IsoFit Documentation and User's Guide Version 1.2

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Version 1.2

Contents

Glossary of Terms

Terms used in the various equations of this manual are defined as follows:

- m : the total number of laboratory measurements.
- C_i : the i^{th} aqueous concentration $[M/L^3]$ $(i = 1...m)$.
- q_i : the i^{th} *estimated* sorbed mass fraction, estimated via an isotherm expression.
- $\mathbf{X}$: A vector of isotherm parameters.
- $f(\mathbf{X}, C_i)$: an expression for q_i that depends on the corresponding concentration (C_i), the selected isotherm and it's associated parameters $(\mathbf{X})$.
- Φ : the weighted sum of squared error (WSSE) objective function to be minimized by IsoFit
- w_i : the weight given to observation i
- $q_{i,obs}$: the laboratory measured sorbed mass fraction
- p : the number of isotherm parameters, which depends on the type of isotherm
- X_j : the value of the j^{th} isotherm parameter $(j = 1...p)$
- X_j^L : the lower bound of X_j
- X_j^H : the upper bound of X_j
- Q_0 : the maximum sorption density $[M/M]$
- b : the affinity of adsorbent to the adsorbate $[L^3/M]$

- S_w : the aqueous solubility of the sorptive material.
- $(1/n_f)$: the Freundlich exponent [no units].
- K_f : the Freundlich isotherm parameter $[\big((M/M)/(M/L^3)\big)^{(1/n)}]$
- K_p : a linear partitioning parameter $[L^3/M]$ used by the linear isotherm and several dual-mode isotherms (i.e. Freundlich w/ Partitioning, Langmuir w/ Partitioning, and Polanyi w/ Partitioning).
- $(1/n_g)$: the Generalized Langmuir-Freundlich exponent [no units].
- A : a lumped Polanyi isotherm parameter
- B : a lumped Polanyi isotherm parameter
- n_t : the Toth exponent [no units]

Chapter 1

Introduction

IsoFit is a program that fits isotherm parameters to a given set of laboratory data by minimizing the weighted sum of squared error between laboratory measured data and corresponding isotherm computed values. The general form of the isotherm expression is

$$q_i = f(\mathbf{X}, C_i) \text{ , i = 1..m} \tag{1.1}$$

Where the form of $f(\mathbf{X}, C_i)$ depends on the type of isotherm. At present, IsoFit implements the following isotherm expressions (1) Brunauer-Emmett-Teller (BET), (2) Freundlich, (3) Freundlich with Linear Partitioning, (4) Generalized Langmuir-Freundlich, (5) Langmuir, (6) Langmuir with Linear Paritioning, (7) Linear, (8) Polanyi, (9) Polanyi with Linear Partitioning, or (10) Toth. For isotherm expression(s) not currently supported by IsoFit, two software packages developed by the British Geological Survey may prove useful: ISOTHERM (Kinniburgh, 1985) and FIT (Kinniburgh, 1999).

IsoFit treats the isotherm fitting process as a minimization optimization problem, which can be described as:

$$\begin{aligned} &\text{Minimize} \\ &\quad \Phi = WSSE = \sum_{i=1}^{m} \left[w_i (q_i - q_{i,obs}) \right]^2 \\ &\text{Subject to} \\ &\quad X_j^L \leq X_j \leq X_j^H \text{ , j = 1..p} \end{aligned} \tag{1.2}$$

Equation 1.2 calls for the adjustment of uncertain isotherm parameters so that the difference between model-predicted and field-observed sorbed mass fractions is minimized. To solve the optimization problem, IsoFit utilizes a

hybrid optimization search procedure that couples a global search heuristic [particle swarm optimization, Kennedy and Eberhart (1995)] with a non-linear regression procedure [Levenberg-Marquardt, Levenberg (1944) and Marquardt (1963)]. IsoFit first uses particle swarm optimization (PSO) to identify promising solutions while circumventing local minima; this is followed by a regression-based "polishing" step that refines the PSO parameter estimates and generates regression statistics [e.g. Katare et al. (2004)].

The remainder of this manual (i) briefly describes each of the isotherm expressions supported by IsoFit, (ii) describes the syntax for the IsoFit input file, and (iii) demonstrates IsoFit by applying it to an example problem. Additional isotherm details may be found throughout the literature and include the studies of Allen et al. (2003), Allen-King et al. (2002), Bartelt-Hunt et al. (2005), Kinniburgh (1986), Padmesh et al. (2006), and Rabideau at al. (in review); these studies compare numerous isotherms in the context of several environmental systems.

1.1 BET Isotherm

The BET isotherm expression (Brunauer et al., 1938) was originally developed to describe the adsorption of gases, but has since been extended to aqueous-phase sorption. The BET isotherm expression is:

$$f(\mathbf{X}, C_i) = \frac{Q_0 b C_i}{(S_w - C_i)\big[1 + (b-1)(C_i/S_w)\big]} \tag{1.3}$$

Where the isotherm parameters are $\mathbf{X} = [Q_0, b]^T$. Figure 1.1 contains a representative BET isotherm fit.

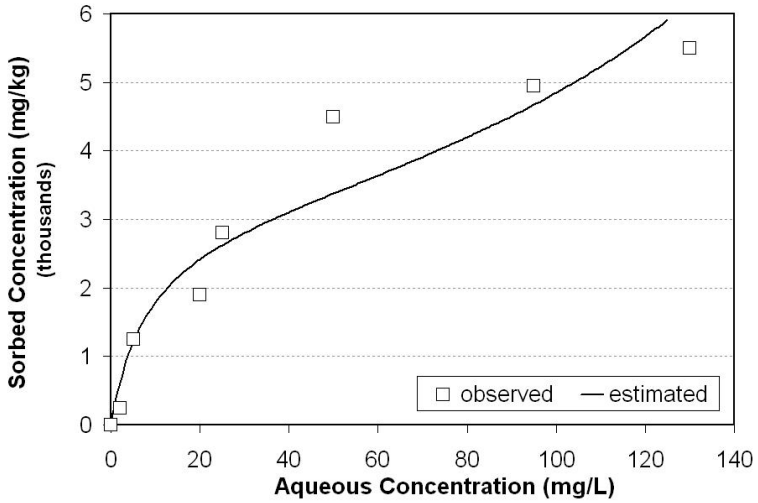

Figure 1.1: Example BET Isotherm Fit

1.2 Freundlich Isotherm

The Freundlich isotherm expression (Freundlich, 1924) is

$$f(\mathbf{X}, C_i) = K_f C_i^{(1/n_f)} \tag{1.4}$$

Where the isotherm parameters are $\mathbf{X} = [K_f, (1/n_f)]^T$. Figure 1.2 illustrates the shape of a typical Freundlich isotherm fit.

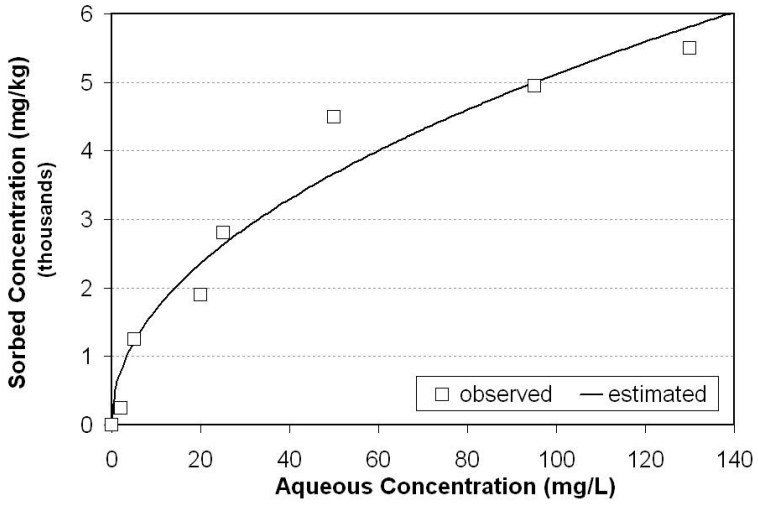

Figure 1.2: Example Freundlich Isotherm Fit

1.3 Freundlich Isotherm w/ Linear Partitioning

The Freundlich isotherm with linear partitioning (Weber at al., 1992) is expressed as a dual-mode formulation that incorporates both Freundlich and Linear isotherm behavior:

$$f(\mathbf{X}, C_i) = K_f C_i^{(1/n_f)} + K_p C_i \tag{1.5}$$

Where the isotherm parameters are $\mathbf{X} = [K_f, (1/n_f), K_p]^T$. Figure 1.3 illustrates the shape of a typical Freundlich w/ Linear Partitioning isotherm fit.

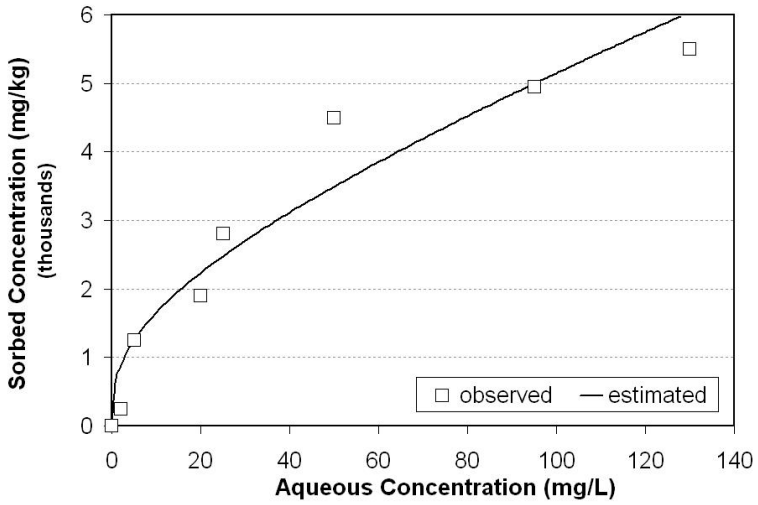

Figure 1.3: Example Freundlich w/ Linear Partitioning Isotherm Fit

1.4 Generalized Langmuir-Freundlich Isotherm

The Generalized Langmuir-Freundlich isotherm (Kano et al., 2000) is expressed as a combination of various components of the Langmuir and Freundlich isotherms:

$$f(\mathbf{X}, C_i) = \frac{Q_0 (bC_i)^{(1/n_g)}}{1 + (bC_i)^{(1/n_g)}} \tag{1.6}$$

Where the isotherm parameters are $\mathbf{X} = [Q_0, b, (1/n_g)]^T$. Figure 1.4 illustrates the shape of a typical Generalized Langmuir-Freundlich isotherm fit.

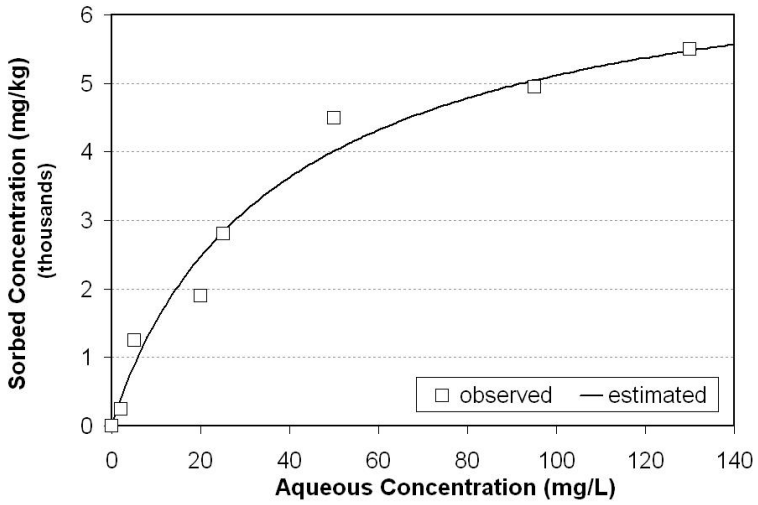

Figure 1.4: Example Generalized Langmuir-Freundlich Isotherm Fit

1.5 Langmuir Isotherm

The Langmuir isotherm (Langmuir, 1916) is written as

$$f(\mathbf{X}, C_i) = \frac{Q_0 b C_i}{1 + b C_i} \tag{1.7}$$

Where the isotherm parameters are $\mathbf{x} = [Q_0, b]^T$. Figure 1.5 contains a representative Langmuir isotherm fit.

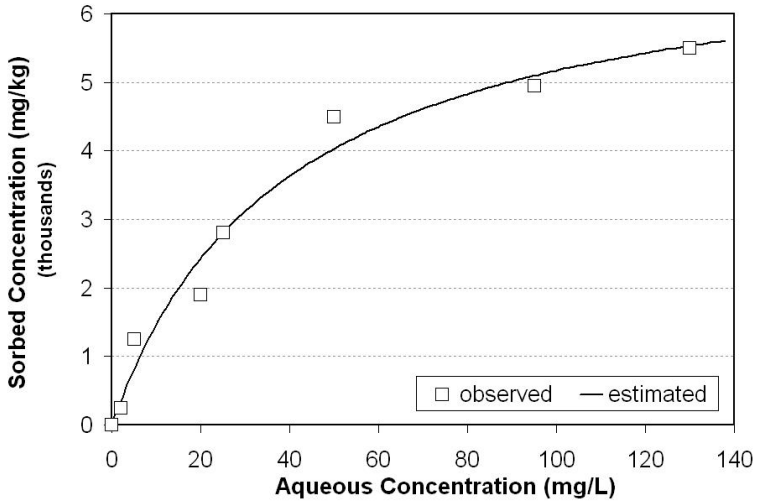

Figure 1.5: Example Langmuir Isotherm Fit

1.6 Langmuir Isotherm with Linear Paritioning

The Langmuir isotherm with linear partitioning (Xing et al., 1996) is expressed as a dual-mode formulation that incorporates both Langmuir and Linear isotherm behavior:

$$f(\mathbf{X}, C_i) = \frac{Q_0 b C_i}{1 + bC_i} + K_p C_i \tag{1.8}$$

Where the isotherm parameters are $\mathbf{X} = [Q_0, b, K_p]^T$. Figure 1.6 illustrates the shape of a typical Langmuir w/ Linear Partitioning isotherm fit.

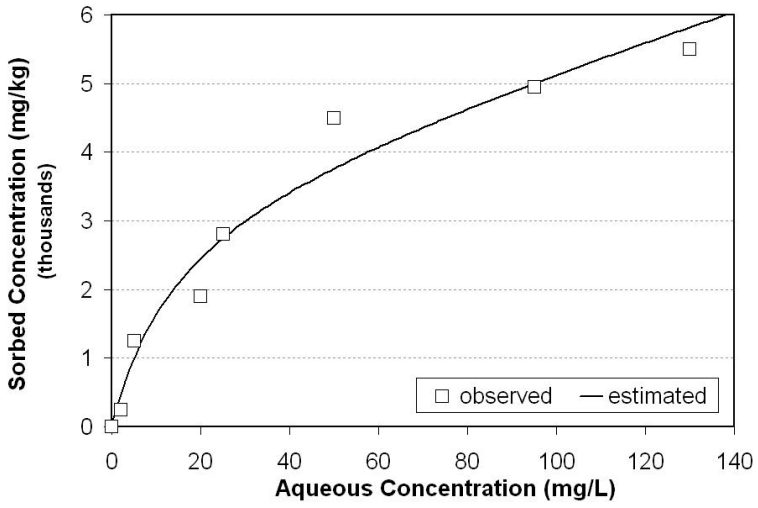

Figure 1.6: Example Langmuir w/ Linear Partitioning Isotherm Fit

1.7 Linear Isotherm

The formula for the linear isotherm is

$$f(\mathbf{X}, C_i) = K_p C_i \tag{1.9}$$

Where the isotherm parameter is $\mathbf{X} = [K_p]$. Figure 1.7 contains an example linear isotherm fit.

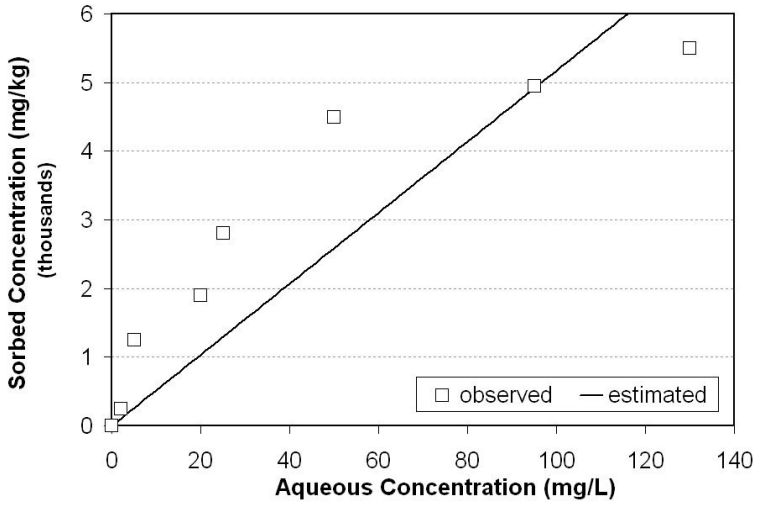

Figure 1.7: Example Linear Isotherm Fit

1.8 Polanyi Isotherm

The Polanyi isotherm, as applied to solid-water interactions [e.g. Xia and Ball (1999 and 2000)], may be expressed as:

$$f(\mathbf{X}, C_i) = Q_0 10^{-A\left[log\left(S_w/C_i\right)\right]^B} \tag{1.10}$$

Where the isotherm parameters are $\mathbf{X} = [Q_0, A, B]^T$. Figure 1.8 illustrates the shape of a typical Polanyi isotherm fit.

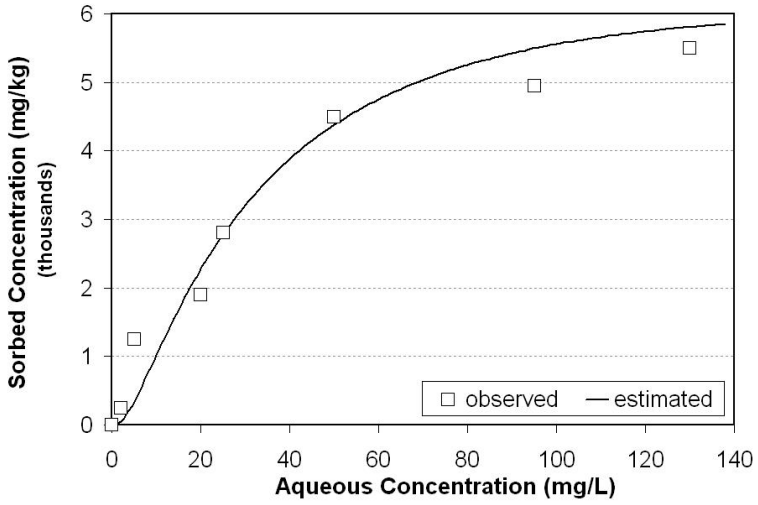

Figure 1.8: Example Polanyi Isotherm Fit

1.9 Polanyi Isotherm with Linear Partitioning

The Polanyi isotherm with linear partitioning (Xia and Ball, 1999 and 2000) is a dual-mode expression that incorporates both Polanyi and Linear isotherm behavior:

$$f(\mathbf{X}, C_i) = Q_0 10^{-A\left[log\left(S_w/C_i\right)\right]^B} + K_p C_i \tag{1.11}$$

Where the isotherm parameters are $\mathbf{X} = [Q_0, A, B, K_p]^T$. Figure 1.9 illustrates the shape of a typical Polanyi w/ Linear Partitioning isotherm fit.

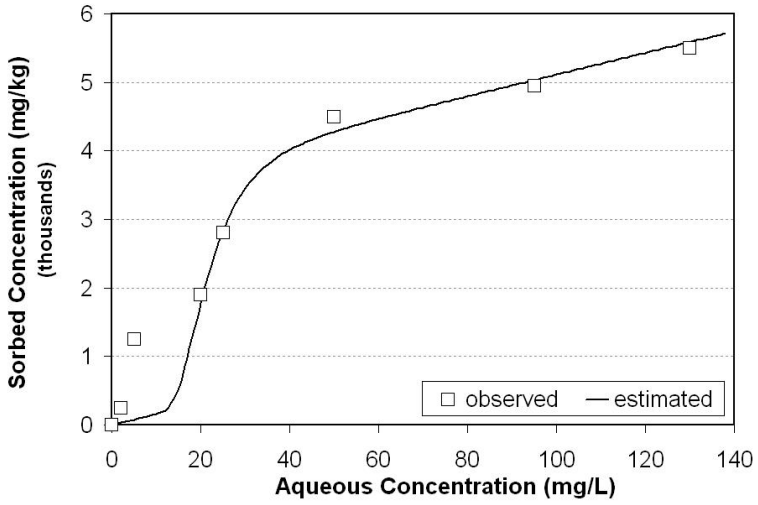

Figure 1.9: Example Polanyi w/ Linear Partitioning Isotherm Fit

1.10 Toth Isotherm

The Toth isotherm (Toth, 1971) is expressed as

$$f(\mathbf{X}, C_i) = \frac{Q_0 b C_i}{\left[1 + (bC_i)^{n_t}\right]^{(1/n_t)}} \tag{1.12}$$

Where the isotherm parameters are $\mathbf{X} = [Q_0, b, n_t]^T$. Figure 1.10 illustrates the shape of a typical Toth isotherm fit.

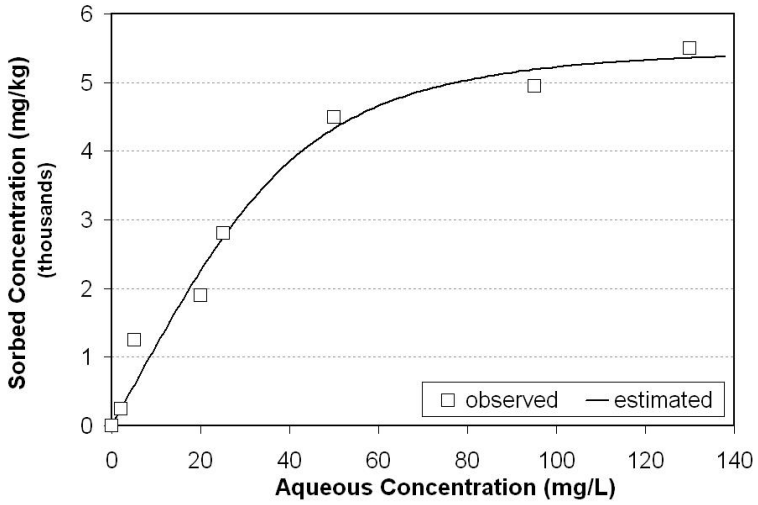

Figure 1.10: Example Toth Isotherm Fit

Chapter 2

Input File

The input file must be named `IsoFitIn.txt` and is formatted such that each line of user-supplied information uses syntax of the form:

`<variable>[TAB]<value>[CR]`

Where,

- `<variable>` is a user-configurable IsoFit variable
- `[TAB]` is the tab character
- `<value>` is the user-specified value of the variable
- `[CR]` is the carriage return-line feed character sequence

Using this general syntax, the user specifies the isotherm type, weighting scheme, and laboratory data, as described in the following sections. Additional optional input file syntax can be used to fine-tune the behavior of the IsoFit search procedure and its treatment of isotherm parameters.

2.1 Entering Comments Into the Input File

Users may include helpful comments in the IsoFit input file by using the `#` character; designated as the comment character. When IsoFit parses the input file, any text that follows a comment character is ignored. For example, in the following line the text '`this is an embedded comment`' would be ignored:

```
IsothermType FreundlichIsotherm # this is an embedded comment
```

Similarly, the entire line of text below would be ignored (since the comment character is the first character to appear in the line):

```
# this entire line is treated as a comment
```

2.2 Specifying the Isotherm Type

The user selects the isotherm type by setting the `IsothermType` variable to one of the following self-explanatory values:

- `AllIsotherms` (fits all isotherms, one at a time)
- `BET_Isotherm`
- `FreundlichIsotherm`
- `Freundlich-PartitionIsotherm`
- `LinearIsotherm`
- `LangmuirIsotherm`
- `Langmuir-FreundlichIsotherm` (the generalized Langmuir-Freundlich isotherm)
- `Langmuir-PartitionIsotherm`
- `PolanyiIsotherm`
- `Polanyi-PartitionIsotherm`
- `TothIsotherm`

NOTE: If the user selects the `AllIsotherms` options, IsoFit will loop through each isotherm, one at a time. After completing each fit, the name of the corresponding isotherm will be appended to any output files that are generated; this makes it easy to determine which output files correspond to a given isotherm.

If required by the chosen isotherm expression (i.e. BET, Polanyi, and Polanyi-Partition), the user must also specify the aqueous solubility of the sorptive material by including the following line in the input file:

```
Solubility    <val>
```

Where <val> is the aqueous solubility.

2.3 Specifying the Weighting Scheme

The user selects a weighting scheme by including a line that uses *one* of the following forms:

- WeightingScheme[TAB]Uniform[TAB]<val>[CR]
- WeightingScheme[TAB]SorbedRelative[TAB]<val>[CR]
- WeightingScheme[TAB]AqueousRelative[TAB]<val>[TAB]<conv>[CR]
- WeightingScheme[TAB]IndividualStdDevs

Where the different weighting schemes are:

- Uniform : uniform observation weights (i.e. $w_i =$ <val>, for $i = 1..m$)
- SorbedRelative : the i^{th} observation weight (w_i) is assigned relative to the corresponding sorbed mass fraction ($q_{i,obs}$).
- AqueousRelative : the i^{th} observation weight (w_i) is assigned relative to the corresponding aqueous concentration (C_i).
- IndividualStdDevs : observation weights are assigned using individual estimates of observation error (expressed in terms of standard deviations)

For the relative weighting schemes, <val> corresponds to the relative error associated with each observation. By relating this relative error to a 95% confidence interval for each observation, IsoFit calculates each corresponding weight as the inverse of the standard deviation ($1/sd_i$) using the following formulas:

For the SorbedRelative scheme:

$$w_i = \frac{1}{sd_i} = \frac{1.96}{\texttt{<val>} \times q_{i,obs}} \tag{2.1}$$

For the AqueousRelative scheme:

$$w_i = \frac{1}{sd_i} = \frac{1.96}{\texttt{<val>} \times C_i \times \texttt{<conv>}} \tag{2.2}$$

where <conv> is a conversion factor that converts aqueous concentrations to an equivalent sorbed mass fraction.

NOTE: When the IndividualStdDevs weighting scheme is selected, the standard deviation (sd_i) for each observation must be entered alongside each laboratory data point (see section 2.4).

2.4 Entering the Lab or Field Measured Data

The user lists laboratory (or field) measured aqueous concentration and sorbed mass fraction values in a section wrapped by the following statements: BeginLabData....EndLabData, as shown below.

```
BeginLabData
<C1>[TAB]<q1>[TAB]<sd1>
<C2>[TAB]<q2>[TAB]<sd2>
.
.
.
<Cm>[TAB]<qm>[TAB]<sdm>
EndLabData
```

Where, <C1>...<Cm> are aqueous concentrations and <q1>...<qm> are corresponding sorbed mass fractions. If the IndividualStdDevs weighting scheme is selected, <sd1>...<sdm> are estimated standard deviations of each sorbed mass fraction measurement ($q_{i,obs}$). If the IndividualStdDevs weighting scheme is *not* selected, IsoFit won't read the <sd1>...<sdm> items and they may be safely omitted.

NOTE: the current version of IsoFit treats measured aqueous concentrations, C_i, as if they are error free. If errors in C_i are significant (i.e. on the order of the errors in $q_{i,obs}$), then one should consider using alternative regression techniques, such as those discussed by Alper and Gelb (1990), Barker and Diana (1974), Carroll and Ruppert (2006), Kinniburgh (1986), McCammon (1973), Orear (1982), and Rubichev (1993).

2.5 Adjusting Isotherm Parameter Treatment

To enhance the performance of IsoFit, users may wish to adjust the manner in which parameters are treated by the hybrid search procedure. The following aspects of a given parameter may be adjusted:

- Parameter Transformation : Users can direct the PSO search procedure to apply a transformation (e.g. log_{10}) to a given parameter. Once the PSO search is complete, all parameter transformations are removed (i.e. set to `none`) in preparation for the polishing step and subsequent post-regression statistics.

- Finite Difference (FD) Step Size : Users can adjust the step size (δX_j) used in the calculation of the Jacobian, which is computed using value-relative finite-differences as shown in Equation 2.3

$$J_{i,j} = \frac{\partial q_i}{\partial X_j} \approx \frac{\Delta q_i}{\Delta X_j} = \frac{f(X_j, C_i) - f\big(X_j(1+\delta X_j), C_i\big)}{X_j \times \delta X_j} \tag{2.3}$$

- Lower and Upper Bounds : Users can specify lower (X^L) and upper (X^H) bounds for each parameter.

- Parameter Lumping: For the BET, Langmuir, Langmuir-Partitioning, and Toth isotherms, users have the option to lump the Q_0 term with the b term, forming a composite $b * Q_0$ parameter. This lumping may avoid excessive parameter correlation; a characteristic that can interfere with the "polishing" step of the IsoFit search procedure. By default, IsoFit will NOT employ parameter lumping. To activate this feature, users should include the following line in the input file:

  ```
  LumpedQ0*b    yes
  ```

To override the default parameter settings, the user lists the new configuration of each parameter in a section that is wrapped by the following statements: `BeginRanges...EndRanges`, as shown below:

```
BeginRanges
<name1>  <low1>  <high1>  <trans1>  <step_size1>
<name2>  <low2>  <high2>  <trans2>  <step_size2>
.
.
.
<nameN>  <lowN>  <highN>  <transN>  <step_sizeN>
EndRanges
```

Where `<name>` is the name of an isotherm parameter, `<low>` is the lower bound, `<high>` is the upper bound, `<trans>` is the transformation type (either '`log10`' or '`none`'), and `step_size` is the value-relative FD step size (δX). Valid choices for `<name>` depend on the isotherm specified in `IsothermType` and whether or not parameter lumping is employed:

`BET_Isotherm`
'`b*Q0`' (if lumping), '`Q0`' (if not lumping), and/or '`b`'
`FreundlichIsotherm`
'`Kf`' and/or '`(1/n)`'
`Freundlich-PartitionIsotherm`
'`Kf`', '`(1/n)`', and/or '`Kp`'
`LinearIsotherm`
'`Kp`'
`LangmuirIsotherm`
'`b*Q0`' (if lumping), '`Q0`' (if not lumping), and/or '`b`'
`Langmuir-FreundlichIsotherm`
'`Q0`', '`b`', and/or '`(1/n)`'
`Langmuir-PartitionIsotherm`
'`b*Q0`' (if lumping), '`Q0`' (if not lumping), '`b`', and/or '`Kp`'
`PolanyiIsotherm`
'`Q0`', '`a`', and/or '`b`'
`Polanyi-PartitionIsotherm`
'`Q0`', '`a`', '`b`', and/or '`Kp`'
`TothIsotherm`
'`b*Q0`' (if lumping), '`Q0`' (if not lumping), '`b`', and/or '`n`'

NOTE: if the user selects `AllIsotherms` for the Isotherm type, then a specific parameter-range wrapper for each isotherm must be included to override the default parameter settings. These isotherm-specific wrappers replace the normal `BeginRanges...EndRanges` wrappers, and use the following syntax:

- For BET : `BeginBET_Ranges...EndBET_Ranges`
- For Freundlich : `BeginFreundlichRanges...EndFreundlichRanges`
- For F-P : `BeginFreundlich-PartitionRanges...EndFreundlich-PartitionRanges`
- For GLF : `BeginLangmuir-FreundlichRanges...EndLangmuir-FreundlichRanges`
- For Langmuir : `BeginLangmuirRanges...EndLangmuirRanges`

- For L-P : `BeginLangmuir-PartitionRanges...EndLangmuir-PartitionRanges`
- For Linear : `BeginLinearRanges...EndLinearRanges`
- For Polanyi : `BeginPolanyiRanges...EndPolanyiRanges`
- For P-P : `BeginPolanyi-PartitionRanges...EndPolanyi-PartitionRanges`
- For Toth : `BeginTothRanges...EndTothRanges`

Where F-P = Freundlich w/ Partitioning, GLF = Generalized Langmuir-Freundlich, L-P = Langmuir w/ Partitioning, and P-P = Polanyi w/ Partitioning.

IsoFit will use the default isotherm parameter settings given in Table 2.1 (located on the following page) unless the user overrides them in the parameter ranges section.

Isotherm	Parameter	Transformation	FD Step Size	Lower	Upper
BET	Q_0 , $b * Q_0$ b	log_{10}	0.001	1×10^{-6} 1.00	1×10^{6}
Freundlich	K_f $(1/n)$	log_{10} none	0.001	1×10^{-6}	1×10^{6} 1.00
F-P	K_f K_p $(1/n)$	log_{10} none	0.001	1×10^{-6}	1×10^{6} 1.00
GLF	Q_0 b $(1/n)$	log_{10} none	0.001	1×10^{-6}	1×10^{6} 1.00
Langmuir	Q_0 , $b * Q_0$ b	log_{10}	0.001	1×10^{-6}	1×10^{6}
L-P	K_p Q_0 , $b * Q_0$ bVal	log_{10}	0.001	1×10^{-6}	1×10^{6}
Linear	K_p	log_{10}	0.001	1×10^{-6}	1×10^{6}
Polanyi	Q_0 A B	log_{10} none	0.001	1×10^{-6}	1×10^{6} 1.00 10.00
P-P	K_p Q_0 A B	log_{10} none	0.001	1×10^{-6}	1×10^{6} 1.00 10.00
Toth	Q_0 , $b * Q_0$ b n	log_{10} none	0.001	1×10^{-6}	1×10^{6} 1.00

Table 2.1: Default Isotherm Parameter Configurations

2.6 Adjusting the IsoFit Search Procedure

The user can adjust two parameters of the IsoFit search procedure by including the following syntax in the input file:

`MaxGens` `<gens>` (default value is $20 \times np$)
`PopSize` `<pop>` (default value is $20 \times np$)

Where `<gens>` is the maximum number of generations to use in the particle swarm optimization procedure, `<pop>` is the number of particles (i.e. parameter sets) to evaluate during each generation, and np is the number of isotherm parameters.

Chapter 3

IsoFit Output Files

IsoFit uses the OSTRICH calibration/optimization program to perform the minimization of equation (1.2) and, as a result, the output is stored in a file named `OstOutput0.txt`. This output file will contain the following elements (i) a GNU Public License disclaimer, (ii) a summary of the basic configuration variables, (iii) a run record detailing each iteration of the optimization algorithm, (iv) the resulting optimal isotherm parameters and objective function value, and (v) a comprehensive list of regression statistics, including:

- Error variance and standard error of the regression, providing a rough indication of the goodness-of-fit of the chosen isotherm type.
- Observation residuals and correlation between measured and fitted observations (R_y).
- 95% linear confidence intervals for each isotherm parameter.
- Parameter variance-covariance matrix, parameter standard error and parameter correlation coefficients.
- Normality of residuals analysis, a test of the assumption that residuals are normally distributed.
- Cook's D and DFBETAS influential observation measures, identifying observations having the greatest impact on the isotherm fit.
- Parameter sensitivities, measures of the sensitivity of simulated observations (q_i) to changes in isotherm parameter values.
- Beale and Linssen measures of model non-linearity.

- Regression matrices, including the Jacobian, normal, and inverse-normal matrices.
- A Runs Test for determining whether residuals are serially autocorrelated, computed following the guidelines of Sweed and Eisenhart (1943). For the Runs Test to be meaningful, the lab data should be entered in an appropriate order (e.g. ordered by increasing value of observation) within the `LabData` section of the input file.
- The Durbin-Watson test for serial autocorrelation of residuals, computed following the guidelines of White (1992) and Durbin and Watson (1971). As with the Runs Test, the Durbin-Watson test is only meaningful if the lab data is entered in an appropriate order.
- Multi-Model Ranking (MMR) Statistics that compute alternative measures of model fit. MMR measures are designed to help with the identification of the "best" isotherm for a given data set, and are based on statistics derived from information theory. Each MMR measure may be viewed as an estimate of the amount of information that is lost when a model (i.e. an isotherm) is used to approximate reality. As such, isotherms with low MMR measures are preferred. IsoFit reports the following MMR measures:
  - Akaike Information Criterion (AIC) (Akaike, 1974)
  - Corrected Akaike Information Criterion (AICc) (Hurvich and Tsai, 1994)
  - Bayesian Information Criterion (BIC) (Schwarz, 1978)
  - Hannan and Quinn's Criterion (HQ) (Hannan and Quinn, 1979)
  - Kashyap's Information Criterion (KIC) (Kashyap, 1992)

  Poeter and Anderson (2005) reviewed these measures in the context of groundwater flow modeling and preferred the AICc measure.

Detailed descriptions of the elements of the `OstOutput0.txt` output file are provided in the OSTRICH manual, which is available online at

`www.groundwater.buffalo.edu/software/Ostrich/OstrichMain.html`

In addition to the `OstOutput0.txt` file, users may be interested in viewing the `IsothermOut.txt` file. On completion of IsoFit, this file will contain the optimal parameter values of the user-specified isotherm, along with the laboratory data that was used by the fitting procedure. Figure 3.1 contains an example `IsothermOut.txt` output file.

```
Isotherm Output File

IsothermType Langmuir
b*Q0   2.075377E+001
b      2.096651E+000
Q0     9.898533E+000
NumObs 11

i     Concentration    q
0     1.614204E-307    3.350082E-306
1     3.000000E-002    5.857685E-001
2     6.900000E-002    1.251026E+000
3     1.180000E-001    1.963232E+000
4     1.660000E-001    2.555648E+000
5     2.170000E-001    3.095293E+000
6     2.700000E-001    3.578017E+000
7     3.250000E-001    4.011496E+000
8     3.880000E-001    4.440287E+000
9     4.530000E-001    4.821797E+000
10    5.120000E-001    5.124671E+000
```

Figure 3.1: Example `IsothermOut.txt` Output File

Chapter 4

Running IsoFit

After creating the input file, IsoFit is run by typing `<path>/IsoFit.exe` at a command line prompt, where `<path>` is the path to the location of the IsoFit.exe executable. As IsoFit runs, the progress of the search procedure is displayed in a DOS console window. If the user wishes to abort the IsoFit program before the search procedure completes, this can be accomplished in a graceful fashion by creating an empty text file named `OstQuit.txt`; when OSTRICH detects the existence of such a file, it will (i) finish up the current step of the search procedure, (ii) generate output files, and (iii) quit.

Chapter 5

Example Problem

The following example is derived from a research project conducted by Dr. Shannon L. Bartelt-Hunt; wherein various materials were considered as possible amendments to conventional landfill liners. The materials considered were known to have high sorptive capacities for organic compounds commonly found in landfill leachate, and it was hypothesized that amendment of traditional clay liners with such materials could substantially retard diffusive flux of organic contaminants from the landfill into underlying groundwater. The IsoFit input file used for this example is provided in the Demo directory of the IsoFit download.

C_i(mg/L)	$q_{i,obs}$ (mg/kg)
0.00	0.00
15.71	43,928.35
32.01	137,758.63
48.03	197,583.55
68.80	252,327.78
97.02	314,850.34
161.47	370,194.85
217.76	406,402.19
508.57	437,013.71

Table 5.1: TCE sorption onto liner amended with GAC

In this example, a series of column experiments were performed to determine the sorption of trichloroethylene (TCE) onto a compacted clay liner amended with granular activated carbon (GAC). Table 5.1 contains the lab

measurements from the column experiments and Figure 5.1 contains the corresponding `IsoFitIn.txt` input file for the Freundlich isotherm type.

```
IsothermType     FreundlichIsotherm
WeightingScheme  Uniform  1.00

BeginLabData
0.00    0.00
15.71   43928.35
32.01   137758.63
48.03   197583.55
68.80   252327.78
97.02   314850.34
161.47  370194.85
217.76  406402.19
508.57  437013.71
EndLabData

MaxGens   50
PopSize   50

Solubility  1000

BeginRanges
Kf     0.0  1.00e06  none  0.001
(1/n)  0.0  1.00     none  0.001
EndRanges
```

Figure 5.1: GAC-TCE Freundlich Isotherm Input File

Figure 5.2 shows the OSTRICH setup summary, run record, optimal parameter set and some of the basic statistical output from the IsoFit output file (`OstOutput0.txt`). Although Figure 5.2 suggests that the OSTRICH program ran only two iterations of the Levenberg-Marquardt algorithm, in actuality IsoFit runs OSTRICH twice. The first run uses a Particle Swarm Optimization algorithm to place the starting point for the subsequent Levenberg-Marquardt algorithm very close to the global minimum. This procedure helps prevent the Levenberg-Marquardt algorithm from falling into a local minima, a distinct possibility, given the non-linear form of many isotherm expressions.

```
Ostrich Setup
Model                  : Isotherm()
Algorithm              : Levenberg-Marquardt
Objective Function     : WSSE
Number of Parameters   : 2
Number of Tied Params  : 0
Number of Observations : 9

Ostrich Run Record
iter  obj. function  Kfval          (1/n)val       lambda
0     2.020642E+010  4.710056E+004  3.781439E-001  1.000000E+001
1     2.020642E+010  4.710056E+004  3.781439E-001  9.090909E+000

Optimal Parameter Set
Objective Function : 2.020642E+010
Kfval              : 4.710056E+004
(1/n)val           : 3.781439E-001

Statistical Output
********** NOTE **********
Insensitive observations (1) and/or parameters (0)
were detected and have not been included in the
following statistical calculations.
**********

Adjusted Obj.Func. : 2.020642E+010

Parameter      Value            Sensitive?
Kfval          4.710056E+004    YES
(1/n)val       3.781439E-001    YES

Observation Residuals
Observation    Measured       Simulated      Weighted Residual   Sensitive?
obs0           0.000000E+000  0.000000E+000  +0.000000E+000      NO
obs1           4.392835E+004  1.334605E+005  -8.953215E+004      YES
obs2           1.377586E+005  1.746790E+005  -3.692040E+004      YES
obs3           1.975835E+005  2.036478E+005  -6.064300E+003      YES
obs4           2.523278E+005  2.332915E+005  +1.903630E+004      YES
obs5           3.148503E+005  2.656719E+005  +4.917840E+004      YES
obs6           3.701948E+005  3.221088E+005  +4.808600E+004      YES
obs7           4.064022E+005  3.606768E+005  +4.572540E+004      YES
obs8           4.370137E+005  4.970683E+005  -6.005460E+004      YES

Correlation between measured and simulated observations
Ry         :  0.924

Error Variance and Standard Error of the Regression
S^2 : 3.367737E+009
S   : 5.803221E+004

MMRI (Alternative Measures of Model Fit)
Corrected Akaike Information Criterion (AICc) : 179.598599
```

Figure 5.2: Partial List of IsoFit Output

Isotherm	Param	Estimate	CI_{low}	CI_{high}	Isotherm	Param	Estimate	CI_{low}	CI_{high}
BET	bQ_0	1.25×10^{7}	-8.27×10^{6}	3.32×10^{7}	L-P	bQ_0	6,670	5,000	8,880
	b	45.7	-39.2	131		b	0.0125	8.22×10^{-3}	0.0189
	Q_0	2.73×10^{5}	n/a	n/a		Q_0	5.35×10^{5}	n/a	n/a
Freundlich	K_f	4.71×10^{4}	1,970	9.22×10^{4}		K_p	5.18×10^{-9}	n/a	n/a
	$(1/n_f)$	3.78E-01	0.198	0.558	Polanyi	Q_0	4.40×10^{5}	4.27×10^{5}	4.52×10^{5}
F-P	K_f	4.71×10^{4}	1,980	9.23×10^{4}		A	-0.144	-0.162	-0.126
	$(1/n_f)$	0.378	0.198	0.558		B	3.21	2.91	3.50
	K_p	6.29×10^{-4}	n/a	n/a	P-P	Q_0	4.35×10^{5}	3.79×10^{5}	5.00×10^{5}
GLF	Q_0	4.52×10^{5}	4.30×10^{5}	4.74×10^{5}		A	-0.141	-0.188	-0.093
	b	0.0174	0.0158	0.0191		B	3.25	2.59	3.90
	$(1/n_g)$	1.55	1.35	1.75		K_p	9.24	-118	137
Langmuir	bQ_0	6,670	5,000	8,880	Toth	bQ_0	4,340	3,580	5,260
	b	0.0125	8.22×10^{-3}	0.0189		b	9.84×10^{-3}	8.19×10^{-3}	0.0115
	Q_0	5.35×10^{5}	n/a	n/a		Q_0	4.41×10^{5}	n/a	n/a
Linear	K_p	1,240	739	2070		n_T	2.12	1.12	3.11

Figure 5.3: Summary of Parameter Estimates for the Example Problem

By adjusting the `IsothermType` parameter in the `IsoFitIn.txt` file, IsoFit runs were performed for all ten isotherms. Figure 5.3 summarizes the resulting parameter estimates for each isotherm, along with linear confidence intervals. Note that the parameter lumping option was enabled for the BET, Langmuir, L-P and Toth isotherms.

Figure 5.4 summarizes some of the diagnostic statistics computed by IsoFit and reported in the `OstOutput0.txt` output file. The $AICc$ values indicate that the Polanyi isotherm expression provides the best fit of the sorption data.

Iso-therm	Multi-Model Ranking (AICc)	Correlation Between Measured and Simulated Observations (R^2_y)	Correlation Between Residuals and Normality (R^2_N)	Linssen Measure of Non-Linearity (M^2)	Linearity Assessment
Polanyi	145	0.999	0.908	0.009	Linear
GLF	150	0.998	0.968	0.014	Linear
P-P	155	0.999	0.913	2.062	Non-Linear
Toth	159	0.995	0.749	2.606	Non-Linear
Lang-muir	166	0.978	0.947	0.013	Linear
L-P	166	0.978	0.947	0.013	Linear
Freund-lich	180	0.854	0.911	2.211	Non-Linear
F-P	180	0.854	0.911	2.210	Non-Linear
BET	184	0.741	0.944	1.479	Non-Linear
Linear	193	0.614	0.752	0.013	Linear

Figure 5.4: Summary of Selected Diagnostics for the Example Problem

Bibliography

Akaike H. 1974. A new look at the statistical model identification.*IEEE Transactions on Automatic Control*, vol. 19, pg. 716723.

Allen SJ, Gan Q, Matthews R, Johnson PA. 2003. Comparison of Optimized Isotherm Models for Basic Dye Adsorption bye Kudzu. *Bioresource Technology*, vol. 88, pg. 143-152.

Allen-King RM, Grathwohl P, Ball WP. 2002. New modeling paradigms for the sorption of hydrophobic organic chemicals to heterogeneous carbonaceous matter in soils, sediments, and rocks. *Advances in Water Resources*, vol. 25, pg. 9851016.

Alper Js, Gelb RI. 1990. Standard Errors and Confidence Intervals in Nonlinear Regression: Comparison of Monte Carlo and Parametric Statistics. *Journal of Physical Chemistry*, vol. 94, pg. 4747-4151.

Barker DR, Diana LM. 1974. Simple Method for Fitting Data when Both Variables Have Uncertainties. *American Journal of Physics*, vol. 42, pg. 224-227.

Bartelt-Hunt SL, Smith JA, Burns SE, Rabideau AR. 2005. Evaluation of granular activated carbon, shale and two organoclays for use as sorptive amendments in clay landfill liners. *Journal of Geotechnical and Geoenvironmental Engineering*, vol. 131, no. 7, pg. 848-856, DOI:10.1061/(ASCE)1090-0241(2005)131:7(848).

Brunauer SP, Emmett PH, Teller E. 1938. Adsorption of Gases in Multimolecular Layers. *Journal of the American Chemical Society*, vol. 60, pg. 309-319.

Carroll RJ, Ruppert DR. 2006. *Measurement Error in Nonlinear Models: a modern perspective*, Chapman and Hall: London, UK.

Durbin J, Watson GS. 1971. Testing for Serial Correlation in Least Squares Regression III. *Biometrika*, vol. 58, no. 1, pg. 1-19.

Freundlich H. 1924. *The Elements of Colloidal Chemistry*, translated by George Barger. Dutton and Company Publishers: New York, NY, pp. 58-61.

Hannan E, Quinn B. 1979. The determination of the order of an autoregression. *Journal of the Royal Statistical Society, Series B*, vol. 41, no. 1, pg. 190-195.

Hurvich CM, Tsai C-L. 1994. Autoregressive model selection in small samples using a bias-corrected version of AIC. In: Bozdogan H, editor. *Proceedings of the First U.S./Japan Conference on the Frontiers of Statistical Modeling: An Informational Approach*. Kluwer Academic Publishers: Dordrecht, Netherlands, pg. 137-157.

Kano F, Abe I, Kamaya H, Ueda I. 2000. Fractal Model for Adsorption on Activated Carbon Surfaces: Langmuir and Freundlich Adsorption. *Surface Science*, vol. 467, pg. 131-138.

Kashyap R. 1992. Optimal choice of AR and MA parts in autoregressive moving average models. *IEEE Transactions on Pattern Analysis and Machine Intelligence*, vol. 4, no. 2, pg. 99-104.

Katare S, Kalos A, West D. 2004. A hybrid swarm analyzer for efficient parameter estimation. In *Proceedings of the IEEE Congress on Evolutionary Computation*, vol. 244, no. 1, pg. 309-315.

Kennedy J, Eberhart RC. 1995. Particle swarm optimization. *Proceedings of IEEE International Conference on Neural Networks*, Piscataway, NJ. pg. 1942-1948.

Kinniburgh DG. 1985. ISOTHERM: A Computer Program for Analysing Adsorption Data. *Report WD/ST/85/02*; British Geological Survey: Wallingford, UK.

Kinniburgh DG. 1986. General Purpose Adsorption Isotherms.*Environmental Science and Technology*, vol. 20, pg. 895-904.

Kinniburgh DG. 1999. FIT User Guide. *Report WD/93/23*; British Geological Survey: Keyworth, UK.

Langmuir I. 1916. The Constitution and Fundamental Properties of Solids and Liquids. Part I. Solids. *Journal of the American Chemical Society*, vol. 38, no. 11, pg. 2221-2295.

Levenberg K. 1944. A Method for the Solution of Certain Problems in Least Squares. *Quarterly of Applied Mathematics*, vol. 2, pg. 164-168.

Marquardt D. 1963. An Algorithm for Least-Squares Estimation of Nonlinear Parameters. *SIAM Journal on Applied Mathematics*, vol. 11, pg. 431-441.

McCammon RB. 1973. Nonlinear Regression for Dependent Variables. *Mathematical Geology*, vol. 5, no. 4, pg. 365-375.

Orear J. 1982. Least squares when both variables have uncertainties. *American Journal of Physics*, vol. 50, no. 10, pg. 912-916.

Padmesh TVN, Vijayaraghavan K, Sekaran G, Velan M. 2006. Application of Two- and Three-Parameter Isotherm Models: Biosorption of Acid Red 88 onto *Azolla microphylla*. *Bioremediation Journal*, vol. 10, no. 1-2, pg. 37-44.

Poeter E, Anderson D. 2005. Multimodel ranking and inference in groundwater modeling. *Ground Water*, vol. 43, no. 4, pg. 597-605.

Rabideau AJ, Jiang Z, Matott LS, Allen-King R. 2006. Modeling groundwater transport with nonlinear isotherms. *Advances in Water Resources*, in review.

Rubichev NA. 1993. Least-squares fitting with errors of measurement in both variables. *Measurement Techniques*, vol. 36, no. 12, pg. 1311-1315.

Schwarz G. Estimating the dimension of a model. *Annals of Statistics*, vol. 6, no. 2, pg. 461-464.

Sweed FS, Eisenhart C. 1943. Tables for testing randomness of grouping in a sequence of alternatives. *The Annals of Mathematical Statistics*, vol. 14, no. 1, pg. 66-87.

Toth J. 1971. State Equations of the Solid-Gas Interface Layer. *Acta Chem. Acad. Hung.*, vol. 69, pg. 311-317.

Weber WJ, McGinley PM, Katz L. 1992. A distributed reactivity model for sorption by soils and sediments. 1. Conceptual basis and equilibrium

assessments. *Environmental Science & Technology*, vol. 26, no. 10, pg. 19551962.

White KJ. 1992. The Durbin-Watson Test for Autocorrelation in Nonlinear Models. *The Review of Economics and Statistics*, vol. 74, no. 2, pg. 370-373.

Xia G, Ball WP. 1999. Adsorption-Partitioning Uptake of Nine Low-Polarity Organic Chemicals on a Natural Sediment. *Environmental Science & Technology*, vol. 33, pg. 262-269.

Xia G, Ball WP. 2000. Polanyi-Based Models for the Competetive Sorption of Low-Polarity Organic Contaminants on a Natural Sorbent. *Environmental Science & Technology*, vol. 34, pg. 1246-1253.

Xing B, Pignatello JJ, Gigliotti B. 1996. Competitiive sorption between atrazine and other organic compounds in soils and model sorbents. *Environmental Science & Technology*, vol. 30, no. 8, pg. 24322440.