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

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ABSTRACT

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 (X_i) to the amount of DOC adsorbed or released from soil surfaces. The Langmuir isotherm is also used with final concentration (X_f). The IM isotherm failed to meet theoretical assumptions and provided poor fits to experimental data. The non-linear and Langmuir X_i approaches had good fits to experimental data, and the Langmuir X_i approach had the most robust estimates of desorption capacity. Both Langmuir X_i and X_f isotherms hold the advantage of estimating the maximum adsorption capacity, yet the X_f 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 (X_i). Isotherms are generally created with a constant pH and ionic strength across X_i 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 (X_f). 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 (X_i), rather than the final equilibrium concentration (X_f), 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 X_i 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 X_i 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 X_i concentration range, choosing between linear and non-linear approaches, as well as considering the advantages of using either X_i or X_f approaches. Few studies have compared DOC sorption characteristics derived from batch incubation using different isotherm approaches (Rennert and Mansfeldt, 2003; Vandenbruwane et al., 2007). To our knowledge, no

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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 X_i, (ii) a non-linear isotherm using X_i, previously used by Rennert and Mansfeldt (2003), (iii) the Langmuir isotherm using X_i, and (iv) the Langmuir isotherm using X_f. 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 (X_i) or final (X_f) 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}, a pH of 4.8 and conductivity of 100 µS cm^{-1}. From this concentrated leachate solution, we created 7 solutions ranging in DOC concentration from 0 to ~120 mg L^{-1} by dilution with a 0 mg L^{-1} solution of similar pH and ionic strength (10 mg L^{-1} NaCl, 20 mg L^{-1} $CaCl_2$ $2H_2O$, and 24 mg L^{-1} K_2SO_4) for a total final ionic strength of 0.001 mmol L^{-1}.

The batch incubations were performed by adding 0.03 L of the initial DOC solutions to 3 g of soil in a 0.05 L centrifuge vial. Vials were hand shaken to ensure that soil and solution was in a slurry, and laid flat on a horizontal shaker for 24 h at 4 °C, at a speed of 60 rpm. 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 (X_i), 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.

$$\mathrm{RE} = m \cdot X_i - b. \quad (1)$$

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)).

$$\mathrm{Kd} = \left(\frac{m}{1-m}\right) \cdot \frac{V}{M}. \quad (2)$$

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.

$$\mathrm{RE} = p1 \cdot X_i^{p2} - b. \quad (3)$$

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

Table 1
Mean and standard deviation of sorption characteristics derived from the linear initial mass (IM) isotherm, the non-linear isotherm, Langmuir isotherm plotted with initial concentration (X_i), and the Langmuir isotherm plotted with final concentration (X_f), for 52 samples grouped into 9 soil horizons

Sorption characteristic (n)	Ae/Ahe (4/1)	Ah (7)	Bf/Bcc (8/1)	Bfh (4)	Bfj (8)	Bg (9)	Bm (7)	Bt (2)	C (2)
Linear initial mass isotherm									
b (mg kg^{-1})	125±17	37±27	13±11	30±45	8±25	23±25	−1±13	26±9	3±1
np (mg kg^{-1})	2483±1505	283±200	32±33	79±64	45±120	209±292	−1±85	122±75	−14±6
m	0.07±0.04	0.16±0.07	0.40±0.10	0.44±0.13	0.34±0.12	0.17±0.05	0.24±0.14	0.24±0.07	0.19±0.01
Kd (mg kg^{-1} 10^{-2})	0.07±0.05	0.19±0.09	0.70±0.29	0.88±0.49	0.57±0.33	0.21±0.08	0.36±0.29	0.32±0.12	0.23±0.02
RE1000 (mg kg^{-1})	−59±49	117±64	328±95	412±140	332±137	148±78	241±140	213±80	192±13
R^2	0.48±0.48	0.95±0.03	0.94±0.08	0.97±0.02	0.95±0.02	0.89±0.10	0.89±0.09	0.97±0.02	0.88±0.03
Non-linear isotherm									
b (mg kg^{-1})	143±58	88±52	125±47	195±99	106±71	96±60	93±43	100±23	147±31
np (mg kg^{-1})	3673±1876	206±125	140±66	267±203	126±161	203±177	75±38	215±61	42±9
$p1$	62±86	9±13	6±3	8±6	9±7	21±28	19±19	4±2	61±13
$p2$	0.3±0.3	0.5±0.2	0.6±0.1	0.6±0.1	0.6±0.1	0.5±0.3	0.4±0.2	0.6±0.1	0.2±0.0
RE1000 (mg kg^{-1})	−26±17	94±58	334±89	299±168	331±146	140±88	238±143	169±53	160±7
Langmuir (X_i) isotherm									
b (mg kg^{-1})	70±51	64±40	101±40	160±86	63±48	47±31	41±13	85±15	40±2
np (mg kg^{-1})	204±63	215±122	143±65	270±193	126±168	202±157	81±38	224±64	51±4
k (10^{-3})	5.1±3.1	1.1±0.1	1.6±2.4	0.8±0.6	0.7±0.3	0.2±0.2	0.2±0.1	0.1±0.0	4.0±0.8
Q_{max} (mg kg^{-1})	82±40	260±101	962±400	1140±560	1107±489	950±1468	504±310	556±117	241±20
RE1000 (mg kg^{-1})	−34±16	91±56	310±86	290±166	334±145	143±95	232±130	165±45	150±9
Langmuir (X_f) isotherm									
b (mg kg^{-1})	92±4	77±48	332±87	543±37	231±197	142±115	127±80	182±55	168±84
np (mg kg^{-1})	220±50	340±310	120±50	140±250	110±160	180±130	80±40	200±30	40±30
k (10^{-3})	43.2±29.0	5.6±7.7	3.8±3.1	13.6±9.6	0.7±0.6	0.8±0.8	0.6±0.5	0.3±0.1	2.0±1.2
Q_{max} (mg kg^{-1})	105±51	355±246	1833±1753	1968±1984	921±520	500±644	501±253	530±31	567±263
RE1000 (mg kg^{-1})	20±50	100±52	386±137	2025±2663	388±176	82±76	262±167	197±313	360±313