Adsorption of dissolved organic carbon to mineral soils: A comparison of four isotherm approaches

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A B S T R A C T

The partitioning of dissolved organic carbon (DOC) within mineral soils is primarily controlled by adsorption to soil particle surfaces. We compare the theoretical limitations and modeling accuracy of four isotherm approaches to describe DOC partitioning to soil surfaces. We use 52 mineral soil samples to create linear initial mass (IM), non-linear, and Langmuir isotherms, all relating the initial solution concentration (Xi) to the amount of DOC adsorbed or released from soil surfaces. The Langmuir isotherm is also used with final concentration (Xf). The IM isotherm failed to meet theoretical assumptions and provided poor fits to experimental data. The non-linear and Langmuir Xf approaches had good fits to experimental data, and the Langmuir Xi approach had the most robust estimates of desorption capacity. Both Langmuir Xi and Xf isotherms hold the advantage of estimating the maximum adsorption capacity, yet the Xi isotherm is a better reflection of adsorption processes.

1. Introduction

The cycling of dissolved organic carbon (DOC) within soils is influenced by a combination of chemical, physical and biological processes. While processes controlling DOC cycling in organic soil horizons are primarily microbial, control on DOC retention within mineral horizons is primarily by adsorption to soil surfaces (Kalbitz et al., 2000). Adsorption is rapid, occurring within seconds to minutes, and thus occurs more rapidly than microbial decomposition (Qualls and Haines, 1992). Predicting DOC partitioning between mineral soils and the solution phase requires a reliable means of estimating the DOC adsorption capacity and desorption potential. Batch incubations are a common means of establishing sorption isotherms, whereby the soil is allowed to come to equilibrium with the solute in solution, across a range of initial concentrations (Xi). Isotherms are generally created with a constant pH and ionic strength across Xi solutions, to reduce confounding influences. The sorption isotherm can then be used to establish relationships between sorption characteristics and key soil properties (Moore et al., 1992; Kaiser et al., 1996).

Traditionally, the Langmuir isotherm has been used to relate the amount of a species adsorbed to a solid (RE), to the final solution concentration (Xi). When describing the solid-solution partitioning of naturals soils, the presence of pre-existing native species of organic carbon should be considered. Thus, the linear initial mass (IM) isotherm was developed by Nodvin et al. (1986), which uses the initial solution concentration (Xi), rather than the final equilibrium concentration (Xf), plotted against the amount of a species adsorbed or desorbed to soil surfaces (RE). The IM isotherm allows for an estimation of desorbed species when the Xi concentration is 0 mg kg⁻¹.

The IM isotherm has been widely used to describe DOC adsorption and desorption to mineral soils (e.g. Vance and David, 1989; Moore et al., 1992; Kaiser et al., 1996; Ussiri and Johnson, 2004; Kawahigashi et al., 2006). A non-linear approach has also been used by Rennert and Mansfeldt (2003) to describe DOC sorption to mineral soils. The non-linear approach is similar to the IM approach, whereby desorption of native species is considered, and a non-linear relationship between Xi and RE can be easily described. The sorption of DOC to mineral soils has been described by a modified version of the traditional Langmuir isotherm, which also accounts for native species (Lilienfein et al., 2004) and, unlike the IM or non-linear approach, the modified Langmuir allows for an estimation of the maximum adsorption capacity.

Several decisions must be made when choosing the most appropriate isotherm approach to describe DOC adsorption to mineral soils. These include choosing the experimental Xi concentration range, choosing between linear and non-linear approaches, as well as considering the advantages of using either Xi or Xf approaches. Few studies have compared DOC sorption characteristics derived from batch incubation using different isotherm approaches (Rennert and Mansfeldt, 2003; Vandenbruwene et al., 2007). To our knowledge, no
study has compared isotherm approaches to describe DOC adsorption using a wide range of mineral soils.

The objective of this study is to compare four isotherm approaches used to establish the partitioning of DOC within mineral soils. These include (i) the linear IM isotherm (Nodvin et al., 1986) with Xf, (ii) a non-linear isotherm using Xf, previously used by Rennernt and Mansfeldt (2003), (iii) the Langmuir isotherm using Xf, and (iv) the Langmuir isotherm using Xf. We apply each of the four isotherm approaches to batch incubation experiments, using 52 mineral soil samples collected from across Canada. We establish the theoretical attributes and limitations of the four approaches, test the best fit to experimental data, and evaluate the suitability of using the initial (Xf) or final (Xf) soil solution concentration.

2. Materials and methods

2.1. Batch incubations

Fifty-two mineral soil samples were collected from 17 soil profiles from Podzols, Brunisols, Gleysols, Luvisols, and one Organic soil (Canadian Soil Survey Committee, 1998). Soils were passed through a 2 mm sieve, air-dried and stored at 4 °C. DOC was extracted from the LFH organic horizons of a Podzol collected from Mt. St. Hilaire, Quebec. The intact organic LFH horizon was soaked in deionized water for 5 days and the suspension was filtered with 0.45 µm glass fiber filters and stored at 4 °C. This initial DOC extract solution had a concentration of ~180 mg C L⁻¹. The tubes were placed upright to settle for ~30 min prior to filtration with a 0.45 µm glass fiber filter. The filtrate was acidified to pH 3 to 4 with dilute HCl, and analyzed for non-purgeable organic carbon, operationally considered DOC here, with a Shimadzu TOC 5050 total carbon analyzer.

2.2. Isotherms

The initial mass (IM) isotherm (Eq. (1)) establishes a linear relationship between the mass of the absorbent (DOC) removed from or released into the solution phase (RE), normalized for soil mass (mg kg⁻¹), and the concentration of the initial solution (Xf), also normalized for soil mass (mg kg⁻¹). The RE was calculated as the difference in DOC concentrations found within the initial and final solution phases. The amount of adsorbent desorbed into solution at a starting concentration of 0 mg kg⁻¹ (y-intercept) is defined as the desorption term (b), expressed in units of mg kg⁻¹. The slope of the regression (m) is the partition coefficient, and is unitless.

\[ \text{RE} = m \cdot X_f^- b. \]  

(1)

The m of the linear IM isotherm was used to determine the distribution coefficient or Kd (Nodvin et al., 1986), whereby the ratio between the volume (V) of solution, and mass of soil (M) used in batch incubations, are incorporated (Eq. (2)).

\[ \text{Kd} = \left( \frac{m}{1-m} \right) \frac{V}{M}. \]  

(2)

Solution concentrations for all isotherms are expressed in mass-based units of mg DOC kg⁻¹ soil, as done with the linear IM isotherm. The non-linear isotherm (Eq. (3)) incorporates two parameters, p1 and p2, which establish the extent of curvature in the line.

\[ \text{RE} = p1 \cdot X_f^{p2} - b. \]  

(3)

The Langmuir isotherm is modified to correct for native adsorbed solute on the soil surface of mineral soils by adding the desorption term, b (Eq. (4)). The Langmuir isotherm is used here to express a

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Table 1

<table>
<thead>
<tr>
<th>Sorption characteristic (a)</th>
<th>Ae/AHe (4/1)</th>
<th>Ah (7)</th>
<th>Bf/Bcc (8/1)</th>
<th>Bfh (4)</th>
<th>Bfl (8)</th>
<th>Bg (9)</th>
<th>Bm (7)</th>
<th>Br (2)</th>
<th>C (2)</th>
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<tr>
<td>b (mg kg⁻¹)</td>
<td>125±17</td>
<td>37±27</td>
<td>13±11</td>
<td>30±45</td>
<td>8±25</td>
<td>23±25</td>
<td>11±13</td>
<td>26±9</td>
<td>3±1</td>
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<tr>
<td>n (mg kg⁻¹)</td>
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<td>238±200</td>
<td>32±33</td>
<td>79±64</td>
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<td>209±292</td>
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<td>m</td>
<td>0.07±0.04</td>
<td>0.16±0.07</td>
<td>0.40±0.10</td>
<td>0.44±0.13</td>
<td>0.34±0.02</td>
<td>0.17±0.05</td>
<td>0.24±0.14</td>
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<td>0.19±0.01</td>
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<td>0.19±0.09</td>
<td>0.70±0.29</td>
<td>0.88±0.49</td>
<td>0.57±0.33</td>
<td>0.21±0.08</td>
<td>0.36±0.29</td>
<td>0.32±0.12</td>
<td>0.23±0.02</td>
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<td>RE1000 (mg kg⁻¹)</td>
<td>59±49</td>
<td>117±64</td>
<td>328±95</td>
<td>412±140</td>
<td>332±137</td>
<td>148±78</td>
<td>241±140</td>
<td>213±80</td>
<td>192±13</td>
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<td>b (mg kg⁻¹)</td>
<td>143±58</td>
<td>88±52</td>
<td>125±47</td>
<td>195±99</td>
<td>106±71</td>
<td>96±60</td>
<td>93±43</td>
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<td>147±31</td>
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<td>206±123</td>
<td>140±66</td>
<td>267±203</td>
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<td>75±38</td>
<td>215±61</td>
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<td>9±13</td>
<td>6±3</td>
<td>8±6</td>
<td>9±7</td>
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<td>0.5±0.3</td>
<td>0.4±0.2</td>
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<td>RE1000 (mg kg⁻¹)</td>
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<td>94±58</td>
<td>334±89</td>
<td>299±168</td>
<td>331±140</td>
<td>148±78</td>
<td>238±143</td>
<td>169±53</td>
<td>160±7</td>
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<tr>
<td>b (mg kg⁻¹)</td>
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<td>64±40</td>
<td>101±40</td>
<td>160±86</td>
<td>63±48</td>
<td>47±31</td>
<td>41±13</td>
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<td>215±122</td>
<td>143±65</td>
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<td>202±157</td>
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<td>1.1±0.1</td>
<td>1.6±2.4</td>
<td>0.8±0.6</td>
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<td>0.1±0.0</td>
<td>4.0±0.8</td>
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<td>Qmax (mg kg⁻¹)</td>
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<td>260±101</td>
<td>962±400</td>
<td>1140±560</td>
<td>1107±489</td>
<td>950±1468</td>
<td>504±310</td>
<td>556±117</td>
<td>241±20</td>
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<tr>
<td>RE1000 (mg kg⁻¹)</td>
<td>34±16</td>
<td>91±56</td>
<td>310±86</td>
<td>290±166</td>
<td>334±145</td>
<td>143±395</td>
<td>223±130</td>
<td>165±45</td>
<td>150±9</td>
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<td>Langmuir (Xf) isotherm</td>
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<tr>
<td>b (mg kg⁻¹)</td>
<td>92±4</td>
<td>77±48</td>
<td>332±87</td>
<td>543±37</td>
<td>231±197</td>
<td>142±115</td>
<td>127±80</td>
<td>182±55</td>
<td>168±84</td>
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<td>n (mg kg⁻¹)</td>
<td>220±50</td>
<td>340±310</td>
<td>120±50</td>
<td>140±250</td>
<td>110±160</td>
<td>180±130</td>
<td>80±40</td>
<td>200±30</td>
<td>40±30</td>
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<td>k (10⁻¹)</td>
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<td>5.6±7.7</td>
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<td>Qmax (mg kg⁻¹)</td>
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<td>335±246</td>
<td>1833±1733</td>
<td>1968±1984</td>
<td>921±520</td>
<td>500±644</td>
<td>501±253</td>
<td>530±11</td>
<td>567±263</td>
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relationship between the amount adsorbed (RE), in mg kg$^{-1}$, and the initial DOC starting concentration ($X_i$), mg kg$^{-1}$, the binding affinity ($k$), and the maximum adsorption capacity ($Q_{\text{max}}$), in mg kg$^{-1}$:

$$RE = \frac{(k \cdot Q_{\text{max}} \cdot X_i)}{(1 + k \cdot X_i)} - b.$$  \hspace{1cm} (4)

We also include the traditional Langmuir isotherm (Eq. (5)) replacing $X_i$ from Eq. (4), with the final equilibrium concentration, $X_f$:

$$RE = \frac{(k \cdot Q_{\text{max}} \cdot X_f)}{(1 + k \cdot X_f)} - b.$$  \hspace{1cm} (5)

The null point (np) was calculated for all isotherm approaches as the $X_i$ or $X_f$ where no net change in DOC concentration occurs, and where RE is equal to 0 mg kg$^{-1}$.

2.3. Model fitting and evaluation

All non-linear seven-point adsorption isotherms relating RE with $X_i$ or $X_f$ were fit using the G-Newton iterative method with step halving, which includes a least-squares function to estimate the best fit (JMP IN 5.1, SAS Institute). The linear isotherm was fit as a simple linear regression. The error associated with the desorption parameter ($b$), is called $b$ error, and was compared across four isotherm approaches. The error associated with the $Q_{\text{max}}$ term, called $Q_{\text{max}}$ error, was compared between Langmuir isotherm approaches ($X_i$ and $X_f$). Model performance was evaluated by three methods. The root mean squared error (RMSE) is the root of an estimate of the variance of the residual error, and should be minimized when estimating how well a model fits the data (Eq. (6)). The $n$ is the number of samples, $P_i$ are predicted values, and $O_i$ are observed values.

$$\text{RMSE} = \left(\frac{1}{n} \sum_{i=1}^{n} (P_i - O_i)^2\right)^{\frac{1}{2}}.$$  \hspace{1cm} (6)

The coefficient of residual mass (CRM) is an analysis of the difference between the observed and predicted values (Eq. (7)) (Loague and Green, 1991)

$$\text{CRM} = \left(\frac{n}{\sum_{i=1}^{n} O_i - \sum_{i=1}^{n} P_i}\right) \left(\frac{\sum_{i=1}^{n} O_i}{\sum_{i=1}^{n} O_i}\right).$$  \hspace{1cm} (7)

The modeling efficiency (EF) has a maximum value of 1, describing a perfect fit to experimental data (Eq. (8)), where $\bar{O}$ is the mean of observed values.

$$\text{EF} = \left(\frac{1}{n} \sum_{i=1}^{n} (O_i - \bar{O})^2 - \sum_{i=1}^{n} (P_i - O_i)^2\right) \left(\frac{\sum_{i=1}^{n} O_i^2}{\sum_{i=1}^{n} O_i}\right).$$  \hspace{1cm} (8)

The EF can have negative values, whereby the predicted values are worse than simply using the observed mean (Loague and Green, 1991).

3. Results

Adsorption characteristics using four isotherm approaches were obtained for the 52 soil samples, grouped into 9 mineral soil horizon categories (Table 1).

Fig. 1. (a) The desorption ($b$) term estimate derived from the linear IM isotherm plotted by soil horizons, (b) a comparison of desorption estimates derived from the non-linear and Langmuir isotherm approaches using the initial solution concentration ($X_i$), and (c) the error associated with the desorption $b$ term ($b$ error) for non-linear and Langmuir ($X_i$) isotherm approaches (line in box is the median, with the box representing the 25% and 75%, limits, and whiskers representing 10% and 90% limits).
3.1. Desorption and null point estimates

Negative desorption term \( (b) \) estimates were derived for 11 out of 52 soil samples when the linear IM isotherm was used (Fig. 1a), which implies that adsorption occurred when the initial solution concentration was 0 mg C L\(^{-1}\). In contrast, the non-linear and Langmuir \( (X_i) \) isotherms provided positive desorption estimates, with the exception of one negative \( b \) term derived from the Langmuir \( (X_i) \) approach (Fig. 1b). The error associated with the linear IM \( b \) term resulted from poor modelled fit to experimental data points. A Brunisol Bfj soil horizon collected from Vancouver Island, provides an example of a soil with strong adsorption affinity based on the IM isotherm \( (m=0.48) \), strong linear regression \( (R^2=0.97) \), and yet estimates adsorption rather than desorption at the \( y \)-intercept \( (b=12.4 \text{ mg kg}^{-1}; \text{Fig. 2a}) \). Soils with low levels of pre-existing soil carbon were more susceptible to producing negative desorption terms, while soil horizons such as the Ah and Bfh indicated high desorption levels despite poor model fits (Table 1).

While the non-linear isotherm produced theoretically feasible desorption estimates comparable to the Langmuir \( (X_i) \) estimates, there were six outliers, which contributed to a larger \( b \) error (Fig. 1b and c). Larger \( b \) values were estimated by the non-linear approach, while the corresponding \( b \) values derived by the Langmuir \( X_i \) provided a better fit. For the Bfj soil horizon mentioned earlier, the \( b \) term estimated by the non-linear approach is 207.8 mg kg\(^{-1}\), compared to 82.8 mg kg\(^{-1}\) from the Langmuir \( (X_i) \) approach (Fig. 2b and c). Consequently, the most reliable estimate of desorption was from the Langmuir \( (X_i) \). The \( b \) term derived from the Langmuir \( (X_i) \) isotherm is not a meaningful estimate of desorption potential, as discussed further in Section 4.1.

The null point \( (np) \) is the starting concentration \( (X_i) \), or final concentration \( (X_f) \), of DOC where there is no change in the amount adsorbed or desorbed (RE). As with the \( b \) term, the same 11 soil samples produced theoretically impossible negative np values when the linear IM approach was used. These negative np estimates did not occur with the non-linear isotherm (Fig. 3a). The np predicted from non-linear and Langmuir \( X_i \) isotherm approaches were almost identical (Fig. 3b), and likewise for the Langmuir \( X_i \) and \( X_f \) (not shown).

![Fig. 2. Comparison of four isotherm approaches used to describe the amount of DOC adsorbed (RE) for the Bfj horizon of a Brunisol, collected from Vancouver Island, British Columbia including the (a) linear IM, (b) non-linear, (c) Langmuir \( X_i \), and (d) Langmuir \( X_f \) isotherm approaches.](image)

![Fig. 3. The null point (np) derived from (a) the linear IM isotherm compared to the non-linear isotherm, and (b) the non-linear isotherm compared to the Langmuir isotherm using the initial starting concentration (\( X_i \)).](image)
3.2. Binding affinity

The relationship between the linear IM isotherm slope \((m)\) and partition coefficient \((K_d)\) is non-linear (see Eq. (2)). The relative increase in \(m\) decreases with increasing \(K_d\), especially at high values of \(K_d\). Of the two parameters controlling the extent of curvature in the non-linear isotherm \((p_1, p_2)\), only \(p_2\) had a significant relationship to the linear \(m\) term at the \(p < 0.05\) level \((m = 0.32\cdot p_2 + 0.09, R^2 = 0.17)\). The binding affinity \((k)\) from the Langmuir \(X_i\) isotherm had a significant relationship with the linear \(m\), also at the \(p < 0.05\) level \((m = 32.5\cdot k - 0.31, R^2 = 0.16)\). The \(k\) derived from the Langmuir \(X_i\) and \(X_f\) isotherms were significantly correlated \((\text{Langmuir } X_i k = 0.13 - \text{Langmuir } X_f k + 0.0, R^2 = 0.43; p < 0.0001)\). Langmuir \(X_i\) isotherms were consistently more linear in shape than the corresponding \(X_f\) isotherms (example, Fig. 2c and d).

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Equation</th>
<th>(R^2)</th>
<th>(p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear IM, (m/\text{RE1000})</td>
<td>(m = 0.00086 - \text{RE1000} + 0.06)</td>
<td>0.95</td>
<td>&lt;0.0001</td>
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<td>Non-linear, (p_1/\text{RE1000})</td>
<td>No relationship with \text{RE1000}</td>
<td>0.09</td>
<td>&gt;0.05</td>
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<tr>
<td>Non-linear, (p_2/\text{RE1000})</td>
<td>No relationship with \text{RE1000}</td>
<td>0.09</td>
<td>&gt;0.05</td>
</tr>
<tr>
<td>Langmuir ((X)<em>i, k/Q</em>{max})</td>
<td>(\log k = -0.82 - \log Q_{max} + 0.55)</td>
<td>0.61</td>
<td>&lt;0.0001</td>
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<tr>
<td>Langmuir ((X)<em>i, k/Q</em>{max})</td>
<td>(\log k = -0.64 - \log Q_{max} + 1.68)</td>
<td>0.33</td>
<td>&lt;0.0001</td>
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Fig. 4. Comparison of (a) the maximum adsorption capacity \((\log Q_{max})\) estimated from the Langmuir isotherm using the initial solution concentration \((X_i)\), and the final equilibrium solution concentration \((X_f)\), and (b) the error associated with the \(Q_{max}\) estimate \((Q_{max} \text{ error})\) for the Langmuir \(X_i\) and \(X_f\) isotherms.

3.3. Adsorption

A measure of adsorption, called the \(\text{RE1000}\), was created to compare isotherm approaches. The \(\text{RE1000}\) provides an estimate of the relative amount of DOC adsorbed at an \(X_i\) of 1000 mg kg\(^{-1}\). \(\text{RE1000}\) values derived from the linear and non-linear isotherms were strongly correlated \((R^2=0.92, p < 0.0001)\), with an even tighter relationship between the non-linear and Langmuir \((X_f)\) isotherms \((R^2=0.99, p < 0.0001)\).

Significant relationships also exist between the \(\text{RE1000}\) and the \(\log Q_{max}\) values, derived from both the Langmuir \(X_i\) and \(X_f\) isotherms \((R^2=0.57\) and 0.48 respectively, both \(p < 0.0001)\). The \(Q_{max}\) derived from both Langmuir approaches, \(X_i\) and \(X_f\), were not directly comparable, yet produced a significant relationship (Fig. 4a). Furthermore, the error associated with predicting the \(Q_{max}\) value \((Q_{max} \text{ error})\),

![Graph](image-url)

Fig. 5. Modeling errors associated with four different isotherm approaches, (a) root mean squared error (RMSE), (b) the coefficient of determination of residual mass (CD) and (c), the modeling efficiency (ME). The line within boxes represents the median, while boxes represent the 25% and 75% limits, and whiskers represent 10% and 90% distribution limits.
was not significantly different between the \( X_i \) and \( X_i \) approach (paired Student’s t-test, \( p=0.05 \), Fig. 4b).

A comparison of the relationship between adsorption (RE1000, \( Q_{\text{max}} \)) and binding (\( m, p_1, p_2, k \)) affinity was made for all four isotherm approaches (Table 2). The strongest relationship was observed between the IM isotherm \( m \) and RE1000, while the non-linear isotherm did not have significant relationships between either \( p_1 \) or \( p_2 \) and the RE1000 (Table 2). A significant relationship existed between the \( k \) and \( Q_{\text{max}} \) of the Langmuir \( X_i \) isotherm, while a weaker, but still significant, relationship occurred between the \( k \) and \( Q_{\text{max}} \) of the Langmuir \( X_i \) isotherm (Table 2).

3.4. Model errors

The non-linear and Langmuir (\( X_i \)) isotherms resulted in the lowest RMSE (all pairs, Tukey–Kramer t-test at 0.05) with means of 11.7 and 11.6 respectively, whereas the linear IM and Langmuir (\( X_i \)) RMSE values were 26.1 and 20.7, respectively (Fig. 5a). The CD, was poorest for the linear IM isotherm, while the non-linear, Langmuir isotherms \( X_i \) and \( X_i \) had a CD closest to 1 (Fig. 5b). The average EF, which can have a maximum value of 1 for a perfect fit, was greatest for the non-linear isotherm (mean=0.99 ± 0.005), and the Langmuir \( X_i \) isotherm (mean=0.98 ± 0.005) (Fig. 5c). The EF of the Langmuir \( X_i \) was greater (mean=0.97 ± 0.004), than the linear IM isotherm (mean=0.94 ± 0.005).

4. Discussion

4.1. Desorption and null point

Limitations to the linear IM isotherm were immediately apparent from theoretically impossible negative desorption (\( b \)) and null point (\( n_p \)) estimates derived for 11 out of 52 soil samples (Figs. 1a and 3a), which was due to poor fit to data at a low \( X_i \) (Fig. 2a). Sorption characteristics derived from the linear IM isotherm, including the \( b \) term and \( n_p \), have been widely used in the past (e.g. Vance and David, 1989; Kaiser et al., 1996; Ussiri and Johnson, 2004), and could potentially be implemented here if the starting concentration range was reduced. The linear IM isotherm was originally developed to describe the initial component of the classical Langmuir sorption isotherm, which is almost linear within the low \( X_i \) concentration range (Nodvin et al., 1986). The \( X_i \) range used by Nodvin et al. (1986) was 0 to 480 mg DOC kg\(^{-1}\), which is substantially lower than 0 to 1200 mg DOC kg\(^{-1}\) used here. If a lower \( X_i \) range is used, the curvature in data points is reduced, and the linear IM isotherm provides a better fit to experimental data, along with more accurate estimates of \( b \) and \( n_p \).

The linear IM isotherm is most frequently used to describe DOC adsorption to mineral soils because it incorporates a desorption term, which accounts for the release of native soil organic carbon. As shown here, and elsewhere, isotherms such as the non-linear, Langmuir, Freundlich and asymptotic negative exponential are easily modified to incorporate a desorption term (Rennert and Mansfeld, 2003; Lilienfein et al., 2004; Vandenbruwane et al., 2007). The \( b \) term (or \( y \)-intercept) simply adjusts the isotherm along the \( y \)-axis to account for desorbed species of the adsorbent at a low \( X_i \).

While the non-linear approach has the advantage of being flexible and capable of fitting to the natural bend observed in soil-DOC isotherms, an overestimation of \( b \) was observed for six mineral soils, which resulted from a sharp bend of the curve within the low \( X_i \) range of the isotherm. This \( b \) error could be reduced by ensuring a \( X_i \) data point as close to 0 mg kg\(^{-1}\) as possible. The combination of two parameters, \( p_1 \) and \( p_2 \), contributes to the amount of curvature observed within the non-linear isotherm. The exponent \( p_2 \) term can reach a maximum value of 1, whereby the non-linear isotherm would be converted into a linear isotherm. Since the maximum predicted value of \( p_2 \) was 0.93, the non-linear isotherm always provided a better fit to experimental data than the linear IM isotherm.

The most accurate and theoretically sound isotherm approach for estimation of the desorption term (\( b \)) was the Langmuir \( X_i \) approach. In contrast, the \( b \) term associated with the Langmuir \( X_i \) isotherm term is meaningless. Most mineral soils contain some level of soil organic carbon, thus even when the initial solution DOC concentration is 0 mg kg\(^{-1}\), some organic carbon is desorbed into solution, resulting in an \( X_i \) greater than zero. So from a practical perspective, the \( y \)-intercept (\( b \)), or an \( X_i \) of 0 mg kg\(^{-1}\) cannot be achieved experimentally, or in nature. Thus the \( b \) term of the Langmuir \( X_i \) isotherm is simply a requirement of the equation to provide a good fit to data points. The lack of a meaningful desorption term may be considered a limitation of using the Langmuir \( X_i \) isotherm. The Langmuir \( X_i \) and \( X_i \) approaches were considered equally suitable for calculating the \( n_p \).

4.2. Binding affinity

The binding affinity of the linear IM isotherm (\( m \)), was not directly comparable to \( p_1, p_2 \) and \( k \) derived from the non-linear and Langmuir isotherms, due to the different means of obtaining these estimates. In particular, the non-linear isotherm uses two parameters (\( p_1, p_2 \)) to define the shape of the curve, making it difficult to compare with single parameters, \( m \) and \( k \). Observed differences in the log \( k \) values derived from the Langmuir \( X_i \) and \( X_i \) isotherms (Fig. 4b) resulted from the variable function of the \( x \)-axis, which inherently controls the shape of an isotherm. Langmuir \( X_i \) isotherms were more linear than the Langmuir \( X_i \) (example, Fig. 2c and d). Nodvin et al. (1986) made a similar observation, which was the motivation for using the \( X_i \) rather than \( X_i \) concentration for the linear IM isotherm.

4.3. Adsorption

The RE1000 was developed as a simple means of comparing the amount adsorbed (RE) at a \( X_i \) of 1000 mg kg\(^{-1}\). The RE at a single \( X_i \) concentration allows for a simple and direct comparison of estimates derived from each of the four isotherm approaches, especially since the linear and non-linear isotherms do not have a comparable measure of sorption capacity such as the \( Q_{\text{max}} \). An \( X_i \) value of 1000 mg kg\(^{-1}\) was selected as a high concentration, which still lies within the experimental \( X_i \) range. Similar RE1000 values obtained from the non-linear and Langmuir \( X_i \) approaches suggest that either approach is equally reliable. In contrast, the linear approach produced RE1000 values that deviated from the experimental values.

An advantage to the Langmuir approach is the estimate of \( Q_{\text{max}} \), which is a valuable means of establishing the relative maximum capacity for mineral soils to adsorb DOC. Poorly adsorbing mineral soils, such as Ah/Ahe/Ae horizons, often achieved the sorption maximum (\( Q_{\text{max}} \)) within the experimental \( X_i \) range. In contrast, highly adsorbing soils, such as the Bf horizons of Podzol and volcanic soils, had projected \( Q_{\text{max}} \) values in a concentration range up to five times greater than the experimental range. Consequently, \( Q_{\text{max}} \) estimates associated with strongly adsorbing horizons held a greater amount of uncertainty than poorly adsorbing soils. This uncertainty in \( Q_{\text{max}} \) estimates is especially apparent if the \( X_i \) concentration range is adjusted, or the number of data points along the isotherm is modified. In addition, small experimental errors within the low \( X_i \) concentration range can exacerbate the uncertainty associated with \( Q_{\text{max}} \). While the \( X_i \) concentration range used here exceeds natural conditions, the confidence in \( Q_{\text{max}} \) estimates improves with a larger experimental \( X_i \) range. For example, Lilienfein et al. (2004) used the Langmuir (\( X_i \)) isotherm with an initial solution DOC concentration range of 0 to 300 mg kg\(^{-1}\), plus an additional solution of 2000 mg kg\(^{-1}\).

Natural soil solutions entering mineral horizons from the Oa layer typically contain DOC ranging between 20 and 90 mg L\(^{-1}\), while B horizons typically have 2 to 35 mg L\(^{-1}\) (Michalzik et al., 2001). The maximum initial DOC concentration used here was 120 mg L\(^{-1}\), with a soil (3 g) to solution (30 mL) ratios yielding a maximum \( X_i \) of 1200 mg
kg$^{-1}$. While this concentration is likely beyond the range found in natural soils, the typical range of soil to solution ratios found under ambient conditions is highly variable with hydrology. For example, an unsaturated soil can have a very low soil to solution ratio ($<1$). Saturated conditions with rapid movement of water may result in ratios far exceeding 1. Since the movement of water through soils is dynamic, the range of potential soil to solution ratios, along with DOC concentration (mg L$^{-1}$) is also large, and highly variable. Thus, a wide $X_i$ range reflects the variable concentration range found in natural soils.

By converting initial and final DOC concentrations to mass-based units (mg kg$^{-1}$, or mmol kg$^{-1}$), isotherms using differing soil to solution ratios are more easily compared. The effect of variable soil to solution ratios has been tested, and was considered negligible with respect to the linear IM binding affinity ($m$); however, levels of desorption increased with soil to solution ratios (Kaiser et al., 2001). Consequently, some effort should be made to use consistent soil to solution ratios in batch experiments.

All four isotherms used here make a false inherent assumption of homogeneous binding sites, and a homogeneous adsorbent (DOC). An inherent theoretical flaw in the linear IM isotherm is the assumption that adsorption (e.g., RE1000) is directly related to the binding affinity ($m$) (Eq. (1), and Table 2). The non-linear isotherm is flawed since there is no single estimate of sorption affinity ($p_1$ and $p_2$). The relationship between $k$ and $Q_{max}$ was strong for the Langmuir, and weaker for the $X_i$. While the affinity of DOC adsorption to mineral soils is a mean of numerous of soil–solution interactions, including ligand exchange, cation bridging, and weaker van der Waals interactions (Sposito, 2004), the sorption capacity is based on the maximum number of available binding sites. Thus, there is no theoretical requirement for sorption capacity to be a direct consequence of binding affinity, or the opposite. Consequently, the lack of dependence between DOC sorption affinity and capacity observed for the Langmuir $X_i$ is theoretically justified.

Traditionally, isotherms such as the Langmuir have been plotted with the $X_i$ against RE; however, there is some advantage to the IM isotherm plotted with the $X_i$. For instance, when modeling DOC transport through soils, the flux or concentration of DOC leaving the soil and soil horizon may be the only available input parameter ($X_i$) for predicting the soil–solution partitioning of DOC within the mineral soil. Neff and Asner (2001) created a model describing DOC transport in soils using IM isotherm sorption parameters.

### 4.4. Model errors

The linear IM isotherm provided the weakest fit to experimental data based on the RMSE, CD and EF (Fig. 5), despite often producing impressive regression coefficients ($R^2 > 0.90$ for 76% of soil samples). In addition, a maximum $p_2$ term of 0.93 for the non-linear isotherm (Eq. (3)) implies that none of the isotherms were truly linear (where $p_2 = 1$). Consequently, all isotherms had a better fit to experimental data when the non-linear or Langmuir isotherms were used compared to the linear approach. Soil horizons with poor fits to experimental data included the Ae horizons, which generally did not adsorb DOC within the concentration range, and produced isotherms of irregular shape. Soils with weak sorption affinity, such as the Bg horizons of Gleysols, were clearly non-linear, even within a low $X_i$ range (0 to 500 mg kg$^{-1}$). Several strongly adsorbing soils with large DOC sorption capacity, such as B horizons of Podzols, appeared to have a fairly linear relationship between RE and $X_i$ with a concentration range of 0 to 800 mg kg$^{-1}$, before the increase in RE with respect to $X_i$ started to level off, and highlight the non-linear shape. These strongly adsorbing soils may have been better described by the linear IM isotherm within a lower concentration range. Vandenbruwane et al. (2007) also compared the IM isotherm with the Langmuir isotherm and concluded that the IM isotherm cannot be used in a concentration range where the sorption maximum is likely to be reached. The advantage to incorporating a larger $X_i$ range to 1200 mg kg$^{-1}$, as done here, is to reveal the non-linear component of the isotherm, and provide deeper insight into differing DOC sorption capacity between minerals soils.

The Langmuir $X_i$ isotherm is falsely represented by modeling error estimates of RMSE, CD and EF compared to other $X_i$ isotherms approaches (Fig. 5). Since the $X_i$ is a concentration taken after equilibration, it incorporates an additional level of experimental manipulation, and potential for error, compared to $X_i$ approaches. Thus, estimates of RMSE, CD and EF for the Langmuir $X_i$ are not directly comparable to isotherms using $X_i$. A visual example of experimentally derived error is evident in Fig. 2(d), where isotherm points plotted with $X_i$ are misaligned, compared to isotherms using $X_i$ (Fig. 2a, b and c). Using the Langmuir isotherm with $X_i$ holds great advantage over $X_i$, in so far as the x-axis represents the product of adsorption and desorption processes at near equilibrium. In contrast, $X_i$ is simply the concentration of solutions created at specified intervals, prior to adsorption. In another comparative study where all isotherms were based on the $X_i$, Vandenbruwane et al. (2007) concluded that the Langmuir isotherm was the most appropriate approach for DOM adsorption to mineral soils, compared to the linear IM, Freundlich and an exponential isotherm.

### 5. Conclusions

The frequently used linear IM isotherm approach was found to have limited use for the determination of sorption characteristics of DOC to mineral soils. Three alternative non-linear isotherm approaches were easily modified to account for native organic species by incorporating a desorption $b$ term. It should be noted that the initial DOC concentration range ($X_i$) used within this study (0 to 1200 mg kg$^{-1}$) was outside the linear portion of sorption isotherms, which was the intended design of the IM isotherm. Thus, partitioning of DOC within a lower $X_i$ range may be effectively described by the binding affinity ($m$), or the partitioning coefficient (Kd), from the linear IM isotherm. While the linear IM isotherm is easy to use, the error associated with fitting to experimental data was always reduced when the non-linear and Langmuir $X_i$ approaches were used. The non-linear and Langmuir $X_i$ approaches produced closely comparable null point (np) and RE1000 estimates, however the Langmuir $X_i$ isotherm produced more robust estimates of $b$. Estimates of binding affinity were not comparable between isotherm approaches. Since an additional level of error is incorporated in the determination of $X_i$, the modelling error associated with the Langmuir $X_i$ approach could not be fairly compared with $X_i$ approaches. While the Langmuir $X_i$ approach was best suited for the estimation of desorption capacity, the traditional Langmuir $X_i$ approach provides a more meaningful description of DOC adsorption to mineral soils.

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