Systems Modeling of Nonequilibrium Chemical Reactions Using STELLA

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ABSTRACT
Understanding mathematical models of chemical reactions is central to the fields of geology, geochemistry, and contaminant hydrogeology. Unfortunately, many students struggle with understanding the relationships between the mathematics and the physical reality. Even upper-level undergraduate students often misunderstand fundamental concepts such as chemical equilibrium. To address the question of how to provide students with strong conceptual and quantitative reinforcement of systems in general and how to better understand chemical reactions in particular, we developed an exercise using STELLA to model a sorption-reaction system. STELLA enables students to build dynamic systems graphically from a physically based conceptual model independent of the governing differential equations. Using their STELLA models, students can gain insights into the system, observe relationships among model parameters and results, and discover new insights into what chemical equilibrium means and implies. Students can also explore their STELLA models to discover connections to the mathematical representation, thereby gaining a deeper appreciation of the mathematics behind the model and ultimately strengthening their mathematical skills.

Keywords: Education – computer assisted; education – graduate; education – undergraduate; geochemistry; hydrogeology and hydrology; miscellaneous and mathematical geology.

Introduction
Upper-level undergraduate and graduate-level hydrogeology and geochemistry courses, as well as many other geology courses, depend heavily on a student's ability to understand natural systems and the mathematics that describe them. Although they are developed from basic physical and chemical principles, the mathematical statements that describe the fate and transport of contaminants are often complex. As a result, students can easily fail to understand links between real-world processes and the equations. Even if students can analytically solve the simplest forms of these equations, the physical implications of those solutions may still be difficult to grasp, and students' understanding of the processes is therefore not enriched despite their technical mastery of calculus.

Computer programs that solve various governing differential equations have become an increasingly important part of earth-science courses. These programs can be used to solve much more complex equations than can be solved analytically and allow even students without any calculus skills to explore the nature and implications of Earth systems. The advantage of such programs is that they enable students to learn why the mathematics are important by discovery and thereby avoid the contradiction of not being able to solve anything unless they first use the mathematics. Even in introductory geology classes, we have found that this approach seems to encourage interest.

Another aspect of these programs is that they allow students and researchers to take a "what if..." approach to the system in question (Butler, 1988). Students can test hypotheses and make predictions much more easily than with analytical or physical models (De Wet, 1994). Packaged computer models that allow students to explore important questions and test hypotheses are available; however, many of these models require no true understanding of the systems represented and serve merely as "black boxes." Alternatively, students can use their understanding of systems to construct their own computer models using such software as STELLA II® (Structural Thinking Experimental Learning Laboratory with Animation).

STELLA can be used to develop a quantitative model from a conceptual model of a system. Therefore, it is an excellent tool for teaching about simple dynamic systems in introductory earth-science classes (Mayer, 1990; Moore and Derry, 1995; De Wet, 1994). STELLA allows modeling of dynamic systems. Feedback loops that force systems to equilibrium are easily incorporated with graphical connections between reservoirs and rates of flow (Mayer, 1990; Mayer, 1992). Students may in fact derive the greatest benefit by linking their mathematical understanding of a system with the computer approach (Moore and Derry, 1995). Thus, using STELLA to model physical systems can enable students to gain a deeper understanding of the governing differential equations.

Fundamental Concepts
STELLA is essentially a high-level programming language that uses a visual toolbox. The visual toolbox establishes the allowable syntax of the programming language, which coincides with the language of natural systems. The toolbox consists of reservoirs, pipes, rate controllers, information flows, and functions (Figure 1). Reservoirs represent quantities, physical entities that can be measured, such as the amount of water or the height of a mountain. Pipes determine how the "material" in the reservoir moves from or to reservoirs. Rate controllers determine how fast the flow into or out of a reservoir occurs. Information
flows determine how one part of the system interacts with another and, most importantly, how rates are affected by other parts of a system. Functions may describe a physical constant or a statistical function or merely be a conversion from one unit to another (Mayer, 1990).

The STELLA programming language differs from that of programs such as Mathematica that also solve differential equations in that STELLA does not inherently represent the mathematical formulation of a physical system but rather represents the “logic” of the physical system. Thus while Mathematica may be useful in reinforcing the mathematics of a system, STELLA reinforces an understanding of the system itself. For example, students often have a fundamental misunderstanding of what is meant by a “system in equilibrium” and their confusion is not always cleared up by a purely mathematical approach. Equilibrium concepts are particularly well described by STELLA (Mayer, 1992).

Because geochemical models and contaminant-transport equations often invoke the assumption of chemical equilibrium, a clear understanding of this assumption is required. STELLA-based modeling can be used to teach about equilibrium versus kinetic reactions and thus allows one to examine the implications of nonequilibrium systems (Mayer, 1992). This approach is demonstrated here by presenting an exercise meant to explore reversible, linear, kinetic sorption. This exercise is used in a small contaminant-hydrogeology class consisting of both upper-level undergraduate and graduate students. Although the exercise pertains specifically to sorption, the general concepts can be applied to a wide variety of reactions.

Sorption Processes and Mathematical Models

Contaminant hydrogeology is concerned with the transport and fate of solutes or colloids through porous media. Sorption reactions refer to a variety of processes in which solutes or colloids are attracted and attached to the surfaces of the solids comprising the porous media (Fetter, 1999). These reactions play an important role in controlling ground-water chemistry and contaminant transport. Sorption reactions are particularly important for cations attracted to negatively charged clay-mineral surfaces and for dissolved organic contaminants attracted to solid organic surfaces (Fetter, 1999). Sorption reactions can be divided into those that are reversible and those that are irreversible. During irreversible sorption, a solute becomes attached to a solid surface and is irreversibly removed from solution. From the standpoint of monitoring a contaminant’s dissolved concentration, irreversible sorption is indistinguishable from a decay or degradation process. During reversible sorption reactions, on the other hand, solutes move back and forth between the dissolved and the solid phases and are never permanently lost from the dissolved system. Reversible sorption results in apparent retardation of average solute velocity and spreading relative to water and to a nonreactive solute. Sorption reactions can, therefore, be beneficial by decreasing contaminant movement and allowing greater time for degradation processes to occur. However, retardation caused by sorption can also slow down any aquifer-remediation efforts that involve water withdrawal and removal of dissolved-phase contaminants.

Reversible sorption reactions can be further divided into equilibrium and kinetic reactions. Equilibrium reactions are those that occur at rates that are fast relative to ground-water-flow velocities, allowing equilibrium to be reached between the dissolved and sorbed phases. When equilibrium sorption reactions occur, there is a direct relationship between the sorbed and dissolved-phase contaminant concentrations, and one can express the concentration of a sorbed contaminant as a function of its concentration in solution (Langmuir, 1997). The simplest such function is a linear one expressed as:

$$C = K_d C$$

where

$C$ is the sorbed-phase concentration (mass of sorbate/mass of aquifer sediment);

$C$ is the dissolved-phase concentration (mass of solute/volume of water); and

$K_d$ is the empirically determined partitioning coefficient between the dissolved and sorbed phases (volume of water/mass of aquifer sediment) (Fetter, 1999).

Kinetic sorption reactions are slow relative to ground-water flow. Modeling systems with kinetic reactions requires knowledge of the forward (dissolved to sorbed-phase) and reverse (sorbed to dissolved-phase) reactions rates; these rates vary in time as a function of the changing dissolved- and sorbed-phase concentrations. Kinetic models are rare in field applications due to the difficulty in determining the rate expressions (Domenico and Schwartz, 1998).
Improperly assuming equilibrium conditions may lead to erroneous predictions of contaminant fate (Bahr, 1989).

The equations governing the change in dissolved- and sorbed-phase concentrations due to a kinetic, or non-equilibrium, linear sorption process are

\[
\frac{dC}{dt} = \frac{\rho_b}{n} k_f C - k_r C
\]  

(2)

and

\[
\frac{dC}{dt} = \frac{n}{\rho_b} k_r C - k_f C
\]  

(3)

where

\( k_f \) and \( k_r \) are the forward (dissolved to sorbed) and reverse (sorbed to dissolved) reaction-rate constants (time\(^{-1}\));

\( \rho_b \) is the aquifer-sediment bulk density (mass of aquifer sediment/volume of aquifer); and

\( n \) is the aquifer porosity.

It is also possible to rewrite Equations 2 and 3 in terms of changes in mass of the solute \((M_f)\) or sorbate \((M_s)\). Equation 2 is rewritten by multiplying both sides by the volume of water \((nV)\), where \( V \) is the aquifer volume; Equation 3 is rewritten by multiplying both sides by the mass of aquifer sediment \((\rho_b V)\).

\[
\frac{dM_f}{dt} = \rho_b V k_f C - k_r C n V = k_f M_s - k_r M_f
\]  

(4)

and

\[
\frac{dM_s}{dt} = n V k_r C - \rho_b V k_f C = k_f M_f - k_r M_s
\]  

(5)

Note that Equations 4 and 5 differ only by a factor of \(-1\). At equilibrium, the rates of change become zero, resulting in the following relationships:

\[
M_s = \frac{k_f}{k_r} M_f
\]  

(6)

and

\[
C = \frac{k_f}{k_r \rho_b} \frac{n}{M_s} C
\]  

(7)

The factor \( \frac{k_f}{k_r \rho_b} \) is equivalent to the equilibrium, linear sorption constant \( K_d \) from Equation 1.

The STELLA Approach Towards Understanding Sorption Processes: A Student Exercise

The student STELLA exercise is presented in full in Appendix A. In this exercise, students model an aquifer/ground-water-contaminant system. The system is initially out of equilibrium; all of the contaminant is initially in the dissolved phase. Students must build the model using the appropriate constants and relationships and run the model to equilibrium. To help the reader to more fully appreciate the systems approach, we compare the STELLA and mathematical representations for each concept that we want to teach (Table 1). The concepts are discussed below. To better evaluate whether our approach enriches the conceptual foundations of chemical reactions, the reader may follow our discussion while referring to Appendix A and Table 1. The numbers in the first column of Table 1 correspond to the exercise numbers in Appendix A.

Recall that although the sorption process can be taught using the mathematical representation presented in Equations 2 through 5, students can only model sorption using STELLA based on their understanding of the physical system. There is no way to simply “plug and chug” as one can with equations.

The STELLA model is constructed using rectangles representing the reservoirs (the sorbed and dissolved masses) and flows (adsorption and desorption) representing the transfers between these reservoirs. Like most natural systems, the sorption process contains feedback loops in which the transfer rates control the reservoir quantities and the reservoir quantities, in turn, control the transfer rates. STELLA is especially suited to incorporating feedback loops into modeled systems. In this case, the system contains two negative-feedback loops; the greater the dissolved mass, the greater its outflow or sorption rate, and the greater the sorbed mass, the greater its outflow or desorption rate. These negative-feedback loops are central to understanding the system and, in fact, are what drive the system towards equilibrium.

Once the STELLA model is completed, students can use it to explore the system and discover the connections among model parameters, initial conditions and resulting changes in concentrations. By exploring a model that they themselves have built based on a qualitative conceptualization, students can come to a greater understanding of the system and of chemical equilibria. As a final step, students can use their physically based STELLA model to discover its connection to the mathematical representation, thereby gaining a deeper appreciation of the mathematics.

The specific objectives, which directly parallel the steps in the exercise (Appendix A), are for students to:

1. conceptualize the sorption system as one of masses found in two different phases with transfers occurring between those phases at varying, but quantifiable, rates;
2. build a diagram that represents their conceptualization of the system;
3. convert their diagram into a quantitative and executable model;
4. use their model to explore the nature and meaning of chemical equilibrium; and
5. explore the connections between their STELLA model and the differential equations governing the system to develop an appreciation of the elegance of the mathematical approach.

The fourth objective, to discover the meaning of equilibrium, can be broken down into several specific
### Table 1. Outline of STELLA sorption-system modeling exercise.

<table>
<thead>
<tr>
<th>Concept</th>
<th>Action</th>
<th>STELLA model</th>
<th>Mathematical analog</th>
</tr>
</thead>
<tbody>
<tr>
<td>The sorption system consists of masses in two distinct phases.</td>
<td>Add reservoirs to the STELLA model</td>
<td>Dissolved mass Sorbed mass</td>
<td>Let $M_d$ = the dissolved mass. Let $M_s$ = the sorbed mass.</td>
</tr>
<tr>
<td>Mass is transferred back and forth between the two phases at certain rates representing adsorption and desorption. Adsorption adds to the sorbed mass and decreases the dissolved mass. Desorption does the opposite.</td>
<td>Add pipes to the STELLA model allowing mass transfer.</td>
<td></td>
<td>$\frac{dM_d}{dt} = -V\frac{dC}{dt}$</td>
</tr>
<tr>
<td>Adsorption and desorption rates are proportional to the dissolved and sorbed masses, respectively. These proportionalities are the negative feedback loops that drive the system towards equilibrium.</td>
<td>Add the feedback loops to the STELLA model.</td>
<td></td>
<td>Adsorption rates: $M_d$ Desorption rates: $M_s$</td>
</tr>
<tr>
<td>The constants of proportionality are the adsorption (forward) and desorption (reverse) rate constants, usually empirically defined.</td>
<td>Add the rate constants to the STELLA model.</td>
<td></td>
<td>$\frac{dM_d}{dt} = k_r M_s - k_f M_d$ $\frac{dM_s}{dt} = k_f M_d - k_r M_s$</td>
</tr>
<tr>
<td>Dissolved and sorbed masses are typically expressed in terms of concentrations of µg/mL and µg/g, respectively.</td>
<td>Add functions to the STELLA model to convert masses to concentrations.</td>
<td></td>
<td>$\frac{dC}{dt} = \frac{\rho_b}{V} k_r \bar{C} - k_f \bar{C}$ $\frac{d\bar{C}}{dt} = \frac{n}{\rho_b} k_f \bar{C} - k_r \bar{C}$</td>
</tr>
<tr>
<td>To explore the model and gain insights into the system, we need to quantify the parameters and set initial conditions.</td>
<td>Quantify the system with hypothetical values.</td>
<td></td>
<td>$V = 1,000,000$ cm$^3$ $\rho_b = 1.5$ g/cm$^3$ $n = 0.3$ $k_r = 0.01$ day$^{-1}$ $k_f = 0.005$ day$^{-1}$ $M_d + M_s = 9,000,000$ µg</td>
</tr>
<tr>
<td>The STELLA model can now be used to explore the system and discover relationships. STELLA allows graphs and tables to be easily made.</td>
<td>Run the STELLA model with different initial conditions and parameter values</td>
<td></td>
<td>Example of a STELLA graph:</td>
</tr>
<tr>
<td>Run the STELLA model with different initial conditions and parameter values</td>
<td>Example of a STELLA graph:</td>
<td></td>
<td>To get the mathematical model to run now requires translation into a computer program and additional graphing in order to view the results.</td>
</tr>
</tbody>
</table>

sub-objectives, which the students can achieve by carefully observing the effects of changing the model parameter values and initial conditions. These sub-objectives include:

4a) realizing that a system in equilibrium does not mean that the reactions have ceased or that the dissolved and sorbed concentrations or masses are equal;

4b) realizing that a system in equilibrium does mean that the net rate of concentration or mass change is zero and the forward- and reverse-reaction rates are equal;

4c) understanding that for a given amount of total mass, the system will always reach the same equilibrium concentrations, no matter what the starting concentrations;

4d) discovering that changing the magnitudes of the reaction-rate constants, without changing their ratio, affects only the amount of time needed for the system to reach equilibrium; and

4e) discovering that while the absolute magnitudes of the forward and reverse reaction-rate constants do not control the final equilibrium concentrations, equilibrium concentrations are controlled by the ratio of the forward- and reverse-reaction constants.

The critical incorporation of the negative-feedback loops occurs in step 3 of the exercise (Appendix A) where the rates of adsorption and desorption are related to the dissolved mass and the sorbed mass, respectively. Because mathematics are actually underneath the STELLA syntax, it seems clear to us that the systems approach to teaching these concepts is far more effective than relying solely on the mathematical equations.

Expected Results of the STELLA Exercise

The methodical progression from a simple physical conceptualization of the system to a fully operational STELLA model that can be used to simulate dissolved and sorbed concentrations given various scenarios is shown in Table 1 and steps 1 through 5 of the exercise (Appendix A). The rest of the STELLA exercise is designed to address objectives 4 and 5 through model exploration and relating the STELLA model to the mathematical approach.

Initially, all of the contaminant is in the dissolved phase. The modeled contaminant will move from the dissolved to the sorbed phase and, once sorption begins, from the sorbed to the dissolved phase. The system approaches equilibrium as the mass transfer rates become equal. Exercise steps 6 and 7 (Appendix A) ask the students to run the model for a simulated period of 800 days and graph the results. STELLA allows automatic, point-and-click graphing of any model component versus time. The graphs that students should produce are presented in Figures 2 and 3. Figure 2 shows how the dissolved concentration starts at 30 µg/mL and falls to the steady-state concentration of 10 µg/mL. The sorbed concentration starts at 0 and climbs to 4 µg/g. Concentrations are within 1% of their equilibrium concentrations in about 350 days. The changing rates of adsorption and desorption are shown in Figure 3. At first, adsorption occurs at a much greater rate than desorption, but by 350 days, both rates have stabilized at about 30,000 µg/day. Students can observe from these graphs that reaching equilibrium does not result in equal dissolved and sorbed masses or concentrations. Nor does reaching equilibrium result in the cessation of the reactions. Instead, students realize that reaching equilibrium means that the adsorption and desorption rates are equal and that the masses and dissolved concentrations reach a constant value.

Exercise step 8 (Appendix A) asks the students to redistribute the initial mass any way they wish as long as they maintain a total mass in the system of nine grams. They find that no matter how they distribute the mass, the same equilibrium concentrations are reached. They discover that the equilibrium established is independent of the initial conditions. Exercise step 9 is designed to help the students learn what
actors do govern the equilibrium concentrations. Through this step, students learn that the steady-state concentrations depend only on the ratio of $k_1$ to $k_2$. They also discover that changing the values of the rate constants without changing their ratio affects how quickly the system reaches equilibrium. Through this step, students are able to better understand that the common equilibrium assumption really means that forward- and reverse-rate constants are both large relative to other rates of interest (for example, the round-water-flow rate).

Exercise step 11 (Appendix A) is the point where students tie together the STELLA systems approach and the mathematical approach. Students are presented with the differential equations governing the system they have modeled. (By the time students do this exercise, the equations have already been developed and developed in lecture.) Step 11 asks the students to apply the equilibrium condition to the equations and express the sorbed concentration as a function of the dissolved concentration. By so doing, the students derive an expression for the equilibrium, linear partition coefficient $K_d$ and show that the STELLA-derived concentrations conform to their mathematical expression. In this step, the students are relating their physically based model to the mathematical expressions, bringing more meaning to those expressions and allowing them to realize the elegance of the mathematical approach.

A strength of STELLA is that, once a simple system is built, it can be expanded upon in ways that would be very difficult to handle mathematically. For example, ground-water flow and simulated pumping can be added to the system presented here to teach about the importance of kinetic versus equilibrium-sorption reactions in contaminant-transport and remediation predictions. Students can explore various pumping schemes to discover that optimal pumping rates depend on the nature and rate of the sorption reactions.

conclusions

Because sorption reactions play a crucial role in contaminant hydrogeology, students should have a fundamental understanding of sorption processes and, specifically, the nature and meaning of equilibrium. A commonly made assumption regarding sorption reactions is that the system is in equilibrium. When appropriate, this assumption can lead to erroneous eductions of contaminant fate and remediation.

STELLA is an effective pedagogical tool that allows students to explore chemical processes, and it can enhance students’ understanding and appreciation of the critical concepts. It is not meant to be a substitute for a purely mathematical approach but is best used in conjunction with the mathematics. STELLA modeling is based on the student’s fundamental conceptualization of the sorption system. Using STELLA, students diagrammatically build a model based on reservoirs of dissolved- and sorbed-contaminant masses, withers between these reservoirs and feedback loops to control the transfer rates and drive the system toward equilibrium. Once the model is built, it is easily quantified and run so that students can explore the effects of changing initial conditions and parameter values. Such exploration is possible for other programs that solve the governing equations; however, unlike with STELLA, these other programs do not involve models that the students have built out of their understanding of the system without direct reference to the mathematics. The exercise in Appendix A is designed to lead the students from building a model of a sorption process through exploration of that model to gain a greater understanding of what is meant by kinetic versus equilibrium reactions. Finally, relating the STELLA model to the mathematical model helps remove conceptual abstraction from the mathematics (Moore and Derry, 1995), allowing students to gain a greater understanding of, and hopefully become more comfortable with, the mathematical approach.

The sorption reaction presented here is just one example of a beneficial use of STELLA modeling. The same approach can be used for many types of chemical and biological reactions including nonequilibrium Langmuir sorption reactions, various-order decay reactions and Monod kinetics. STELLA adds an active, demanding, and rewarding component to the teaching and learning of all these concepts and processes.

References Cited


Computer Software Information

STELLA II is a computer modeling application available in both Macintosh and IBM formats. It is available from High Performance Systems, Inc., 45 Lyme Road, Suite 33, Hanover, NH 03755. Telephone: (603) 642-9636, fax: (603) 643-9502. e-mail: support@hps-inc.com, url: http://www.hps-inc.com.


**APPENDIX A**

**STEELA Modeling of Reversible Nonequilibrium Sorption**

In this exercise, you will use STEELA to model a reversible nonequilibrium-sorption reaction based on fundamental chemical principles. You will then expand the model to apply the simulations to a hypothetical experimental aquifer.

1) You will first build your model qualitatively using STEELA’s world view. Assume you have a certain total mass of a ground-water contaminant contained within a small experimental aquifer. The total mass can be partitioned into a dissolved mass and a sorbed mass. Start building your model with these two masses as your quantities or reservoirs.

2) There is flow between these reservoirs. The transfer of mass from the dissolved phase to the sorbed phase is termed adsorption. The transfer of mass from the sorbed to the dissolved phase is termed desorption. Expand your model by using STEELA pipes to represent these transfers.

3) Thermodynamics dictates that the greater the dissolved mass, the faster the rate at which reactions involving dissolved mass occur. In this case, that means the adsorption rate is proportional to the amount of dissolved mass. Also, the desorption rate is proportional to the amount of sorbed mass.

The constants of proportionality (that is, the rate constants) are $k_f$ for adsorption (the forward reaction) and $k_r$ for desorption (the reverse reaction). Build these controls and feedback loops into your model. State what kind of feedback loops these are and why.

4) Although the modeling of the sorption process is complete, we want to understand the reaction in terms of concentrations as well as masses. The dissolved concentration is in terms of the mass of contaminant per volume of water. The sorbed concentration is in terms of the mass of contaminant per mass of aquifer material. Add links to your model allowing calculation of concentrations given the following aquifer constants: volume, porosity and bulk density.

5) The qualitative model is now complete. You will use it to investigate several questions and scenarios. First, switch into the quantitative-model mode and enter the following values for the constants:

- Aquifer volume: $1 \text{ m}^3$ ($1,000,000 \text{ cm}^3$)
- Aquifer bulk density: $1.5 \text{ g/cm}^3$
- Aquifer porosity: 0.3
- $k_f$: $0.01 \text{ day}^{-1}$
- $k_r$: $0.005 \text{ day}^{-1}$
- Total contaminant mass: $9 \text{ g (9,000,000 \mu g)}$

Assume that, initially, all the mass in the system is in solution. Using units of cm and \mu g, you insure that the concentrations are both equivalent to ppm.

6) Model the system for 800 days. Make a plot of the dissolved-and sorbed-phase masses and a separate plot of the dissolved- and sorbed-phase concentrations. Set your dissolved- and sorbed-mass ranges identically so that the y-axis on the plot is easier to read. Do the same for the concentrations. Approximately how much time is needed for the system to reach equilibrium? What are the equilibrium masses? What are the equilibrium concentrations?

7) Make a plot of the two reaction rates (again, with each at the same scale). Describe what is occurring throughout the 800 days based on this plot.

8) Now redistribute the mass in the system any way you wish. Just be sure to keep total mass at 9 g. Rerun the model a few times, examine your plots and report your results. How do your results compare to your original run?

9) How do the equilibrium masses relate to the forward- and reverse-rate constants? Test your hypothesis by changing the values of the rate constants. Experiment with different values but keep the ratio of the values the same. Also experiment with different ratios. Report your results. How is the system affected when the values change but the ratios are the same?

10) To summarize, explain the meaning of equilibrium for this system. What does it mean in terms of the masses, concentrations, rates and rate constants?

11) Here are the mathematical equations governing the system you have modeled. The right side of each equation comprises the adsorption and desorption reactions:

$$\frac{dC}{dt} = \frac{\rho_s}{n} k_f \bar{C} - k_r \bar{C},$$

and

$$\frac{d\bar{C}}{dt} = \frac{n}{\rho_b} k_f \bar{C} - k_r \bar{C}.$$  

where

- $C$ is the dissolved concentration;
- $\bar{C}$ is the sorbed concentration;
- $k_f$ and $k_r$ are the forward (dissolved to sorbed) and reverse (sorbed to dissolved) reaction-rate constants (time$^{-1}$);
- $\rho_b$ is the aquifer-sediment bulk density (mass of aquifer sediment/volume of aquifer); and
- $n$ is the aquifer porosity.

At equilibrium, the concentrations stop changing, and therefore their derivatives equal zero. Take either equation and apply the equilibrium condition. Write an expression for $\bar{C}$ in terms of $C$. What is the constant of proportionality relating $\bar{C}$ and $C$? This constant is known as $K_d$, the linear-sorption-isotherm partition coefficient. Show that your concentrations from #6 conform to the relationship you have derived.