.47 (activated carbon in pure water) to -2.49 (oxidized graphite in water with NOM) to 7.84 (activated carbon in water with NOM). In the presence of NOM and pores in the system, the differential interactions of target organic compounds with the activated carbon surface and aqueous NOM phase evolved and caused activated carbon to have a higher removal of target organic contaminants that have more hydrogen bond accepting functional groups.

### 5.3.5 Predicting isotherms for another natural water

The pp-LFER equation was developed for one type of activated carbon and one kind of natural water. The type of NOM in different natural water varies tremendously in terms of molecular weights and chemical functional groups. The effect of a difference in NOM composition was

tested by using the pp-LFER equation determined above using SRNOM to predict atrazine isotherms in other natural waters.

Ding et al. measured adsorption isotherms of atrazine in presence of two different natural waters on SA-UF activated carbon. (Ding et al., 2006). The two different natural waters were groundwater from Clinton Water Works (CWW), Clinton, IL and groundwater from a well located next to Newmark Civil Engineering Laboratory (NCEL) at the University of Illinois. The properties of these two natural waters were determined by Ding et al..

In Figure 5.2, it was observed that for higher atrazine initial concentrations, the predicted $K_d$ values were within a factor of 1.5 from the experimental $K_d$ values. For higher NOM initial concentration of 7.5 mg/L, the predicted $K_d$ values were on average, 3 times higher than the experimental $K_d$ values. For a lower NOM initial concentration of 2.5 mg/L, the predicted $K_d$ values were an average of 1.9 higher than the experimental $K_d$ values. The initial concentration of the SRNOM used in this study was 4 mg/L; thus we can speculate that for NOM with an initial concentration that is close to that used in the fitting, the prediction will be better. The initial concentration of the target organic compound is also important. For higher initial concentrations, the predictions were better. However, this exercise was only done for one compound, atrazine, which was used in the fitting process of this study. More adsorption data for other compounds in different natural waters on SA-UF will have to be collected in order to show that one pp-LFER equation will be sufficient to predict adsorption isotherms in different natural waters, on one carbon, with reasonable accuracy.

### 5.3.6 Selection of compounds to develop pp-LFER

The pp-LFER approach has been shown above to be an effective method to predict adsorption isotherms on activated carbon in natural water. However, for each combination of natural water and activated carbon, we will need to develop a pp-LFER equation to predict adsorption isotherms. Thus, it will be valuable to evaluate the selection of compounds required to develop a good pp-LFER.

Six compounds (atrazine, heptanol, nitrobenzene, trichloroethylene, estradiol and diazepam) were selected based on the range of their molecular descriptors. This selected group of compounds covers the wide range of molecular descriptors and aqueous solubility shown in Table 1 ($V$ = 0.71 to 2.19, $B$ = 0.03 to 1.25, $S$ = 0.37 to 1.77, $E$ = 0.21 to 2.08, $A$ = 0 to 0.86 and aqueous solubility = 0.26 mg/L to 1949 mg/L). Using the adsorption isotherms of these six compounds in natural water, the pp-LFER equation was fitted. In Figure 5.3, it was shown that for fitting with 6 compounds, the $K_d$ predictions for bisphenol A, benzene, naphthalene and 2,4-dinitrotoluene were within a factor of 5 from the experimental values.

### 5.3.7 Application to predict elution order of compounds

Granular activated carbon (GAC) columns have been used to remove organic compounds from drinking water. Estimation of an activated carbon adsorber bed's life has been a challenge for the water industries, especially when a new target organic contaminant that is of concern to the public emerges. Snoeyink et al. used isotherm data to predict the remaining lifetime of an

adsorber bed and they showed that reasonable predictions could be made with isotherm data (Snoeyink et al., 1989).

For good estimation of the lifetime of a GAC column, both equilibrium and kinetics data are required (Schideman et al., 2007). But to determine if new compounds will breakthrough a GAC column quickly, or if it will break through before another compound the predictive tool developed in this study will be of great use. By assuming an ideal breakthrough curve, the sequence of the elution of organic compounds will be determined by their $K_d$ values. A higher $K_d$ value will have a longer retention time in the GAC column while a lower $K_d$ will indicate a faster breakthrough. For initial design of GAC column, the pp-LFER equation can help water utilities plan ahead for a variety of organic compounds. When a new organic compound emerges, water utilities can obtain the molecular descriptors and the aqueous concentration of the compound and apply the pp-LFER equation developed to get the $K_d$ value of the new compound. This will help water utilities predict if the new compound will be of great concern and if the GAC column does not have a high capacity for it.

One point to note is that the pp-LFER was determined for simultaneous adsorption of organic compound and NOM on activated carbon. Frequently a GAC column will be preloaded with NOM before the organic contaminant is introduced (Gillogly et al., 1999); (Knappe et al., 1997); (Speth, 1991). Further study of NOM preloading effects on GAC column will have to be done in order to determine the limits of this approach to predict elution order.

## 5.4 Conclusion

- $K_d$ values of adsorption of organic compounds in SRNOM on activated carbon can be predicted by a pp-LFER within a factor of 1.81 from the experimental adsorption isotherms.
- The pp-LFER equation can be extrapolated and used to predict $K_d$ of atrazine in two different natural waters on SAUF carbon within a factor of 3.
- To predict adsorption isotherms effectively, at least 6 organic compounds adsorption isotherms will have to be determined, in order to predict $K_d$ values that are within a factor of 5 from the experimental value.
- The pp-LFER equation can be applied to predict the elution order of organic compounds from a GAC column.

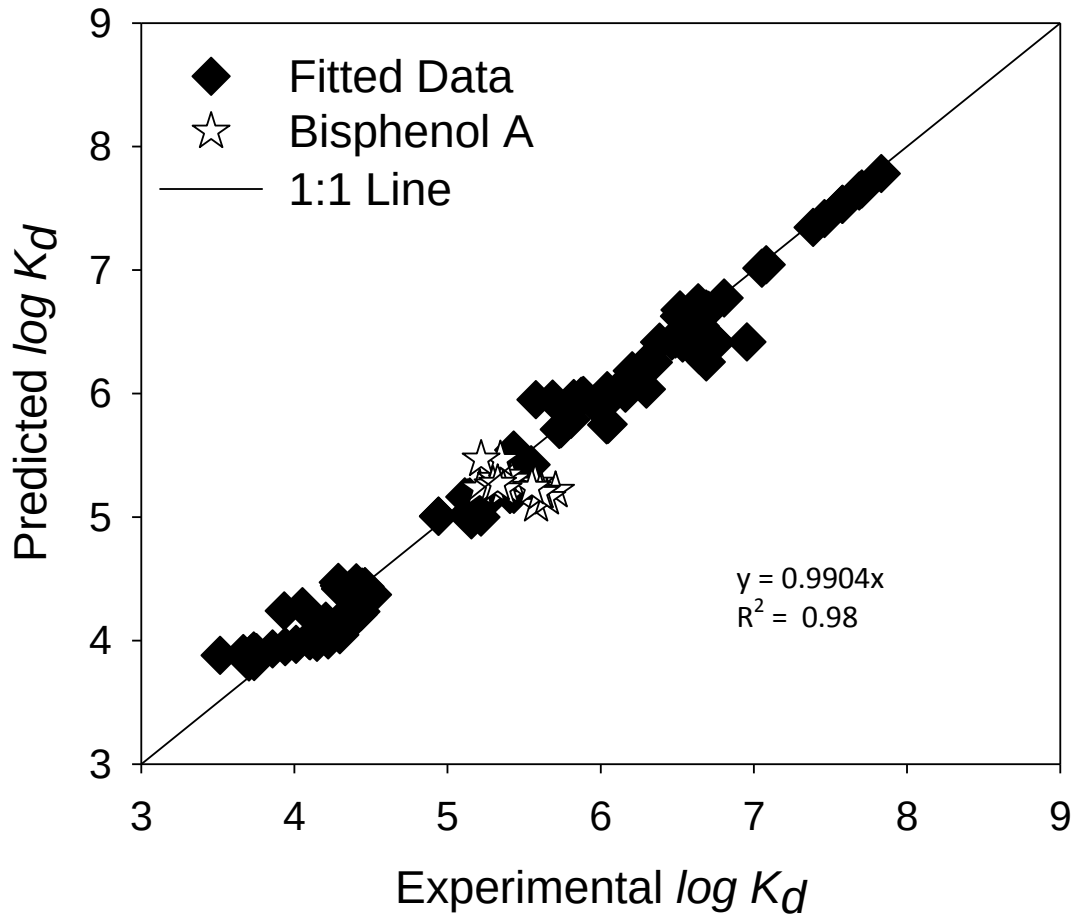


**Figure 5.1: Plot of *log $K_d$* values predicted by pp-LFER equation fitted using isotherms of 9 organic compounds against the experimental *log $K_d$* values of the 9 organic compounds. *log $K_d$* values of Bisphenol A (not used in fitting) were predicted and compared with the experimental values on this plot marked as stars.**

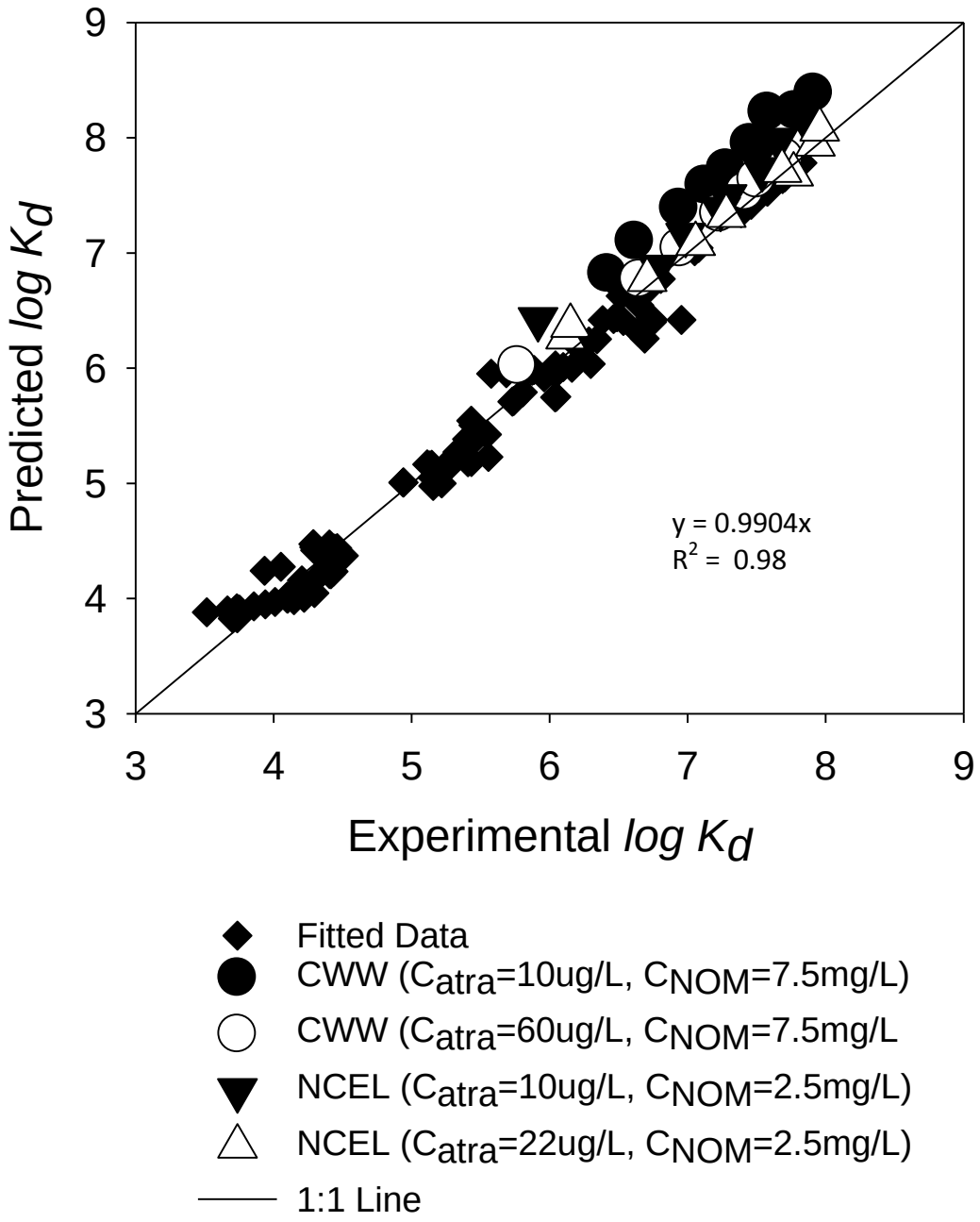


**Figure 5.2: Comparison of predicted *log $K_d$* values for SA-UF isotherms of atrazine in Clinton Water Works (CWW) and Newmark Groundwater (NCEL) with the experimental *Log $K_d$* values. The total organic carbon (TOC) concentration of CWW was 7.5mg/L and NCEL is 2.5mg/L. Two initial concentrations of atrazine was used for both natural waters (Ding et al., 2006).**

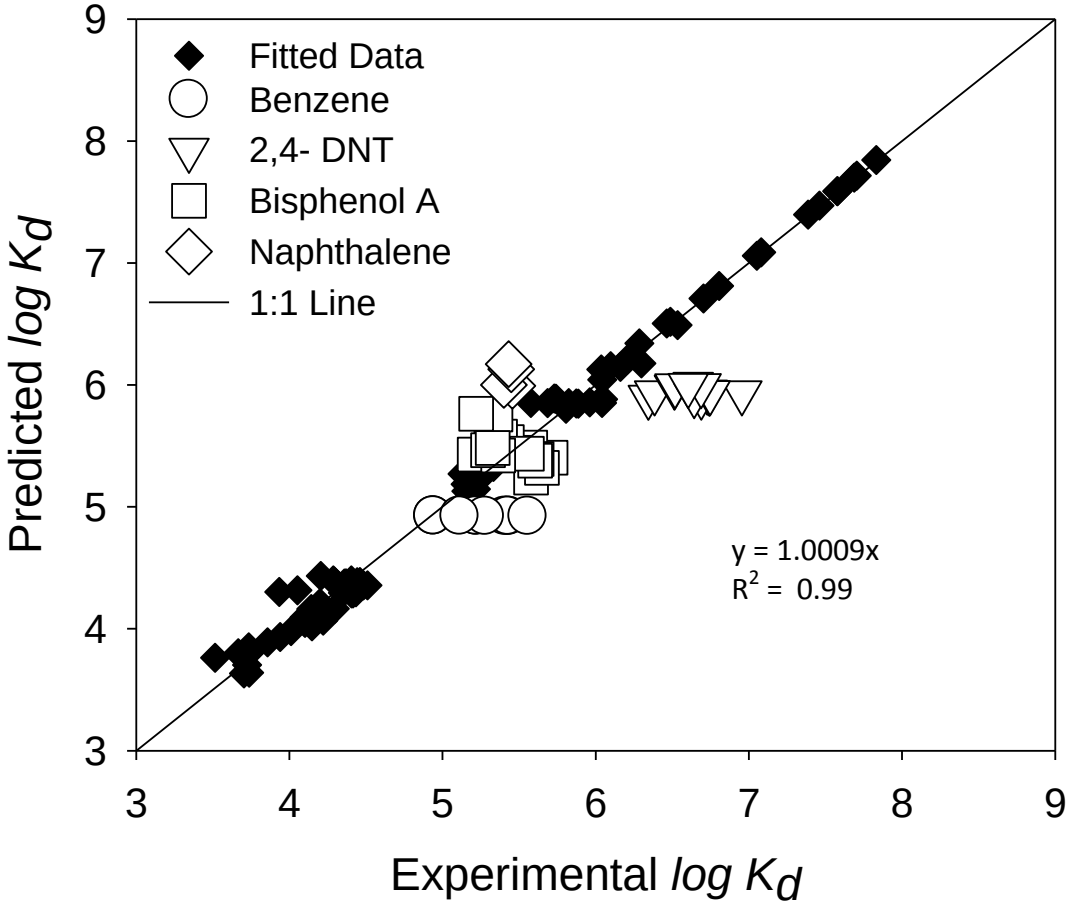


**Figure 5.3: Plot of *log $K_d$* values predicted by pp-LFER equation fitted using isotherms of 6 compounds (atrazine, estradiol, diazepam, trichloroethylene, 1-heptanol, nitrobenzene) against the experimental *log $K_d$* values of the 6 organic compounds. Naphthalene, 2, 4 DNT, Bisphenol A and Benzene *log $K_d$* values in the presence of SRNOM were predicted and compared with the experimental *log $K_d$* on this plot.**

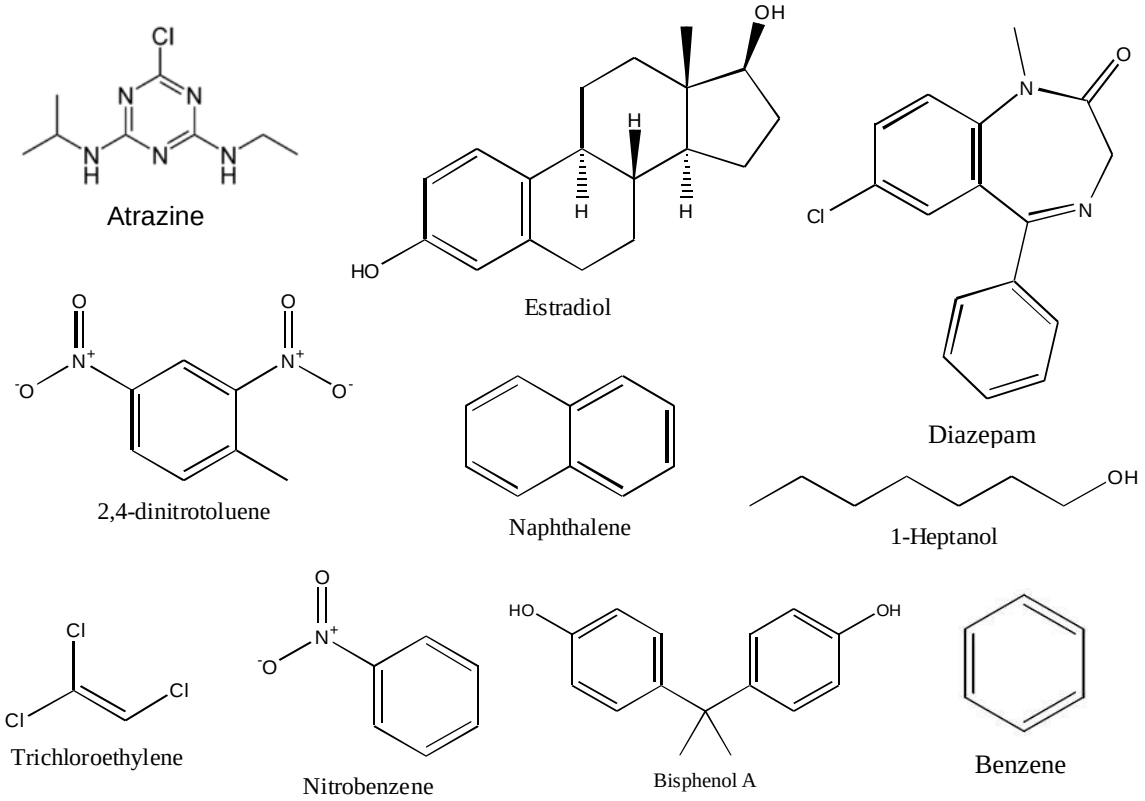


**Table 5.1: Aqueous solubility (Yaw, 1999); (ADME/ Tox WEB) and molecular properties (Abraham et al., 1994a); (Abraham et al., 1994b); (ADME/ Tox WEB) of compounds used for fitting of *log $K_d$* predictive equation.**

| No | Compound | *E* | *S* | *A* | *B* | $V_x$ | Aq. Solubility (mg/L) |
|---|---|---|---|---|---|---|---|
| **1** | Atrazine | 1.95 | 1.64 | 0 | 1.04 | 1.61 | 70 |
| **2** | Estradiol | 1.80 | 1.77 | 0.86 | 1.10 | 2.19 | 0.26 |
| **3** | Diazepam | 2.08 | 1.55 | 0.09 | 1.25 | 2.07 | 50 |
| **4** | Naphthalene | 1.34 | 0.92 | 0 | 0.20 | 1.08 | 30 |
| **5** | 2,4-Dinitrotoluene | 1.17 | 1.27 | 0.07 | 0.51 | 1.20 | 270 |
| **6** | Bisphenol A | 1.60 | 1.56 | 0.99 | 0.94 | 1.86 | 300 |
| **7** | Nitrobenzene | 0.87 | 1.11 | 0 | 0.28 | 0.89 | 1949 |
| **8** | Trichloroethylene | 0.52 | 0.37 | 0.08 | 0.03 | 0.71 | 1280 |
| **9** | Benzene | 0.61 | 0.52 | 0 | 0.14 | 0.71 | 1760 |
| **10** | 1-Heptanol | 0.21 | 0.42 | 0.37 | 0.48 | 1.15 | 1740 |

**Table 5.2: Experimental Freundlich isotherm parameters of 10 compounds on Activated Carbon in the presence of NOM**

| No | Compound | $K_f \times 10^4$ | 1/n |
|---|---|---|---|
| 1 | Atrazine (To et al., 2008) | 12 | 0.36 |
| 2 | Estradiol | 0.114 | 0.48 |
| 3 | Diazepam | 0.895 | 0.43 |
| 4 | Nitrobenzene | 100 | 1.06 |
| 5 | Benzene | 0.751 | 0.54 |
| 6 | 2,4 Dinitrotoluene | 500 | 1.00 |
| 7 | Bisphenol A | 2000 | 1.49 |
| 8 | Trichloroethylene | 1.25 | 0.89 |
| 9 | Naphthalene | 18 | 0.94 |
| 10 | Heptanol | 100 | 2.15 |

**Table 5.3: Experimental Freundlich isotherm parameters of 10 compounds on Oxidized Graphite in the presence of NOM**

| Compound | $K_f$ | 1/n |
|---|---|---|
| Atrazine | 250 | 0.58 |
| Estradiol | 177 | 0.56 |
| Diazepam | 67 | 0.40 |
| Naphthalene | 70 | 0.40 |
| 2,4 Dinitrotoluene | 185 | 0.41 |
| Nitrobenzene | 62 | 0.28 |
| 1-Heptanol | 6 | 0.28 |
| Trichloroethylene | 12 | 0.32 |
| Lindane | 64 | 0.41 |
| Bisphenol A | 80 | 0.34 |

**Table 5.4: Ratio of predicted $K_d$ values and experimental $K_d$ values of the 10th compound (not used in the fitting procedure)**

| No. | Compounds | *Average*($K_d$ Predicted/ $K_d$ Experimental) | Range($K_d$ Predicted/ $K_d$ Experimental) |
|---|---|---|---|
| 1 | Naphthalene | 5.13 | 3.66-6.89 |
| 2 | Bisphenol A | 1.81 | 1.01-3.11 |
| 3 | 2, 4- Dinitrotoluene | 1.80 | 1.03-3.81 |
| 4 | Benzene | 2.22 | 1.08-3.88 |
| 5 | Nitrobenzene | 6.23 | 3.77-10.99 |
| 6 | Trichloroethylene | 1.41 | 1.06-2.54 |
| 7 | Heptanol | 10.18 | 6.47-19.00 |
| 8 | Diazepam | 1.66 | 1.14-2.36 |
| 9 | Estradiol | 2.02 | 1.48-3.68 |
| 10 | Atrazine | 8.17 | 1.09-39.94 |

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# Chapter 6: Summary and Future Research

## 6.1 Summary

Activated carbon has long been used to treat trace organic chemicals and natural organic matter (NOM) in drinking water. Industries have produced many new organic compounds that will eventually make it to our drinking water sources. To be able to assure the public that the current water treatment system is capable of dealing with these new organic compounds, good predictive tools will be useful for a quick initial evaluation of expected activated carbon performance.

Polyparameter linear free energy relationships (pp-LFERs) have been successful in predicting partition coefficients of many environmental systems. There are also many studies that have been done with pp-LFERs and quantitative structure-activity relationships (QSARs) to predict isotherms in organic-free water. But there has not been a good way to predict the expected performance of activated carbon for removal of trace organic compounds in the natural water. In this work, it has been demonstrated that pp-LFERs are applicable to carbon systems and that they can be used to make good predictions of adsorption capacity. Adsorption capacity values can then be used to estimate performance.

The first part of this research demonstrated that pp-LFERs are effective in predicting non-porous oxidized graphite isotherms in waters in absence and presence of NOM. In absence of pores, the surface interactions were greatly influenced by the molecular volume ($V$) and overall hydrogen-

bond basicity (*B*) of the organic compound. Larger compounds with lower hydrogen-bond basicity will adsorb more strongly onto oxidized graphite. In the presence of NOM, similar trends were observed but the magnitude of the dependency on parameters *V* and *B* decreased indicating the influence of surface interactions by NOM adsorption. Both oxidized graphite pp-LFER equations developed for absence and presence of NOM predicted adsorption isotherms that are within a factor of 2 from the experimental isotherms.

The second part of this research demonstrated that pp-LFERs are also effective in predicting activated carbon isotherms in the presence of NOM. In the presence of pores, the pp-LFER equation changed significantly emphasizing the importance of pore size distribution. The signs of parameters *V* and *B* changed signs from what was determined for oxidized graphite. Adsorption of organic compounds is not only determined by surface interactions but also by the amount and size of pores accessible for removal. The pp-LFER predicted adsorption isotherms that are within a factor 2 from the experimental isotherms. The predicted adsorption isotherm data can be used to determine the elution order of organic compounds from a granular activated carbon (GAC) column. It was also shown that atrazine in other natural waters can also be predicted by the same pp-LFER equation with reasonable accuracy.

### 6.2 Future Research

This study has shown that pp-LFERs are effective in predicting adsorption isotherms on one type of activated carbon in the presence of one type of NOM. Future research should focus on extending this study to undertake the following specific tasks:

- To determine if the pp-LFER equation developed using one type of NOM is applicable to other natural waters. The NOM in different natural waters varies widely in terms of chemistry and molecular weight distribution. It was shown in this work that the equation developed using Suwanee River NOM could be applied to atrazine in two other natural waters. Isotherms of more compounds in other natural waters on the same activated carbon must be determined to demonstrate that the effects of NOM variability are not great enough to require the development of a new pp-LFER.

- To determine the limit of the pp-LFER equation to predict isotherms of NOM preloaded activated carbon. Preloading of NOM has been a great problem in GAC columns. Thus, it will be important to determine the amount of NOM preloading that will cause a change in the elution order determined by the pp-LFER equation.

- To determine a parameter that can represent the effects of pore size distribution of activated carbon on adsorption capacity. Different activated carbons have different pore size distribution and that will greatly influence the adsorption process. Thus if a parameter can be determined to represent this in the pp-LFER equation then it will make the pp-LFER equation more useful for predicting adsorption capacity of activated carbon.

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# Appendix:

**Table A1: Oxidized graphite single solute isotherm data of 10 trace organic compounds**

**Atrazine**

| $C_e$ (ug/L) | $C_e$ (mg/L) | q (ug/mg) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 3.466922986 | 0.003467 | 0.020636 | 20.6355 | 5952.109 | 3.774671 |
| 3.026535356 | 0.003027 | 0.020825 | 20.82523 | 6880.88 | 3.837644 |
| 2.911329818 | 0.002911 | 0.02107 | 21.07008 | 7237.27 | 3.859575 |
| 1.253571306 | 0.001254 | 0.010782 | 10.78244 | 8601.374 | 3.934568 |
| 1.255061912 | 0.001255 | 0.010735 | 10.73464 | 8553.074 | 3.932122 |
| 1.325711082 | 0.001326 | 0.010739 | 10.73879 | 8100.402 | 3.908507 |
| 0.895775059 | 0.000896 | 0.008082 | 8.082179 | 9022.554 | 3.955329 |
| 0.894913701 | 0.000895 | 0.008133 | 8.133221 | 9088.274 | 3.958481 |
| 0.859639822 | 0.00086 | 0.008122 | 8.122245 | 9448.428 | 3.97536 |
| 0.813325544 | 0.000813 | 0.006514 | 6.514043 | 8009.146 | 3.903586 |
| 0.631607672 | 0.000632 | 0.006562 | 6.562229 | 10389.72 | 4.016604 |
| 1.278942527 | 0.001279 | 0.00645 | 6.449823 | 5043.091 | 3.702697 |
| 0.507316535 | 0.000507 | 0.005445 | 5.44512 | 10733.18 | 4.030728 |
| 0.519581426 | 0.00052 | 0.005456 | 5.455725 | 10500.23 | 4.021199 |
| 0.560635284 | 0.000561 | 0.005457 | 5.457097 | 9733.774 | 3.988281 |

**Table A1 (cont.)**

**Estradiol**

| $C_e$ (ug/L) | $C_e$ (mg/L) | q (ug/mg) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 0.080438053 | 8.04E-05 | 0.017671 | 17.6706 | 219679.6 | 5.34179 |
| 0.070860888 | 7.09E-05 | 0.016455 | 16.45536 | 232220.7 | 5.365901 |
| 0.082718143 | 8.27E-05 | 0.013245 | 13.24516 | 160124 | 5.204456 |
| 0.07978083 | 7.98E-05 | 0.012973 | 12.97348 | 162614 | 5.211158 |
| 0.053950824 | 5.4E-05 | 0.008719 | 8.71858 | 161602.4 | 5.208448 |
| 0.070920954 | 7.09E-05 | 0.008726 | 8.726462 | 123044.9 | 5.090064 |
| 0.053473957 | 5.35E-05 | 0.006687 | 6.68698 | 125051.2 | 5.097088 |
| 0.021837215 | 2.18E-05 | 0.005458 | 5.45757 | 249920.6 | 5.397802 |
| 0.016816417 | 1.68E-05 | 0.00305 | 3.050279 | 181386.9 | 5.258606 |
| 0.022908315 | 2.29E-05 | 0.002867 | 2.867484 | 125172.2 | 5.097508 |
| 0.007469367 | 7.47E-06 | 0.001579 | 1.579331 | 211441 | 5.325189 |
| 0.007205778 | 7.21E-06 | 0.001598 | 1.597848 | 221745.5 | 5.345855 |
| 0.002798712 | 2.8E-06 | 0.001072 | 1.072409 | 383179.4 | 5.583402 |
| 0.005547319 | 5.55E-06 | 0.00107 | 1.070226 | 192926.7 | 5.285392 |
| 0.006856247 | 6.86E-06 | 0.000798 | 0.797571 | 116327.6 | 5.065683 |
| 0.004361668 | 4.36E-06 | 0.000799 | 0.798554 | 183084.5 | 5.262652 |
| 0.004655032 | 4.66E-06 | 0.000647 | 0.647048 | 138999.6 | 5.143014 |
| 0.005811775 | 5.81E-06 | 0.000642 | 0.641969 | 110460 | 5.043205 |

**Diazepam**

| $C_e$ (ug/L) | $C_e$ (mg/L) | q (ug/mg) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 2.868910794 | 0.002869 | 0.023957 | 23.95675 | 8350.468 | 3.921711 |
| 2.66449695 | 0.002664 | 0.023949 | 23.94924 | 8988.278 | 3.953676 |
| 1.392070876 | 0.001392 | 0.012158 | 12.15795 | 8733.717 | 3.941199 |
| 0.651401441 | 0.000651 | 0.012095 | 12.09503 | 18567.71 | 4.268758 |
| 0.483199393 | 0.000483 | 0.009171 | 9.171038 | 18979.82 | 4.278292 |
| 0.557489987 | 0.000557 | 0.009357 | 9.35653 | 16783.31 | 4.224878 |
| 0.480484649 | 0.00048 | 0.007514 | 7.514141 | 15638.67 | 4.1942 |
| 0.448344503 | 0.000448 | 0.007299 | 7.298523 | 16278.83 | 4.211623 |
| 0.367872845 | 0.000368 | 0.006166 | 6.165786 | 16760.64 | 4.224291 |
| 0.345165512 | 0.000345 | 0.006286 | 6.285671 | 18210.6 | 4.260324 |

**Table A1 (cont.)**

**Naphthalene**

| $C_e$ (ug/L) | $C_e$ (mg/L) | q (ug/mg) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 4.924223976 | 0.004924 | 0.020513 | 20.51308 | 4165.749 | 3.619693 |
| 5.585295767 | 0.005585 | 0.019978 | 19.97805 | 3576.901 | 3.553507 |
| 1.00892852 | 0.001009 | 0.01228 | 12.27977 | 12171.1 | 4.08533 |
| 1.375492831 | 0.001375 | 0.01202 | 12.01979 | 8738.531 | 3.941438 |
| 0.369984941 | 0.00037 | 0.008443 | 8.443229 | 22820.47 | 4.358325 |
| 0.379441351 | 0.000379 | 0.008519 | 8.519113 | 22451.73 | 4.35125 |
| 0.225320781 | 0.000225 | 0.005062 | 5.062379 | 22467.43 | 4.351553 |
| 0.192308278 | 0.000192 | 0.005056 | 5.055718 | 26289.65 | 4.419785 |
| 0.157552578 | 0.000158 | 0.003617 | 3.617212 | 22958.76 | 4.360948 |
| 0.1593956 | 0.000159 | 0.003676 | 3.675724 | 23060.39 | 4.362867 |

**2,4-dinitrotoluene**

| $C_e$ (ug/L) | $C_e$ (mg/L) | q (ug/mg) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 13.13200742 | 0.013132 | 0.06951 | 69.50979 | 5293.158 | 3.723715 |
| 11.78587499 | 0.011786 | 0.069516 | 69.51565 | 5898.218 | 3.770721 |
| 3.493969635 | 0.003494 | 0.036068 | 36.0675 | 10322.79 | 4.013797 |
| 4.403600155 | 0.004404 | 0.036595 | 36.59541 | 8310.339 | 3.919619 |
| 2.082156508 | 0.002082 | 0.028528 | 28.52802 | 13701.19 | 4.136758 |
| 2.687073912 | 0.002687 | 0.027185 | 27.1845 | 10116.77 | 4.005042 |
| 2.198808405 | 0.002199 | 0.02203 | 22.03006 | 10019.09 | 4.000828 |
| 2.328085384 | 0.002328 | 0.022726 | 22.72603 | 9761.681 | 3.989525 |
| 1.804318846 | 0.001804 | 0.018464 | 18.464 | 10233.23 | 4.010013 |
| 1.665794786 | 0.001666 | 0.018485 | 18.48476 | 11096.66 | 4.045192 |

**Table A1 (cont.)**

**Nitrobenzene**

| $C_e$ (ug/L) | $C_e$ (mg/L) | q (ug/mg) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 1308.479069 | 1.308479 | 0.102268 | 102.2679 | 78.15781 | 1.892972 |
| 1268.457913 | 1.268458 | 0.106328 | 106.3282 | 83.82479 | 1.923372 |
| 1202.938061 | 1.202938 | 0.088792 | 88.79196 | 73.81258 | 1.86813 |
| 1189.703357 | 1.189703 | 0.093308 | 93.30774 | 78.42942 | 1.894479 |
| 1084.541751 | 1.084542 | 0.084936 | 84.93573 | 78.31486 | 1.893844 |
| 1063.019228 | 1.063019 | 0.088168 | 88.16833 | 82.94143 | 1.918772 |
| 993.5573082 | 0.993557 | 0.079884 | 79.88407 | 80.40207 | 1.905267 |
| 996.6836764 | 0.996684 | 0.080692 | 80.69202 | 80.96052 | 1.908273 |
| 859.0478924 | 0.859048 | 0.076982 | 76.98185 | 89.61299 | 1.952371 |
| 927.4367696 | 0.927437 | 0.078768 | 78.76754 | 84.93036 | 1.929063 |
| 1075.455654 | 1.075456 | 0.095119 | 95.11863 | 88.44496 | 1.946673 |
| 1141.329819 | 1.14133 | 0.09153 | 91.5297 | 80.19566 | 1.904151 |
| 904.920007 | 0.90492 | 0.088131 | 88.1306 | 97.39048 | 1.988517 |
| 928.3101554 | 0.92831 | 0.089528 | 89.52798 | 96.44189 | 1.984266 |
| 780.2540235 | 0.780254 | 0.079804 | 79.80403 | 102.2796 | 2.009789 |
| 793.1572421 | 0.793157 | 0.080575 | 80.57544 | 101.5882 | 2.006843 |
| 755.4387778 | 0.755439 | 0.074952 | 74.95184 | 99.2163 | 1.996583 |
| 775.7419891 | 0.775742 | 0.07395 | 73.94979 | 95.32782 | 1.97922 |
| 629.4976928 | 0.629498 | 0.070381 | 70.38099 | 111.805 | 2.048461 |
| 596.2008488 | 0.596201 | 0.069032 | 69.03186 | 115.7862 | 2.063657 |

**Lindane**

| $C_e$ (ug/L) | $C_e$ (mg/L) | q (ug/mg) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 4.192221025 | 0.004192 | 0.015221 | 15.22141 | 3630.871 | 3.560011 |
| 3.401835315 | 0.003402 | 0.018244 | 18.24352 | 5362.847 | 3.729395 |
| 1.203364672 | 0.001203 | 0.013358 | 13.35766 | 11100.26 | 4.045333 |
| 0.843460525 | 0.000843 | 0.009454 | 9.453932 | 11208.51 | 4.049548 |
| 0.535121797 | 0.000535 | 0.009938 | 9.937994 | 18571.46 | 4.268846 |
| 0.450631379 | 0.000451 | 0.007612 | 7.612062 | 16891.99 | 4.227681 |
| 0.273805241 | 0.000274 | 0.007729 | 7.72897 | 28227.99 | 4.45068 |
| 0.240479488 | 0.00024 | 0.006277 | 6.277316 | 26103.33 | 4.416696 |
| 0.199136255 | 0.000199 | 0.006296 | 6.296108 | 31617.09 | 4.499922 |

**Table A1 (cont.)**

**Bisphenol A**

| $C_e$ (ug/L) | $C_e$ (mg/L) | q (ug/mg) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 43.09845546 | 0.043098 | 0.074043 | 74.04266 | 1717.989 | 3.23502 |
| 47.24465434 | 0.047245 | 0.072218 | 72.21817 | 1528.6 | 3.184294 |
| 13.19264106 | 0.013193 | 0.041959 | 41.95865 | 3180.458 | 3.50249 |
| 27.10196628 | 0.027102 | 0.040147 | 40.14658 | 1481.316 | 3.170648 |
| 12.67292339 | 0.012673 | 0.032455 | 32.45463 | 2560.942 | 3.4084 |
| 8.491654278 | 0.008492 | 0.031488 | 31.48788 | 3708.097 | 3.569151 |
| 7.359752116 | 0.00736 | 0.026421 | 26.42055 | 3589.869 | 3.555079 |
| 7.636076622 | 0.007636 | 0.026791 | 26.7914 | 3508.529 | 3.545125 |
| 8.150727128 | 0.008151 | 0.020955 | 20.95546 | 2570.993 | 3.410101 |
| 6.157147118 | 0.006157 | 0.021928 | 21.92763 | 3561.329 | 3.551612 |
| 110.9396013 | 0.11094 | 0.126443 | 126.4428 | 1139.744 | 3.056807 |
| 104.2603102 | 0.10426 | 0.128164 | 128.1643 | 1229.272 | 3.089648 |
| 55.80411467 | 0.055804 | 0.078176 | 78.17643 | 1400.908 | 3.14641 |
| 63.35856468 | 0.063359 | 0.079735 | 79.73477 | 1258.469 | 3.099842 |
| 27.64406114 | 0.027644 | 0.061791 | 61.79135 | 2235.249 | 3.349326 |
| 24.7022699 | 0.024702 | 0.059061 | 59.06068 | 2390.901 | 3.378562 |
| 16.80133303 | 0.016801 | 0.047062 | 47.06205 | 2801.09 | 3.447327 |
| 19.83549627 | 0.019835 | 0.046985 | 46.98546 | 2368.756 | 3.37452 |
| 14.24770025 | 0.014248 | 0.03785 | 37.85041 | 2656.598 | 3.424326 |
| 19.34377516 | 0.019344 | 0.03726 | 37.26006 | 1926.204 | 3.284702 |

**1-Heptanol**

| $C_e$ (ug/L) | $C_e$ (mg/L) | q (ug/mg) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 31.46977771 | 0.03147 | 0.005738 | 5.73832 | 182.3438 | 2.260891 |
| 18.16841559 | 0.018168 | 0.00444 | 4.439922 | 244.3758 | 2.388058 |
| 15.23106174 | 0.015231 | 0.003976 | 3.976252 | 261.062 | 2.416744 |
| 20.09884959 | 0.020099 | 0.005354 | 5.353613 | 266.3641 | 2.425476 |

**TCE**

| $C_e$ (ug/L) | $C_e$ (mg/L) | q (ug/mg) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 32.17446037 | 0.032174 | 0.003698 | 3.698468 | 114.9504 | 2.060511 |
| 21.25480943 | 0.021255 | 0.0033 | 3.300018 | 155.2598 | 2.191059 |
| 14.19457195 | 0.014195 | 0.0028 | 2.799979 | 197.257 | 2.295032 |
| 38.95538104 | 0.038955 | 0.005087 | 5.087394 | 130.5954 | 2.115928 |

**Table A2: Oxidized graphite competitive isotherm data of 10 trace organic compounds**

**Atrazine**

| $C_e$ (ug/L) | $C_e$ (mg/L) | q (ug/mg) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 12.14056476 | 0.012140565 | 0.017912382 | 17.9123817 | 1475.415852 | 3.168914445 |
| 11.40409832 | 0.011404098 | 0.018018728 | 18.01872824 | 1580.022176 | 3.198663183 |
| 11.76287693 | 0.011762877 | 0.018136806 | 18.13680574 | 1541.868189 | 3.188047248 |
| 3.963278933 | 0.003963279 | 0.010131219 | 10.13121946 | 2556.272126 | 3.407607084 |
| 3.975100216 | 0.0039751 | 0.010325133 | 10.3251325 | 2597.452125 | 3.414547552 |
| 3.45810308 | 0.003458103 | 0.010414399 | 10.41439864 | 3011.592886 | 3.478796263 |
| 2.788410765 | 0.002788411 | 0.007895152 | 7.895151556 | 2831.416251 | 3.45200372 |
| 2.675983502 | 0.002675984 | 0.007894937 | 7.8949368 | 2950.293526 | 3.469865226 |
| 2.726253356 | 0.002726253 | 0.007913602 | 7.913601605 | 2902.738878 | 3.46280797 |
| 1.988019792 | 0.00198802 | 0.006385821 | 6.385820808 | 3212.151526 | 3.506796024 |
| 1.976706184 | 0.001976706 | 0.006411565 | 6.411565252 | 3243.560071 | 3.511021946 |
| 1.863699936 | 0.0018637 | 0.006398518 | 6.398517933 | 3433.233971 | 3.535703401 |
| 1.496826906 | 0.001496827 | 0.005371764 | 5.371763541 | 3588.767359 | 3.554945306 |
| 1.442913477 | 0.001442913 | 0.005372955 | 5.372954501 | 3723.684466 | 3.570972873 |
| 1.560906557 | 0.001560907 | 0.005357285 | 5.357284585 | 3432.162267 | 3.535567812 |

**Estradiol**

| $C_e$ (ug/L) | $C_e$ (mg/L) | q (ug/mg) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 0.18900723 | 0.000189007 | 0.001055752 | 1.055752462 | 5585.778187 | 3.747083686 |
| 0.120159477 | 0.000120159 | 0.001931092 | 1.93109176 | 16071.07322 | 4.20604488 |
| 0.119362654 | 0.000119363 | 0.000948001 | 0.948001293 | 7942.193464 | 3.899940462 |
| 0.12258624 | 0.000122586 | 0.000958133 | 0.95813267 | 7815.988751 | 3.892983926 |
| 0.089521739 | 8.95217E-05 | 0.000780677 | 0.780676546 | 8720.524836 | 3.940542623 |
| 0.060182744 | 6.01827E-05 | 0.000899143 | 0.899142908 | 14940.21115 | 4.174356735 |
| 0.066884598 | 6.68846E-05 | 0.000653404 | 0.653404214 | 9769.128244 | 3.989855811 |
| 0.065276677 | 6.52767E-05 | 0.000663518 | 0.663518043 | 10164.70306 | 4.007094696 |
| 0.04698694 | 4.69869E-05 | 0.000589183 | 0.589182736 | 12539.28713 | 4.098272847 |
| 0.051719563 | 5.17196E-05 | 0.000571535 | 0.571534869 | 11050.65151 | 4.043387883 |

**Table A2 (cont.)**

**Diazepam**

| $C_e$ (ug/L) | $C_e$ (mg/L) | q (ug/mg) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 21.62891409 | 0.021628914 | 0.013830377 | 13.83037654 | 639.439247 | 2.805799289 |
| 20.71272496 | 0.020712725 | 0.014177934 | 14.17793436 | 684.5035784 | 2.835375723 |
| 8.894670798 | 0.008894671 | 0.010238875 | 10.23887498 | 1151.124669 | 3.061122361 |
| 7.695446825 | 0.007695447 | 0.010307425 | 10.30742477 | 1339.41862 | 3.126916332 |
| 5.206882218 | 0.005206882 | 0.008144991 | 8.144990963 | 1564.274094 | 3.194312853 |
| 2.592998595 | 0.002592999 | 0.006921024 | 6.921024113 | 2669.119886 | 3.426368081 |
| 3.698941119 | 0.003698941 | 0.006935969 | 6.93596928 | 1875.122922 | 3.273029743 |
| 5.217304124 | 0.005217304 | 0.008155204 | 8.155203804 | 1563.106848 | 3.193988666 |
| 2.56598179 | 0.002565982 | 0.005762408 | 5.762408342 | 2245.693389 | 3.35135046 |
| 2.705187457 | 0.002705187 | 0.005832738 | 5.832738105 | 2156.130841 | 3.333675112 |

**Naphthalene**

| $C_e$ (ug/L) | $C_e$ (mg/L) | q (ug/mg) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 12.6292347 | 0.012629235 | 0.010773761 | 10.77376094 | 853.0810615 | 2.930990301 |
| 12.43500505 | 0.012435005 | 0.010458297 | 10.45829723 | 841.0368303 | 2.924815015 |
| 3.961395555 | 0.003961396 | 0.009495531 | 9.495531186 | 2397.016671 | 3.379671054 |
| 5.586216111 | 0.005586216 | 0.008852398 | 8.85239762 | 1584.685849 | 3.19994318 |
| 1.713379641 | 0.00171338 | 0.007371164 | 7.371164268 | 4302.119678 | 3.633682488 |
| 2.594352285 | 0.002594352 | 0.006977526 | 6.977525688 | 2689.505866 | 3.429672496 |
| 1.27633871 | 0.001276339 | 0.004393813 | 4.393812554 | 3442.512964 | 3.536875584 |
| 1.002582059 | 0.001002582 | 0.004466338 | 4.466338245 | 4454.835597 | 3.648831681 |
| 0.790777116 | 0.000790777 | 0.003305257 | 3.305257431 | 4179.758574 | 3.621151197 |
| 0.587345267 | 0.000587345 | 0.003195768 | 3.195767662 | 5441.037571 | 3.735681725 |

**2,4-dinitrotoluene**

| $C_e$ (ug/L) | $C_e$ (mg/L) | q (ug/mg) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 45.193074 | 0.045193074 | 0.051671048 | 51.67104827 | 1143.339979 | 3.05817539 |
| 43.99119107 | 0.043991191 | 0.051538595 | 51.538595 | 1171.566256 | 3.068766854 |
| 13.52667944 | 0.013526679 | 0.031833777 | 31.83377705 | 2353.406627 | 3.371696972 |
| 14.10402588 | 0.014104026 | 0.030081251 | 30.08125059 | 2132.813059 | 3.328952791 |
| 6.85402737 | 0.006854027 | 0.024385422 | 24.38542235 | 3557.823895 | 3.551184448 |
| 6.73624288 | 0.006736243 | 0.024613664 | 24.61366397 | 3653.915753 | 3.56275853 |
| 4.303668959 | 0.004303669 | 0.019715734 | 19.71573374 | 4581.145514 | 3.660974087 |
| 4.916312047 | 0.004916312 | 0.020268442 | 20.26844209 | 4122.692354 | 3.615180928 |
| 3.47112573 | 0.003471126 | 0.016288713 | 16.28871287 | 4692.631191 | 3.671416423 |
| 2.586332894 | 0.002586333 | 0.016764188 | 16.76418795 | 6481.836884 | 3.811698098 |

**Table A2 (cont.)**

**Nitrobenzene**

| $C_e$ (ug/L) | $C_e$ (mg/L) | q (ug/mg) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 1232.105438 | 1.232105438 | 0.06440096 | 64.40096029 | 52.26903341 | 1.718244469 |
| 1226.109706 | 1.226109706 | 0.065287006 | 65.28700597 | 53.2472793 | 1.726297422 |
| 1053.056773 | 1.053056773 | 0.063657506 | 63.65750596 | 60.45021275 | 1.781397834 |
| 1072.570758 | 1.072570758 | 0.063860237 | 63.86023714 | 59.53941654 | 1.774804574 |
| 1008.287546 | 1.008287546 | 0.061480296 | 61.48029624 | 60.97496343 | 1.785151549 |
| 954.0930394 | 0.954093039 | 0.060741611 | 60.74161067 | 63.66424254 | 1.803895576 |
| 862.2532322 | 0.862253232 | 0.058493753 | 58.49375257 | 67.8382526 | 1.831474653 |
| 873.2352291 | 0.873235229 | 0.059158978 | 59.15897791 | 67.7468979 | 1.830889414 |
| 747.9168923 | 0.747916892 | 0.056015545 | 56.0155447 | 74.89541321 | 1.874455221 |
| 735.9998565 | 0.735999857 | 0.057288306 | 57.28830594 | 77.83738737 | 1.89118825 |

**Lindane**

| $C_e$ (ug/L) | $C_e$ (mg/L) | q (ug/mg) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 5.662747816 | 0.005662748 | 0.007183971 | 7.183971158 | 1268.636957 | 3.103337359 |
| 4.788971578 | 0.004788972 | 0.008359093 | 8.359093434 | 1745.488211 | 3.24191692 |
| 2.007158626 | 0.002007159 | 0.005393636 | 5.393635894 | 2687.199619 | 3.429299929 |
| 1.833239764 | 0.00183324 | 0.005304292 | 5.304291993 | 2893.39785 | 3.461408154 |
| 1.010302145 | 0.001010302 | 0.003883826 | 3.883826362 | 3844.222624 | 3.58480853 |
| 1.076013173 | 0.001076013 | 0.003863173 | 3.863172934 | 3590.265464 | 3.555126561 |
| 0.76290487 | 0.000762905 | 0.003075685 | 3.075685096 | 4031.544712 | 3.605471481 |
| 0.660896178 | 0.000660896 | 0.002954029 | 2.954029166 | 4469.732563 | 3.650281539 |
| 3.615569159 | 0.003615569 | 0.005031891 | 5.031890763 | 1391.728533 | 3.143554531 |
| 2.448100856 | 0.002448101 | 0.006193363 | 6.193363191 | 2529.864395 | 3.403097243 |
| 2.875472689 | 0.002875473 | 0.004592715 | 4.592715048 | 1597.203502 | 3.203360254 |
| 2.141092382 | 0.002141092 | 0.00522027 | 5.220269836 | 2438.133861 | 3.387057546 |

**Bisphenol A**

| $C_e$ (ug/L) | $C_e$ (mg/L) | q (ug/mg) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 170.9122581 | 0.170912258 | 0.03992445 | 39.92445027 | 233.5961779 | 2.368465733 |
| 157.6959174 | 0.157695917 | 0.044718699 | 44.7186995 | 283.5755056 | 2.452668715 |
| 81.75083136 | 0.081750831 | 0.034408897 | 34.40889707 | 420.8996593 | 2.624178574 |
| 79.23382989 | 0.07923383 | 0.034886462 | 34.88646228 | 440.2975638 | 2.643746283 |
| 53.09147997 | 0.05309148 | 0.029860811 | 29.86081129 | 562.4407402 | 2.750076771 |
| 59.76186894 | 0.059761869 | 0.0285266 | 28.52659957 | 477.3378087 | 2.678825835 |
| 40.07028924 | 0.040070289 | 0.024486448 | 24.48644773 | 611.0873715 | 2.786103309 |
| 34.53901462 | 0.034539015 | 0.025304478 | 25.30447825 | 732.6346315 | 2.864887444 |
| 25.26629203 | 0.025266292 | 0.021912439 | 21.91243864 | 867.2597708 | 2.938149201 |
| 22.90715995 | 0.02290716 | 0.022273444 | 22.27344415 | 972.3354705 | 2.987816129 |

**Table A2 (cont.)**

**TCE**

| $C_e$ (ug/L) | $C_e$ (mg/L) | q (ug/mg) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 60.85759093 | 0.060857591 | 0.004762022 | 4.762022372 | 78.24861779 | 1.893476675 |
| 48.02925466 | 0.048029255 | 0.004332903 | 4.332903173 | 90.2138333 | 1.955273137 |
| 33.59486403 | 0.033594864 | 0.0039086 | 3.908600413 | 116.3451773 | 2.065748386 |

**1-Heptanol**

| $C_e$ (ug/L) | $C_e$ (mg/L) | q (ug/mg) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 83.31605035 | 0.08331605 | 0.002878115 | 2.878114525 | 34.54453869 | 1.538379397 |
| 50.39603142 | 0.050396031 | 0.002867798 | 2.867797852 | 56.90523184 | 1.755152197 |
| 35.04907678 | 0.035049077 | 0.002401408 | 2.40140766 | 68.51557531 | 1.835789309 |
| 28.03250693 | 0.028032507 | 0.002111353 | 2.111353043 | 75.31802447 | 1.87689892 |

**Table A3: Activated carbon competitive isotherm data of 10 trace organic compounds**

**Atrazine (To et al., 2008)**

| $C_e$ (ug/L) | q (mg/g) | $C_e$ (mg/L) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 30.661507 | 33.778321 | 0.0306615 | 33778.321 | 1101652.3 | 6.0420446 |
| 1.9401091 | 12.401822 | 0.0019401 | 12401.822 | 6392332.4 | 6.8056594 |
| 0.7190289 | 8.6497496 | 0.000719 | 8649.7496 | 12029766 | 7.0802572 |
| 0.2372795 | 5.7839442 | 0.0002373 | 5783.9442 | 24376077 | 7.3869638 |
| 0.1188512 | 4.5001913 | 0.0001189 | 4500.1913 | 37864065 | 7.5782272 |
| 0.0799391 | 3.8967829 | 7.994E-05 | 3896.7829 | 48746899 | 7.687947 |
| 71.986873 | 46.04554 | 0.0719869 | 46045.54 | 639638 | 5.8059343 |
| 16.97323 | 27.252675 | 0.0169732 | 27252.675 | 1605626.9 | 6.2056446 |
| 2.8041184 | 14.176032 | 0.0028041 | 14176.032 | 5055432.8 | 6.7037583 |
| 0.7976834 | 8.9819184 | 0.0007977 | 8981.9184 | 11260004 | 7.0515386 |
| 0.1817246 | 5.2501508 | 0.0001817 | 5250.1508 | 28890703 | 7.4607581 |
| 0.1191763 | 4.5046554 | 0.0001192 | 4504.6554 | 37798242 | 7.5774716 |
| 0.0754183 | 3.8152994 | 7.542E-05 | 3815.2994 | 50588526 | 7.704052 |
| 0.047619 | 3.2287841 | 4.762E-05 | 3228.7841 | 67804467 | 7.8312583 |

**Estradiol**

| $C_e$ (ug/L) | q (mg/g) | $C_e$ (mg/L) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 0.1208699 | 0.0173033 | 0.0001209 | 17.303284 | 143156.24 | 5.1558103 |
| 0.1119093 | 0.0185092 | 0.0001119 | 18.509193 | 165394.64 | 5.2185214 |
| 0.0938763 | 0.0133073 | 9.388E-05 | 13.307339 | 141754.05 | 5.1515355 |
| 0.0564383 | 0.0110608 | 5.644E-05 | 11.06082 | 195980.81 | 5.2922136 |
| 0.05073 | 0.0108894 | 5.073E-05 | 10.889384 | 214653.68 | 5.3317383 |
| 0.0255638 | 0.0089811 | 2.556E-05 | 8.9810597 | 351319.98 | 5.5457028 |
| 0.0432971 | 0.0093108 | 4.33E-05 | 9.3107916 | 215044.42 | 5.3325282 |
| 0.070825 | 0.0128337 | 7.083E-05 | 12.833731 | 181203.3 | 5.2581661 |
| 0.0828102 | 0.0132937 | 8.281E-05 | 13.293697 | 160532.09 | 5.2055619 |
| 0.0650861 | 0.0087898 | 6.509E-05 | 8.7898162 | 135049.01 | 5.1304914 |
| 0.0635909 | 0.008887 | 6.359E-05 | 8.8870341 | 139753.15 | 5.1453616 |

**Table A3 (cont.)**

**Benzene**

| $C_e$ (ug/L) | q (mg/g) | $C_e$ (mg/L) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 4.8174609 | 0.4199928 | 0.0048175 | 419.99275 | 87181.351 | 4.9404236 |
| 4.8057834 | 0.4198564 | 0.0048058 | 419.85643 | 87364.825 | 4.9413366 |
| 1.3251332 | 0.2208847 | 0.0013251 | 220.88471 | 166688.68 | 5.2219061 |
| 1.3941148 | 0.229786 | 0.0013941 | 229.78602 | 164825.75 | 5.2170251 |
| 0.5615831 | 0.1523199 | 0.0005616 | 152.31994 | 271233.12 | 5.4333427 |
| 0.5716649 | 0.1463927 | 0.0005717 | 146.39265 | 256081.21 | 5.4083777 |
| 0.4379333 | 0.1169681 | 0.0004379 | 116.96809 | 267091.14 | 5.4266595 |
| 0.323325 | 0.1165976 | 0.0003233 | 116.59762 | 360620.47 | 5.5570504 |
| 0.4962514 | 0.0942079 | 0.0004963 | 94.207935 | 189839.14 | 5.2783858 |
| 0.7179693 | 0.0931395 | 0.000718 | 93.139542 | 129726.35 | 5.1130282 |

**2,4 dinitrotoluene**

| $C_e$ (ug/L) | q (mg/g) | $C_e$ (mg/L) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 0.1069377 | 0.2362693 | 0.0001069 | 236.2693 | 2209409.9 | 6.3442763 |
| 0.0440742 | 0.2363456 | 4.407E-05 | 236.3456 | 5362447.5 | 6.7293631 |
| 0.0265646 | 0.1186469 | 2.656E-05 | 118.64689 | 4466347.6 | 6.6499525 |
| 0.0489826 | 0.1187201 | 4.898E-05 | 118.72006 | 2423721.1 | 6.3844826 |
| 0.0142054 | 0.0589403 | 1.421E-05 | 58.940313 | 4149149.1 | 6.617959 |
| 0.0181266 | 0.0592168 | 1.813E-05 | 59.216791 | 3266843.5 | 6.5141283 |
| 0.0108695 | 0.0470715 | 1.087E-05 | 47.071451 | 4330605.1 | 6.6365486 |
| 0.0143177 | 0.0471518 | 1.432E-05 | 47.151801 | 3293249.4 | 6.5176246 |
| 0.1049717 | 0.5132185 | 0.000105 | 513.2185 | 4889114.7 | 6.6892302 |
| 0.048716 | 0.4393422 | 4.872E-05 | 439.34219 | 9018445.6 | 6.9551317 |
| 0.0800734 | 0.3518047 | 8.007E-05 | 351.80472 | 4393527.3 | 6.6428133 |
| 0.052731 | 0.2912157 | 5.273E-05 | 291.21569 | 5522665.5 | 6.7421487 |
| 0.0480022 | 0.268013 | 4.8E-05 | 268.01301 | 5583347.9 | 6.7468947 |
| 0.0137541 | 0.0671745 | 1.375E-05 | 67.174494 | 4883972 | 6.6887732 |
| 0.013361 | 0.0537412 | 1.336E-05 | 53.741167 | 4022235.2 | 6.6044675 |

**Table A3 (cont.)**

**TCE**

| $C_e$ (ug/L) | q (mg/g) | $C_e$ (mg/L) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 1.8865851 | 0.0523161 | 0.0018866 | 52.316122 | 27730.592 | 4.4429591 |
| 1.8011818 | 0.0521186 | 0.0018012 | 52.118603 | 28935.781 | 4.4614352 |
| 1.6924186 | 0.033311 | 0.0016924 | 33.310972 | 19682.467 | 4.2940795 |
| 1.3611965 | 0.0345918 | 0.0013612 | 34.591828 | 25412.811 | 4.4050527 |
| 1.3294591 | 0.02576 | 0.0013295 | 25.759981 | 19376.287 | 4.2872706 |
| 3.2726493 | 0.0997438 | 0.0032726 | 99.743845 | 30478.013 | 4.4839866 |
| 3.2684645 | 0.1057376 | 0.0032685 | 105.73765 | 32350.863 | 4.5098859 |
| 2.6177638 | 0.0710348 | 0.0026178 | 71.034769 | 27135.668 | 4.4335405 |
| 2.6090649 | 0.0681288 | 0.0026091 | 68.128754 | 26112.326 | 4.4168456 |
| 2.3305454 | 0.0533241 | 0.0023305 | 53.32405 | 22880.503 | 4.3594656 |
| 2.3017061 | 0.0539032 | 0.0023017 | 53.903211 | 23418.807 | 4.3695648 |
| 2.133466 | 0.0426493 | 0.0021335 | 42.649294 | 19990.613 | 4.3008261 |
| 13.693115 | 0.3484174 | 0.0136931 | 348.41743 | 25444.716 | 4.4055976 |
| 13.777033 | 0.3587083 | 0.013777 | 358.70827 | 26036.686 | 4.4155857 |
| 12.292463 | 0.2747108 | 0.0122925 | 274.71075 | 22347.902 | 4.3492368 |
| 11.149187 | 0.3036141 | 0.0111492 | 303.61411 | 27231.95 | 4.4350787 |
| 7.7624738 | 0.0876543 | 0.0077625 | 87.654296 | 11292.057 | 4.0527731 |
| 10.583787 | 0.0909686 | 0.0105838 | 90.968634 | 8595.0929 | 3.9342506 |

**Table A3 (cont.)**

**1-Heptanol**

| $C_e$ (ug/L) | q (mg/g) | $C_e$ (mg/L) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 31.123394 | 0.4991881 | 0.0311234 | 499.18805 | 16038.998 | 4.2051772 |
| 18.212559 | 0.3602818 | 0.0182126 | 360.28178 | 19782.052 | 4.2962713 |
| 19.922562 | 0.3162354 | 0.0199226 | 316.23541 | 15873.231 | 4.2006653 |
| 17.12611 | 0.2490425 | 0.0171261 | 249.04249 | 14541.685 | 4.1626147 |
| 18.091466 | 0.2514519 | 0.0180915 | 251.45188 | 13898.922 | 4.1429811 |
| 15.773158 | 0.2089068 | 0.0157732 | 208.90684 | 13244.452 | 4.122034 |
| 15.812079 | 0.1990822 | 0.0158121 | 199.08222 | 12590.515 | 4.1000435 |
| 14.711451 | 0.1843357 | 0.0147115 | 184.3357 | 12530.083 | 4.0979539 |
| 14.420731 | 0.1823476 | 0.0144207 | 182.34755 | 12644.821 | 4.1019127 |
| 12.559268 | 0.1287462 | 0.0125593 | 128.74624 | 10251.094 | 4.0107702 |
| 11.418809 | 0.0993787 | 0.0114188 | 99.378691 | 8703.0698 | 3.9396725 |
| 10.465228 | 0.0753504 | 0.0104652 | 75.350392 | 7200.0714 | 3.8573368 |
| 9.0967948 | 0.0514606 | 0.0090968 | 51.460566 | 5656.9998 | 3.7525862 |
| 8.5534286 | 0.0445701 | 0.0085534 | 44.570092 | 5210.7867 | 3.7169033 |
| 7.2218712 | 0.0382585 | 0.0072219 | 38.258474 | 5297.5846 | 3.7240779 |
| 6.3532685 | 0.0346633 | 0.0063533 | 34.663306 | 5455.9801 | 3.7368728 |
| 6.2695648 | 0.0317229 | 0.0062696 | 31.722931 | 5059.8299 | 3.7041359 |
| 14.95411 | 0.2484618 | 0.0149541 | 248.46175 | 16614.948 | 4.220499 |
| 13.595034 | 0.1909229 | 0.013595 | 190.92286 | 14043.574 | 4.1474776 |
| 9.652292 | 0.0523984 | 0.0096523 | 52.398418 | 5428.5985 | 3.7346877 |
| 8.7580464 | 0.0406129 | 0.008758 | 40.612926 | 4637.2129 | 3.666257 |
| 8.1183039 | 0.0266203 | 0.0081183 | 26.620282 | 3279.0448 | 3.5157473 |

**Diazepam**

| $C_e$ (ug/L) | q (mg/g) | $C_e$ (mg/L) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 0.1395722 | 0.2773198 | 0.0001396 | 277.3198 | 1986927.1 | 6.2981819 |
| 0.155966 | 0.2260489 | 0.000156 | 226.04894 | 1449347.3 | 6.1611725 |
| 0.1696491 | 0.1843786 | 0.0001696 | 184.37858 | 1086823.4 | 6.036159 |
| 0.1524556 | 0.1910329 | 0.0001525 | 191.03291 | 1253039.4 | 6.0979647 |
| 0.0398783 | 0.1364937 | 3.988E-05 | 136.49373 | 3422754.7 | 6.5343758 |
| 0.0723668 | 0.1395 | 7.237E-05 | 139.49997 | 1927678.2 | 6.2850345 |
| 0.0377721 | 0.1097509 | 3.777E-05 | 109.7509 | 2905609.4 | 6.4632372 |
| 0.0357111 | 0.1097711 | 3.571E-05 | 109.77111 | 3073869.1 | 6.4876854 |

**Table A3 (cont.)**

**Nitrobenzene**

| $C_e$ (ug/L) | q (mg/g) | $C_e$ (mg/L) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 0.97759 | 1.0751476 | 0.0009776 | 1075.1476 | 1099794 | 6.0413113 |
| 0.9152562 | 0.6112626 | 0.0009153 | 611.26261 | 667859.54 | 5.8246851 |
| 0.9373935 | 0.4556226 | 0.0009374 | 455.62256 | 486052.64 | 5.6866833 |
| 0.9662831 | 0.3643389 | 0.0009663 | 364.33888 | 377051.92 | 5.5764012 |
| 3.195254 | 3.5780046 | 0.0031953 | 3578.0046 | 1119787.2 | 6.0491355 |
| 3.2883414 | 3.6003193 | 0.0032883 | 3600.3193 | 1094873.9 | 6.0393641 |
| 4.102382 | 2.2000825 | 0.0041024 | 2200.0825 | 536293.91 | 5.7294029 |
| 3.9688862 | 2.1835498 | 0.0039689 | 2183.5498 | 550166.9 | 5.7404945 |
| 1.1671864 | 1.0667134 | 0.0011672 | 1066.7134 | 913918.64 | 5.9609075 |
| 0.7884644 | 0.6075339 | 0.0007885 | 607.53387 | 770527.97 | 5.8867884 |
| 0.820682 | 0.6135376 | 0.0008207 | 613.53762 | 747594.79 | 5.8736663 |

**Naphthalene**

| $C_e$ (ug/L) | q (mg/g) | $C_e$ (mg/L) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 0.5502966 | 0.1572073 | 0.0005503 | 157.20732 | 285677.43 | 5.4558759 |
| 0.5429718 | 0.1367315 | 0.000543 | 136.73152 | 251820.67 | 5.4010914 |
| 0.4130808 | 0.1159145 | 0.0004131 | 115.91449 | 280609.75 | 5.4481028 |
| 0.3776519 | 0.1019884 | 0.0003777 | 101.98836 | 270059.18 | 5.4314589 |

**Bisphenol A**

| $C_e$ (ug/L) | q (mg/g) | $C_e$ (mg/L) | q (mg/kg) | $K_d$ | log $K_d$ |
|---|---|---|---|---|---|
| 0.1736978 | 0.0882108 | 1.74E-04 | 88.210803 | 507840.59 | 5.7057274 |
| 0.1314095 | 0.0490923 | 1.31E-04 | 49.092316 | 373582.71 | 5.5723868 |
| 0.1514128 | 0.0449854 | 1.51E-04 | 44.985433 | 297104.62 | 5.4729094 |
| 0.1491466 | 0.0363317 | 1.49E-04 | 36.331745 | 243597.59 | 5.386673 |
| 0.1127538 | 0.0296084 | 1.13E-04 | 29.608409 | 262593.43 | 5.4192839 |
| 0.1597079 | 0.025861 | 1.60E-04 | 25.860979 | 161926.74 | 5.2093186 |
| 0.1087793 | 0.0226485 | 1.09E-04 | 22.648483 | 208205.74 | 5.3184927 |
| 0.0966691 | 0.0229362 | 9.67E-05 | 22.936239 | 237265.51 | 5.3752346 |
| 0.0521536 | 0.0115507 | 5.22E-05 | 11.550738 | 221475.42 | 5.3453255 |
| 0.0512199 | 0.0084793 | 5.12E-05 | 8.479319 | 165547.31 | 5.2189221 |
| 0.3031492 | 0.1148277 | 3.03E-04 | 114.82766 | 378782.7 | 5.5783901 |
| 0.2306125 | 0.1028516 | 2.31E-04 | 102.85155 | 445992.93 | 5.649328 |
| 0.1802571 | 0.0740867 | 1.80E-04 | 74.086676 | 411005.59 | 5.6138477 |
| 0.189101 | 0.0760293 | 1.89E-04 | 76.029262 | 402056.35 | 5.6042869 |
| 0.1555274 | 0.0553231 | 1.56E-04 | 55.323061 | 355712.61 | 5.5510993 |
| 0.1636879 | 0.0378448 | 1.64E-04 | 37.844778 | 231200.84 | 5.3639894 |
| 0.1410478 | 0.0279712 | 1.41E-04 | 27.971248 | 198310.4 | 5.2973455 |
| 0.1325186 | 0.0282018 | 1.33E-04 | 28.201778 | 212813.66 | 5.3279995 |

**A4: XPS Data:**

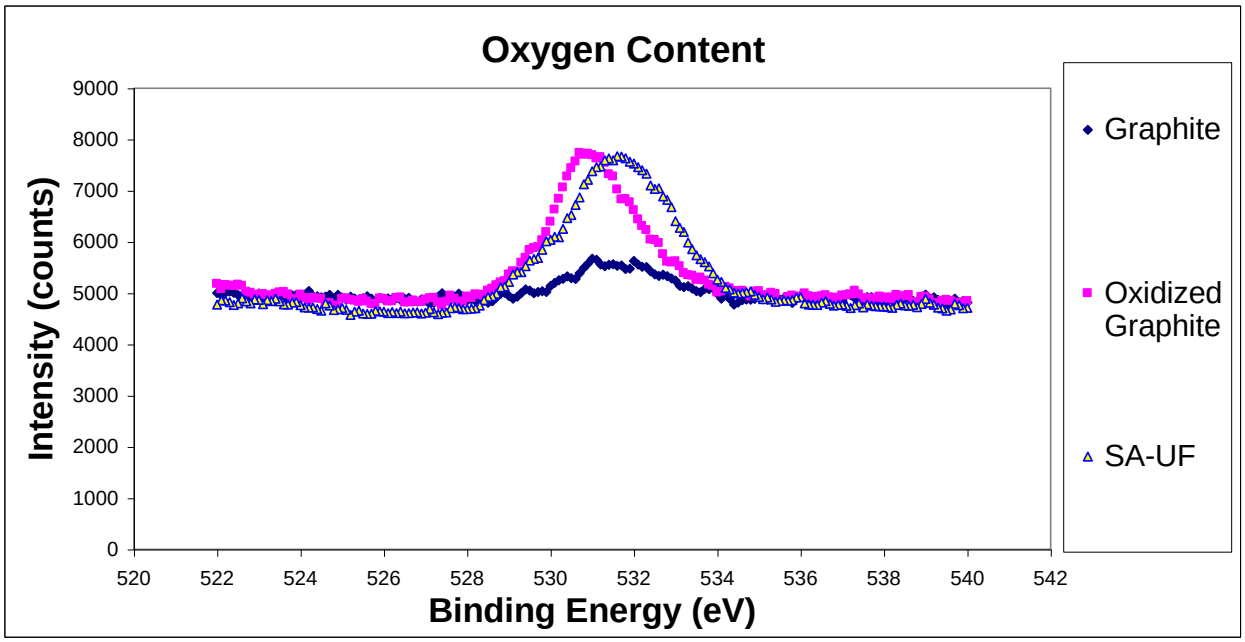


**Figure A1: Oxygen content of carbons measured by XPS**

**Table A4: Mass Concentration of oxygen and carbon on three different carbons**

| Carbon | Graphite | Oxidized Graphite | SA-UF |
|---|---|---|---|
| Mass Conc (%) | | | |
| Oxygen | 1.22 | 4.52 | 7.21 |
| Carbon | 98.78 | 95.48 | 92.79 |