Revisiting a Statistical Shortcoming when Fitting the Langmuir Model to Sorption Data

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The Langmuir model is commonly used for describing the sorption behavior of reactive solutes to surfaces and is often fit to sorption data using nonlinear least squares regression. An important assumption of least squares regression is that the predictor variable is error free. In the case of sorption data, this assumption is not valid, and therefore the potential for parameter bias exists. Although alternative regression methods exist that either explicitly account for error in the predictor variable (Model II regression) or minimize the error in the predictor variable, these methods are not commonly used. Therefore, this paper more fully explores the differences in fitted parameters and model fits between these different data fitting methods by fitting P sorption data collected on 26 different soil samples using three different regression methods. For a majority of soils tested in this study, the differences in model fits between the three regression methods were not statistically significant. Statistical differences were observed in over a third of the soils, however, suggesting that errors in the predictor variable may be large enough to produce biased parameter estimates. These results suggest that multiple regression methods should be used when fitting the Langmuir model to sorption data to better assess the potential impact of error on model fits.

The transport behavior of environmentally significant reactive solutes such as phosphorus and heavy metals is controlled in large part by the sorption behavior of the solute to soil surfaces. A commonly used model for describing sorption behavior of reactive solutes to surfaces is the Langmuir model (Altin et al., 1998; Kleinman and Sharpley, 2002; Kumar and Sivanesan, 2005; Tsai and Juang, 2000; Wang and Harrell, 2005). This nonlinear model was originally developed for describing the adsorption of gases to a surface but has been used extensively for describing solute and metal sorption to soils. This model assumes a finite sorption capacity at the surface; therefore, as the sorption capacity is approached, sorption decreases (Langmuir, 1916). The Langmuir model is expressed as:

$$S = \frac{S_{\max} \times K \times C_e}{1 + K \times C_e} \quad [1]$$

where S is the sorbed concentration (mg kg^{-1}), $S_{\max}$ is the maximum sorption capacity of the soil (mg kg^{-1}), K is the Langmuir binding-strength coefficient (L mg^{-1}), and C_e is the equilibrium concentration (mg L^{-1}).

To obtain estimates of K and $S_{\max}$ for a given soil, the Langmuir model is usually fit to sorption isotherm data by linear or nonlinear least squares regression. Because the transformation of data required for linearization can result in modifications of error structure, introduction of error into the independent variable, and alteration of the weight placed on each data point, several researchers have recommended that linearized versions of the Langmuir equation not be used (Bolster and Hornberger, 2007; Harrison and Katti, 1990; Kinniburgh, 1986; Persoff and Thomas, 1988). Statistical problems also exist, however, when using nonlinear least squares regression for obtaining Langmuir sorption constants (Barrow, 1978; Bothwell and Walker, 1995; Kinniburgh, 1986; Schulthess and Dey, 1996). For example, an important assumption of least squares regression (also known as Model I regression) is that the predictor variable is error free (Draper and Smith, 1998; Seber and Wild, 2003). However, the predictor variable (i.e., C_e) in Eq. [1] is the variable that is experimentally measured and therefore has error associated with it.

When both model variables (i.e., the response and predictor) are subject to experimental error (often referred to as an errors-in-variables model), Model I regression has been shown to generate biased parameter estimates (de Brauwere et al., 2005; Seber and

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Abbreviations: NNLS, normal nonlinear least squares; SSE, sum of the squared errors; VNLS, vertical nonlinear least squares.

Wild, 2003; Valsami et al., 2000). Model II regression, on the other hand, accounts for errors in the predictor and response variables and is therefore more appropriate for fitting errors-in-variables models to data (de Brauwere et al., 2005; Ebert and Russell, 1994; Ko et al., 1997; Seber and Wild, 2003; Valsami et al., 2000). Schulthess and Dey (1996) used a form of Model II regression known as normal nonlinear least squares (NNLS) regression for fitting the Langmuir model to sorption data. With NNLS regression, the distance between observation and model fit in the normal (i.e., shortest) direction is minimized. Using this method, Schulthess and Dey (1996) obtained different parameter estimates than those obtained using Model I regression, although these differences were not statistically compared. In a later study, Wijnja and Schulthess (2000) observed nearly identical model fits using Model I and Model II regression. It is unclear, therefore, whether Model II regression provides significantly different parameter estimates than Model I regression when fitting the Langmuir model to sorption data.

An additional statistical concern when fitting the Langmuir model to sorption data is that the predictor and response variables are not measured independently, and therefore the errors in the response and predictor variables are correlated. Valsami et al. (2000) found that Model I and Model II regression provided unsatisfactory parameter estimates for the Hill protein-binding model (an equation similar to the Langmuir model) when errors in the response and predictor variables were correlated. The authors recommended the use of more sophisticated methods, such as the method of scoring, when errors associated with the two variables are correlated.

Bothwell and Walker (1995) took a different approach to addressing these statistical concerns. As first suggested by Barrow (1978) and later by Kinniburgh (1986), Bothwell and Walker (1995) recognized that because S is a function of C_e and the initial concentration, Eq. [1] could be modified so that the initial concentration replaced the equilibrium concentration as the independent variable in the Langmuir equation. By replacing C_e with the initial concentration—the true independent variable—the errors in the predictor and response variables are no longer correlated, and the predictor variable is usually relatively error free. The authors found that fitting the modified Langmuir equation to cellulose binding data yielded nearly identical parameter estimates but slightly better fits and smaller parameter uncertainties than the original Langmuir equation. Because the authors used only a single data set for comparing the two equations, it is unknown whether this approach yields significantly different fits or parameter estimates than the original Langmuir equation.

Even though the data-fitting methods used by Schulthess and Dey (1996) and Bothwell and Walker (1995) are arguably more statistically valid approaches for fitting the Langmuir model to sorption data than the traditional method of fitting Eq. [1] using Model I regression, it is unclear whether these methods provide significantly different model fits and parameter estimates than the traditional method of fitting the Langmuir model to sorption data because only a few data sets were tested in these studies and statistical comparisons were not performed. Therefore, in this paper I more fully explore the differences in fitted parameters and model fits between these data-fitting methods by fitting P sorption data collected on 26 different soil samples using three regression methods: (i) fitting Eq. [1] using Model I regression, (ii) fitting Eq. [1] using Model II regression, and (iii) fitting a modified version of the Langmuir equation using Model I regression. Results of this study will provide information on how robust Model I regression is to violations of the assumption of an error-free predictor variable.

Methods

Sorption Data

Two sets of sorption data were analyzed as part of this study. The first set of sorption data was obtained from surface soils (0–15 cm depth) collected at seven locations in western Kentucky and one location in Alabama, representing eight different soils series as follows: Belknap (Fluvaquentic Endoaquepts), Collins (Aquic Udifluvents), Hartsells (Typic Hapludults), Lakin (Lamellic Udipsamments), Loring (Oxiaquic Fragiudalfs), Melvin (Fluvaquentic Endoaquepts), Pembroke (Mollic Paleudalfs), and Zanesville (Oxiaquic Fragiudalfs). The second set of sorption data represents soils collected at three depths (0–5, 5–15, and 15–30 cm) from six locations in Mississippi representing three different soil series: Brooksville (Aquic Hapluderts), Okolona (Oxyaquic Hapluderts), and Vaiden (Aquic Dystruderts). For the second data set, soil samples were taken from adjacent fields within each soil series where one field received long-term application of swine effluent (T) and the other field received no manure application (C).

All soils were air dried and passed through a 2-mm sieve before use. Soil samples were equilibrated with a 0.01 mol L^{-1} $CaCl_2$ solution containing various concentrations of P added as KH_2PO_4 in 50-mL centrifuge tubes. Sorption experiments were performed in duplicate for the second data set. The soil mixture was placed on a reciprocating shaker and allowed to equilibrate for 24 h. After equilibration, the mixture was centrifuged at 4000 rpm for 10 min, and the liquid was decanted and filtered through a 0.45-μm filter (Whatman). Dissolved reactive phosphorus was measured colorimetrically (Murphy and Riley, 1962) using a QuickChem Autoanalyzer (Lachat Instruments, Chicago, IL). Further details of the soils and methods can be found in Bolster and Sistani (2008) and Adeli et al. (2008).

Data Analysis

Sorption data were fit by three different methods, and the resultant model fits were statistically compared. For two of the methods, the traditional Langmuir equation (Eq. [1]) was fit to the data using two different objective functions. In the third approach, the modified Langmuir equation of Bothwell and Walker (1995) was fit to the data. This equation uses the initial concentration—the true independent variable—as the predictor variable. The initial concentration can be used as the predictor variable by recognizing that the response variable, S, is determined from the difference between the initial concentration and the equilibrium concentration by the following equation:

$$S = (C_i - C_e) \times V \quad [2]$$

where V (L kg^{-1}) is the solution to soil mass ratio, and C_i (mg L^{-1}) is the initial concentration fixed by the experimenter. Rearranging Eq. [2] and substituting into Eq. [1] yields a quadratic equation with either S or C_e as the response variable and C_i as the predictor variable. The solutions to the resultant quadratic equations are (Bothwell and Walker, 1995):

$$C_e = \frac{-\left(C_i K - 1 - \frac{S_{max} K}{V}\right) - \sqrt{\left(C_i K - 1 - \frac{S_{max} K}{V}\right)^2 + 4 C_i K}}{-2K} \quad [3]$$

$$S = \frac{-\left(1 + K C_i + S_{max} K \frac{1}{V}\right) + \sqrt{\left(1 + K C_i + S_{max} K \frac{1}{V}\right)^2 - 4 S_{max} K^2 C_i \frac{1}{V}}}{-2K \frac{1}{V}} \quad [4]$$

Equations [3] and [4] are mathematically equivalent to the Langmuir equation. Unlike Eq. [1], however, the response and predictor variables in Eq. [3] and [4] are measured independently. Even though some measurement error is associated with the predictor variable, because this error is usually minimal compared with the error associated with S (often referred to as a controlled errors-in-variables model), vertical least squares regression can be safely used for parameter estimation (Ratkowsky, 1990; Seber and Wild, 2003).

Sorption data were fit with Eq. [1], [3], and [4] using unweighted nonlinear least squares regression using Microsoft Excel (Bolster and Hornberger, 2007). Least squares regression seeks to minimize the sum of the squared errors (SSE) between observed and calculated values of the dependent variable:

$$\mathrm{SSE} = \sum_{i=1}^{N} \left[S_{obs} - S_{cal} \right]_i^2 \quad [5]$$

where SSE is the objective function to be minimized, N is the number of observations, and S_{obs} and S_{cal} refer to observed and calculated values, respectively, of the sorbed concentration. Alternative objective functions, and therefore definitions of what constitutes the best model fit, do exist. Indeed, the minimization of alternative objective functions can yield estimates of the Langmuir sorption constants different from those obtained by minimizing Eq. [5] (Allen et al., 2004). Nonetheless, because Eq. [5] is the most commonly used objective function, it was used in this study for quantifying and assessing model fits. Preliminary analyses showed that Eq. [3] and [4] provided identical parameter estimates and parameter uncertainties; therefore, only results from Eq. [4] are shown because this allows direct comparisons of SSE with the original Langmuir equation because both equations predict S.

Initial parameter estimates required for optimization were obtained using two approaches. The first approach involved using a grid point procedure (Draper and Smith, 1998). In this procedure, SSE values were calculated for a range of parameter values (K ranged from 0.1 to 2.6 in increments of 0.5, and S_{max} ranged from 100 to 1200 in increments of 100). The combination of parameter values that gave the lowest SSE values was then used as the initial parameter estimates during optimization. In the second approach, initial values were obtained by fitting transformed data with the Langmuir linearization of Eq. [1] (Langmuir, 1918). Initial values obtained with the two methods yielded identical model fits and parameter estimates, suggesting that the use of initial parameter estimates obtained with the Langmuir linearization will result in model convergence on the global minimum of the objective function.

Equation [1] was also fit to the sorption data with the Model II regression method of Schulthess and Dey (1996) using LLMpro software (Schulthess, 2007). This method is a modification of the traditional normal least squares approach in that the regression results in a model fit in which the data are evenly distributed above and below the curve. To maintain parity of units in the objective function, this method requires an axes conversion factor, which in this study was set equal to the inverse of the soil to solution ratio (V^{-1}). Throughout the remainder of this paper, the three methods used to obtain Langmuir sorption constants are referred to as C_e–VNLS, C_e–NNLS, and C_i–VNLS, representing Eq. [1] with vertical nonlinear least squares regression, Eq. [1] with normal nonlinear least squares regression, and Eq. [4] with vertical nonlinear least squares regression, respectively.

To determine whether the parameter estimates obtained with the three methods were significantly different, model predictions of the data were statistically compared using an F test (Draper and Smith, 1998):

$$\mathrm{SSE}_{95} = \mathrm{SSE}_{min} \left[1 + \frac{P}{N-P} F(0.95, P, N-P) \right] \quad [6]$$

where SSE_{min} is the value of the minimized objective function, SSE_{95} is the maximum SSE value for which the parameter values are within the 95% confidence range of the fitted parameter values, N is the number of data points, and P is the number of fitting parameters (n = 2). The F value was obtained using the FINV command in Excel for a 0.95 probability and P degrees of freedom in the numerator and N-P degrees of freedom in the denominator. Combinations of values of K and S_{max} that yield an SSE value equal to SSE_{95} represent the outer boundary of the 95% confidence region; therefore, all combinations of K and S_{max} resulting in SSE values equal to or less than SSE_{95} are not considered significantly different at the 95% confidence level than the best-fit parameter values. Model fits were statistically compared by calculating values of S using the best-fit parameter estimates obtained from the three regression methods and comparing the resultant SSE values with the SSE_{95} value obtained from Eq. [6]. Statistical comparisons were made for C_e (Eq. [1]) and C_i (Eq. [4]) as the predictor variable.

Results and Discussion

For 23 of the 26 soil samples tested in this study, fitted K values obtained with the C_i–VNLS and C_e–NNLS methods were lower than fitted values obtained with the traditional C_e–VNLS method, with values of K ranging from 9 to 60%

lower for the C_i–VNLS method and 6 to 57% lower for the C_e–NNLS method (Fig. 1A). For these same 23 soil samples, fitted S_{max} values were higher for the C_i–VNLS and C_e–NNLS methods, with increases in S_{max} ranging from 2 to 15% for the C_i–VNLS method and from 2 to 16% for the C_e–NNLS method (Fig. 1B). Schulthess and Dey (1996) also observed that the C_e–NNLS method generally yielded small increases in estimates of S_{max} and relatively large decreases in estimates of K when compared with the C_e–VNLS method. With the exception of the Belknap, Collins, and Hartsells soils, fitted parameter values obtained with the C_i–VNLS and C_e–NNLS methods were more similar to each other than to those obtained with the traditional C_e–VNLS method. Indeed, the C_i–VNLS and C_e–NNLS methods produced nearly identical model fits for most soils (Fig. 2).

Model fits obtained by the different methods were statistically compared using an F-test. When using the best-fit parameter estimates obtained with the C_i–VNLS method to predict values of S using Eq. [1], the resultant SSE values exceeded the SSE_{95} of the C_e–VNLS method in 11 of the soils tested, whereas using the best-fit parameters obtained with the C_e–NNLS method resulted in SSE values exceeding the SSE_{95} of the C_e–VNLS method for nine of the soils tested (Table 1). Statistical differences in model fits between the regression methods are due primarily to large differences in estimates of K between the different methods. When significant differences were observed between the three regression methods, parameter estimates obtained with the C_i–VNLS and C_e–NNLS methods produced better predictions of high concentrations of S at the expense of low concentrations of S, whereas fitted parameter values obtained with the C_e–VNLS method better captured low concentrations of S at the expense of high concentrations of S when C_e was used as the predictor variable (Fig. 2).

Comparisons between the different regression methods were based solely on statistical comparisons of the SSE in the vertical direction. Because this method assumes that error is associated only with the response variable and not with the predictor variable, vertical SSE cannot be used to determine which method provides the best fit; it can only be used to determine whether the differences in SSE are statistically different. Therefore, even though parameter estimates obtained with the C_e–VNLS method provided the lowest SSE values when C_e was used as the predictor variable, this does not mean that the C_e–VNLS method provides the best model fits and parameter estimates.

When sorption data are plotted against the initial concentration, the amount of scatter in the data is noticeably reduced, and the Langmuir model is better able to capture high and low concentrations of S (Fig. 2). Indeed, for all soils tested in this study, SSE values were much lower when C_i was used as the predictor variable rather than C_e, regardless of how the parameter estimates were obtained (Table 1). When using the best-fit parameter estimates obtained with the C_e–VNLS method to predict values of S using Eq. [4], the resultant SSE values exceeded the SSE_{95} of the C_i–VNLS method in 15 of the soils tested, whereas for the C_e–NNLS method, the resultant SSE values never exceeded the SSE_{95} of the C_i–VNLS

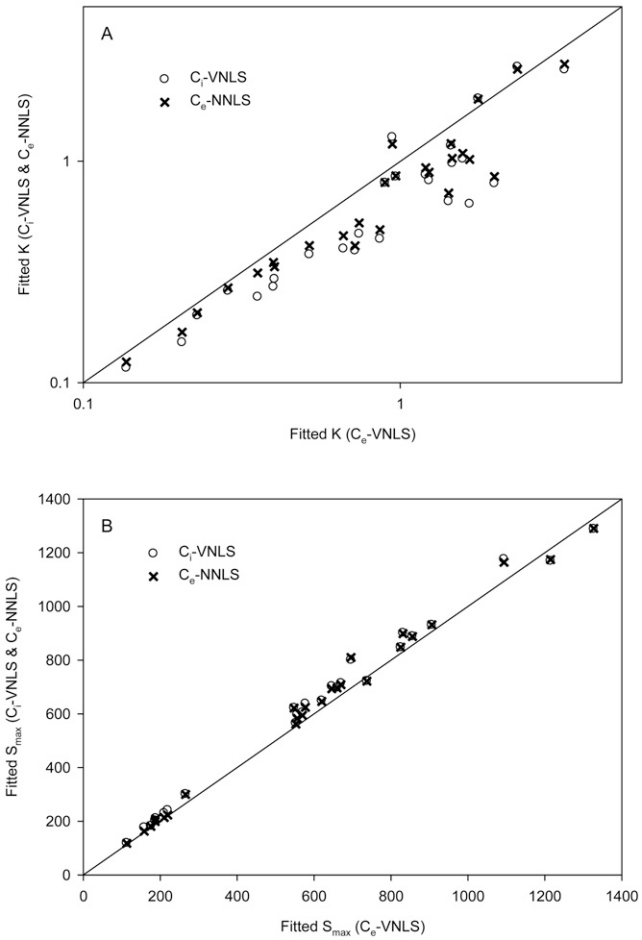

Fig. 1. Fitted values for (A) K and (B) S_{max} for the three regression methods tested in this study. Panel A is plotted with logarithmic axes. Fitted parameter values obtained with the traditional least squares method (C_e–VNLS) are plotted on the *x* axis, and the fitted parameter values obtained with the two alternative methods (C_i–VNLS and C_e–NNLS) are plotted on the *y* axis. The solid line represents a one-to-one line. For 23 of the 26 soils, the C_i–VNLS and C_e–NNLS methods provided lower values of K and higher values of S_{max} than the C_e–VNLS method. For most soils, the C_i–VNLS and C_e–NNLS produce very similar parameter estimates.

method, further highlighting the strong similarities in model fits between these two alternative regression methods.

Previous studies have reported biased parameter estimates when using Model I regression with errors-in-variables models due to the fact that an inherent assumption in vertical least squares regression is that the predictor variable is error free (de Brauwere et al., 2005; Valsami et al., 2000). Because the predictor variable, C_e, in the original Langmuir equation is not error free, the potential exists that Langmuir sorption constants obtained by fitting Eq. [1] to sorption data using vertical least squares regression may be biased. For the majority of soils tested in this study, the differences in model fits between the three regression methods were not statistically significant, indicating that vertical least squares regression is relatively robust to the presence of error in the predictor variable, at least when fitting the Langmuir model to sorption data. For about a third of the samples, however, the C_i–VNLS and C_e–NNLS methods did provide

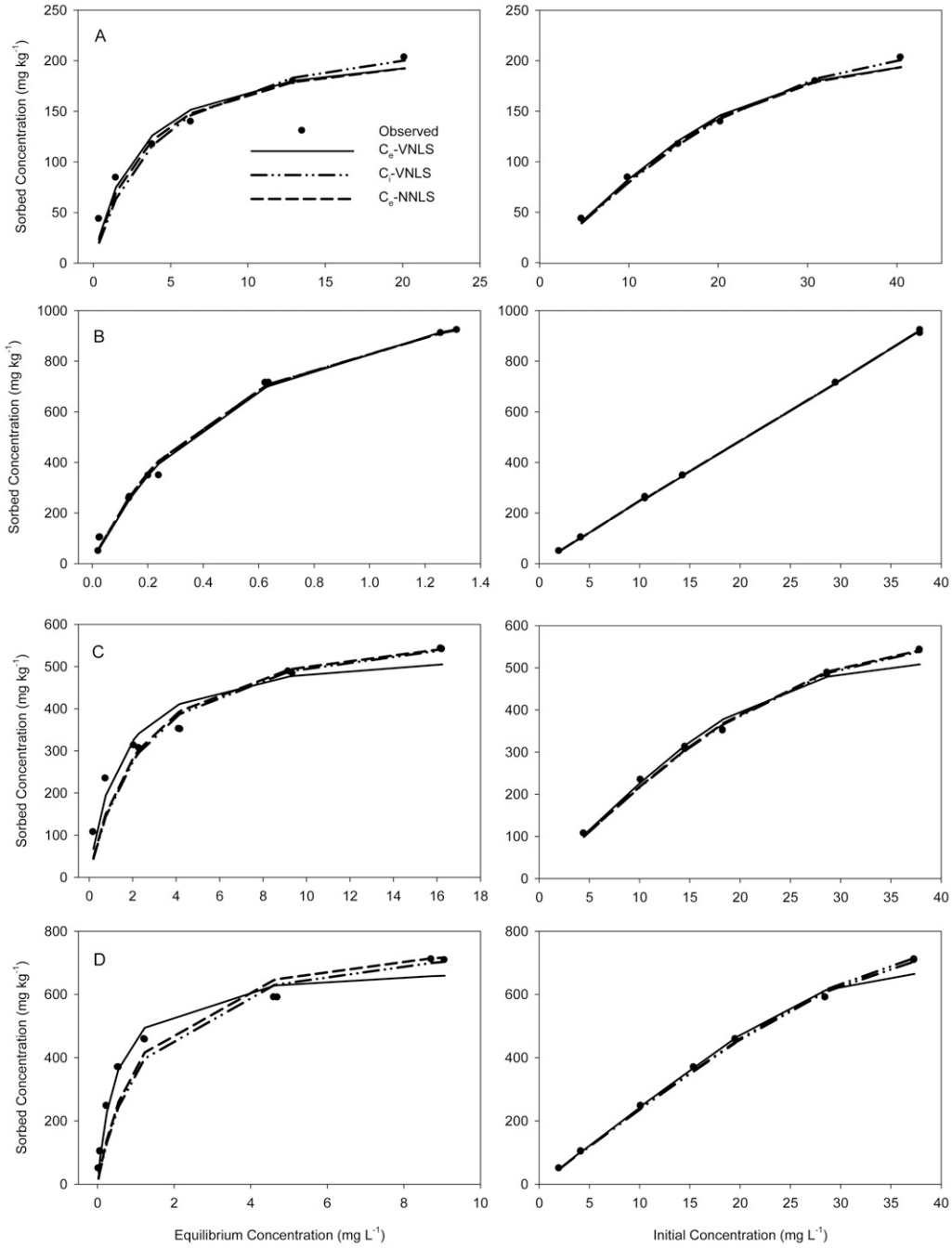

Fig. 2. Observed data and model predictions using the original (left) and modified (right) Langmuir equations. For brevity, only four representative data sets are shown. The Belknap soil (A) is representative of the three soils (Belknap, Collins, and Hartsells) in which the C_e–NNLS method provided more similar parameter estimates to the C_e–VNLS method than the C_i–VNLS. The Vaiden 5- to 15-cm untreated soil (B) is representative of the soils in which all three regression methods provided very similar parameter estimates. The Brooksville 0- to 5-cm untreated (C) and Okolona 15- to 30-cm treated (D) soils are representative of soils in which the C_i–VNLS and C_e–NNLS methods produced significantly different model fits than the C_e–VNLS method.

statistically different model fits than the C_e–VNLS method, suggesting that under some conditions, errors in the predictor variable may be large enough to produce biased parameter estimates.

An additional limitation to using least squares regression for fitting the original Langmuir equation is that S is calculated from measured concentrations of C_e; therefore, S and C_e are not measured independently, and any measurement error in C_e leads to a negatively correlated error in S. Thus, an overestimate of C_e leads to an erroneously low calculated value of S, with the resultant data point being shifted downward and to the right on the isotherm plot. Valsami et al. (2000) reported that neither Model I nor Model II regression could provide good parameter estimates when errors in the response and predictor variables were correlated. In this study, however, fitting the original Langmuir equation using Model II regression yielded nearly identical parameter estimates and model fits as the modi-

fied Langmuir equation, an equation in which the response and predictor variables are measured independently, and thus the errors are uncorrelated. These results, therefore, suggest that the inherent correlation between errors in the predictor and response variables in the original Langmuir equation do not have a significant impact on parameter estimation, at least for the experimental conditions found in this study.

Statistical concerns to using linearized versions of the Langmuir equation have been raised for several decades (Bolster and Hornberger, 2007; Colquhoun, 1969; Colquhoun, 1971; Dowd and Riggs, 1965; Harter, 1984; Kinniburgh, 1986; Kumar and Sivanesan, 2005; Persoff and Thomas, 1988; Schulthess and Dey, 1996). Statistical problems also exist when using regression analysis to fit the nonlinear Langmuir equation to sorption data (Barrow, 1978; Bothwell and Walker, 1995; Kinniburgh, 1986; Schulthess and Dey, 1996). One such problem is that the use of Model I regression assumes an error-free predictor variable, yet this assumption is violated when equilibrium concentrations are used as the predictor variable. The two alternative regression methods tested here specifically address this problem by either explicitly accounting for (C_e–NNLS) or reducing the magnitude of (C_i–VNLS), the error in the predictor variable. For the majority of soils tested in this study, the differences in model fits between the three regression methods were not statistically significant. In about a third of the studies, statistical differences were observed, suggesting that under some conditions errors in the equilibrium concentration may be large enough to produce biased parameter estimates. Therefore, it is recommended that the C_e–NNLS or C_i–VNLS method be used in addition to the C_e–VNLS method when fitting the Langmuir model to sorption data to determine the potential for parameter bias. The modified normal least squares method of Schulthess and Dey (1996) is available at www.alfisol.com (Schulthess, 2007), and an easy-to-use Microsoft Excel spreadsheet capable of fitting Eq. [3] and [4] to sorption data is available at ars.usda.gov/msa/awmru/bolster/Sorption_spreadsheets. Due to its complex structure, the modified Langmuir equation can diverge during optimization if initial estimates are far removed from the best-fit parameter values. Therefore, initial parameter estimates should be obtained with Eq. [1] or the Langmuir linearization of Eq. [1].

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Table 1. Comparisons of sum of squared errors (SSE) for the three nonlinear regression methods: fitting Eq. [1] to sorption data using vertical nonlinear least squares regression (C_e–VNLS), fitting Eq. [4] to sorption data using vertical nonlinear least squares regression (C_i–VNLS), and fitting Eq. [1] to sorption data using normal nonlinear least squares regression (C_e–NNLS).

	SSE (S vs. C_e)			SSE (S vs. C_i)		
Soil	C_e–VNLS	C_i–VNLS	C_e–NNLS	C_e–VNLS	C_i–VNLS	C_e–NNLS
Belknap	737	1025	798	162	69.5	136.8
Collins	750	1044	805	160	68.3	129.2
Hartsells	845	2105	1243	383*	137.1	256.2
Lakin	401	534	460	159	106.8	117.6
Loring	735	1546	1307	290*	91.1	96.7
Melvin	178	241	208	117	93.3	96.3
Pembroke	205	228	219	61	51.4	52
Zanesville	1689	4212	3579	359*	65.3	73.4
Brooksville C5	17,853	28,090*	26,295*	3987*	1096	1157
Brooksville C15	22,823	24,590	24,339	229*	134.2	135
Brooksville C30	6586	11,859*	10,590*	228*	49.5	53.1
Brooksville T5	3724	4234	3936	1108	951	981
Brooksville T15	10,650	24,022*	17,468*	4259*	2693	2808
Brooksville T30	9264	22,370*	18,709*	1507*	724	748
Okolona C5	6234	9797*	7424	2756	2132	2232
Okolona C15	6112	12,739*	9857*	1552*	979	1002
Okolona C30	22,088	39,701*	34,576*	1318*	236	259
Okolona T5	6728	16,458*	11,885*	2126*	1045	1115
Okolona T15	21,321	33,019*	27,350	2545	2391	2450
Okolona T30	12,399	79,101*	66,076*	5133*	1244	1578
Vaiden C5	34,427	35,999	35,846	236*	155	156
Vaiden C15	6152	6824	6685	2.78	2.14	2.15
Vaiden C30	5490	7323	6613	4.93*	2.65	2.78
Vaiden T5	994	1274	1114	373	321	326
Vaiden T15	14153	25491*	20833*	1331*	494	525
Vaiden T30	40072	45456	43129	46.0*	9.29	10.1

* Denotes SSE values that exceed the SSE_{95} value and therefore the fit is considered significantly different at the $p = 0.05$ level.

References

Adeli, A., C.H. Bolster, D.E. Rowe, M.R. McLaughlin, and G.E. Brink. 2008. Effects of long-term swine effluent application on selected soil properties. Soil Sci. 173:223–235.

Allen, S.J., G. Mckay, and J.F. Porter. 2004. Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems. J. Colloid Interface Sci. 280:322–333.

Altin, O., H.O. Ozbelge, and T. Dogu. 1998. Use of general purpose adsorption isotherms for heavy metal-clay mineral interactions. J. Colloid Interface Sci. 198:130–140.

Barrow, N.J. 1978. The description of phosphate adsorption curves. J. Soil Sci. 29:447–462.

Bolster, C.H., and G.M. Hornberger. 2007. On the use of linearized Langmuir equations. Soil Sci. Soc. Am. J. 71:1796–1806.

Bolster, C.H., and K.R. Sistani. 2008. Sorption of phosphorus from swine, dairy, and poultry manures. Commun. Soil Sci. Plant Anal. (in press).

Bothwell, M.K., and L.P. Walker. 1995. Evaluation of parameter estimation methods for estimating cellulase binding constants. Bioresour. Technol. 53:21–29.

Colquhoun, D. 1969. A comparison of estimators for a two-parameter hyperbola. J. R. Stat. Soc. [Ser A] 18:130–140.

Colquhoun, D. 1971. Lectures on biostatistics. Clarendon Press, Oxford, UK.

de Brauwere, A., F. De Ridder, M. Elskens, J. Schoukens, R. Pintelon, and W. Baeyens. 2005. Refined parameter and uncertainty estimation when both variables are subject to error. Case study: Estimation of Si consumption and regeneration rates in a marine environment. J. Mar. Syst. 55:205–221.

Dowd, J.E., and D.S. Riggs. 1965. A comparison of estimates of Michaelis-Menten kinetic constants from various linear transformations. J. Biol. Chem. 240:863–869.

Draper, N.R., and H. Smith. 1998. Applied regression analysis. John Wiley & Sons, New York.

Ebert, T.A., and M.P. Russell. 1994. Allometry and model II non-linear regression. J. Theor. Biol. 168:367–372.

Harrison, F., and S.K. Katti. 1990. Hazards of linearization of Langmuir's model. Chemometr. Intell. Lab. Syst. 9:249–255.

Harter, R.D. 1984. Curve-fit errors in Langmuir adsorption maxima. Soil Sci. Soc. Am. J. 48:749–752.

Kinniburgh, D.G. 1986. General purpose adsorption isotherms. Environ. Sci. Technol. 20:895–904.

Kleinman, P.J.A., and A.N. Sharpley. 2002. Estimating soil phosphorus sorption saturation data from Mehlich-3 data. Commun. Soil Sci. Plant Anal. 33:1825–1839.

Ko, H.C., W.J. Jusko, and W.F. Ebling. 1997. Nonlinear perpendicular least-squares regression in pharmacodynamics. Biopharm. Drug Dispos. 18:711–716.

Kumar, K.V., and S. Sivanesan. 2005. Prediction of optimum sorption isotherm: Comparison of linear and non-linear method. J. Hazard. Mater. B126:198–201.

Langmuir, I. 1916. The constitution and fundamental properties of solids and liquids. Part I. Solids. J. Am. Chem. Soc. 38:2221–2295.

Langmuir, I. 1918. The adsorption of gases on plane surfaces of glass, mica, and platinum. J. Am. Chem. Soc. 40:1361–1403.

Murphy, J., and H.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta 27:31–36.

Persoff, P., and J.F. Thomas. 1988. Estimating Michaelis-Menten or Langmuir isotherm constants by weighted nonlinear least squares. Soil Sci. Soc. Am. J. 52:886–889.

Ratkowsky, D.A. 1990. Handbook of nonlinear regression models. Marcel Dekker, Inc., New York.

Schulthess, C.P. 2007. LMMpro user's manual, version 1.xx. Alfisol, LLC, Coventry, CT.

Schulthess, C.P., and D.K. Dey. 1996. Estimation of Langmuir constants using linear and nonlinear least squares regression analyses. Soil Sci. Soc. Am. J. 60:433–442.

Seber, G.A.F., and C.J. Wild. 2003. Nonlinear regression. John Wiley & Sons, Hoboken, NJ.

Tsai, S.-C., and K.-W. Juang. 2000. Comparison of linear and nonlinear forms of isotherm models for strontium sorption on a sodium bentonite. J. Radioanal. Nucl. Chem. 243:741–746.

Valsami, G., A. Iliadis, and P. Macheras. 2000. Non-linear regression analysis with errors in both variables: Estimation of co-operative binding parameters. Biopharm. Drug Dispos. 21:7–14.

Wang, J.J., and D.L. Harrell. 2005. Effect of ammonium, and sodium cations and phosphate, nitrate, and chloride anions on zinc sorption and lability in selected acid and calcareous soils. Soil Sci. Soc. Am. J. 69:1036–1046.

Wijnja, H., and C.P. Schulthess. 2000. Interaction of carbonate and organic anions with sulfate and selenate adsorption on an aluminum oxide. Soil Sci. Soc. Am. J. 64:898–908.