A Simple Sand Column Laboratory Exercise to Illustrate Pollutant Hydrology in Groundwater Systems

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ABSTRACT

The transport of pollutants in groundwater systems is an important concept taught in contaminant hydrology. Yet, surprisingly, no relevant soil column experiments have been described in the pedagogical literature (*Journal of Chemical Education, Chemical Education Research and Practice, or Journal of Geoscience Education*). This experiment illustrates the transport of tracers in a sand column using the conservative (non-retained and non-reactive) tracer fluorescein, along with a step input of non-conservative (retained/adsorbed) cadmium ion. The experiment is easy to set up, uses inexpensive commercially-available glassware and sand, and is highly reproducible. Step inputs of conservative tracer elute in one pore volume (the volume needed to completely replace the water held in the saturated column), with cadmium eluting in three pore volumes. This experiment can be completed in two, three-hour laboratory periods.

INTRODUCTION AND PURPOSE

Cleanup of polluted groundwater sites is a primary goal of EPA's Superfund budget. While pollutant transport is extensively covered in groundwater modeling lectures, it is completely absent in published laboratory exercises. This is true of most experiments involving soils or sediments, as noted by Tran et al. (2001), who found that of the 92 environmental articles published in the *Journal of Chemical Education* from 1969 to 2000, only approximately 15 percent pertained to soil matrices. Tran et al. (2001) further notes the persistence of a "perception that … soil chemistry is more complex and challenging than water chemistry". Indeed, the relative lack of simple soil experiments may result from the variety of complex chemical and physical properties that can be present in soil and sediment samples (i.e. mineralogy, surficial coatings, organic matter, pH values, and E_H values). Even if an educator develops and publishes an excellent soil experiment, others who follow the published procedure, inevitably with different soils, will likely obtain widely varying results.

Topics covered by the few relevant environmental experiments from the literature that involve soil matrices include various sorption reactions (Xia et al., 2003; Dolan et al., 1998), soil remediation projects (Roundhill, 2004; Harle et al., 2003), and the interaction of acid rain with soil weathering (Schilling et al., 2004). We describe two new laboratory experiments using soil matrices in our manual on instrumental and environmental chemistry (Dunnivant, 2004). One is an experiment to determine the distribution coefficient of a metal in a soil solution. Distribution coefficients are chemical parameters commonly used in modeling the fate and transport of pollutants in groundwater systems. In the second experiment, we describe the Soxhlet pollutant extraction procedure, in which commercially available sand provides the needed analyte recoveries and reproducibility. The new experiment described in this teaching exercise describes a very useful experiment for illustrating the fate and transport of a non-retained and retained chemical tracer in a simulated groundwater system.

The overall goals of these laboratory exercises are to experimentally illustrate fundamental concepts of contaminant hydrology, specifically step inputs of tracers, pollutant distribution coefficients and retardation factors, and pollutant breakthrough curves.

RATIONALE AND APPROACH

The lead author of this article (Dunnivant) has worked on two major groundwater laboratory and field investigations for the Department of Energy (DOE). When presenting the findings of these investigations at national and international meetings, he was asked why there is not a teaching laboratory exercise for these important fate and transport concepts. The answer is simple-it is very difficult to find a pollutant and a geologic media that utilizes these concepts and allows the experiment to fit into the standard three-hour teaching laboratory time slot. For example, one investigation with the DOE (at the Idaho National Engineering Lab, Porro et al., 2000) required several days of continuous monitoring of the effluent from the soil columns, while the second investigation (at the Oak Ridge National Laboratory, Dunnivant et al., 1992a and 1992b) required continuous monitoring periods of weeks to months. Even the most diligent student would balk at these time commitments.

These extremely long experiments present several difficulties in the research lab, most notably designing and maintaining an experimental setup that will operate for the required time without failure; more than one column experiment has prematurely failed. The implications of such failures are even worse considering that the complete effluent profile of pollutant concentration is needed to analyze the data and obtain estimates of pollutant parameters such as the distribution coefficient and soil-specific retardation factor (discussed below). The authoritative publication on designing research-grade column experiments is by Relyea (1982) and provides specific parameters, including (1) the required width of the column (based on it being 40 times the average grain size of geologic media), (2) the column length to width requirements to avoid preferential flow along the column walls, (3) water flow rate guidelines, (4) use of an upward flow regime through the soil column, and (5) requirements of the tracer input function and column hardware as to not allow column expansion or cracking of the packed media during the experiment.

In designing a teaching exercise, some of these guidelines had to be modified (such as the pumping equipment for the solutions, column hardware requirements, media grain size, and column expansion

or media cracking) in order to minimize the monetary cost and time commitments of the experiment. After considerable experimentation we settled on a final design, described in the online instruction material given at http://people.whitman.edu/~dunnivfm/Online-Materials.doc.zip, that allows the column experiment to be operated over a time scale of hours. Modifications needed to obtain our design include slightly reducing the column width requirements (our columns are not 40 times the average sand grain size), the use of a downward flow (necessary for our design), lack of physical packing of the sand media, and a less-than-perfect step addition of the tracers to the head of the column (our step input results in a much larger water volume of transition between pure water and tracer than research experiments would tolerate). The net result of our modifications is a slight broadening of the tracer concentration profile exiting the column, due to increased hydrodynamic dispersion, but the final experimental design is more than adequate to illustrate the most important concepts of pollutant fate and transport in groundwater systems. One final note should be made with respect to the development of this exercise. As you will notice, we use the toxic cadmium ion for our non-conservative (adsorbed) tracer, which generates hazardous waste that must be dealt with at the end of the experiment. Treatment/disposal options are given in the on-line instructions, but you should consult your college/university safety or hazardous waste officer for further instructions. The use of Cd^{2+} was not by choice but necessity. We attempted the experiment with several other potentially non-conservative metal ions, such as calcium, nickel, zinc, and copper, but these eluted from the column with fluorescein or not at all due to the relatively low solubility product constant (K_{sp}) of the metal hydroxide. Thus, while we tried to design a "green" laboratory, the only metal that consistently worked was cadmium.

THEORY AND RELATIONSHIP TO GROUNDWATER TRANSPORT

Several chemical and physical factors determine the transport of pollutants in real-world groundwater systems. Important physical factors include water velocity and mixing or hydrodynamic dispersion in the system. The most important chemical factor determining the retention of metals in a groundwater system is the affinity of the metal for the soil, quantified by the distribution coefficient, K_d, which is the ratio of the concentrations of pollutant adsorbed onto the soil to pollutant dissolved in the aqueous phase (dissolved phase) or C_{soil}/C_{water}. The adsorption mechanism for metals with soils is usually ion exchange, where naturally abundant metal ions (typically Group I and II, including H^+, Na^+, K^+, Ca^{2+}, and Mg^{2+}), which adsorb onto the negatively-charged sand surface, are exchanged with heavy metals such as Cd^{2+}. This exchange occurs as the front of pollutant passes by a given section of the column. Subsequent flushing with cadmium-free water, containing the Group I and II ions, results in these cations exchanging back for the cadmium. Thus the cadmium, experiencing repeated cycles of adsorption and desorption, proceeds slowly through the column.

The degree of adsorption can be determined in the laboratory by measuring the distribution coefficient, K_d. The net retention (a unitless value), R, is related to distribution coefficient by

$$R = 1 + \frac{\rho_b K_d}{\eta} \qquad (1)$$

where r_b represents the bulk density of the soil or fractured rock (in our sand column, the weight of dry sand added to the column divided by the volume of the sand); ($\pi r^2 h$, units of kg/L), K_d is the distribution coefficient measured in the laboratory (as described in the online instructions) (with units of mg Cd^{2+}/kg of dry sand per mg Cd^{2+}/L of water), and η is the porosity of the material in the column or aquifer (a unitless ratio of the volume of the water in the column divided by the total volume of the sand and water). R appears in the solution to the general transport equation for both the pulse and step inputs. The equation of a pulse input of pollutant to a one-dimensional groundwater system is given by (Dunnivant and Anders, 2005)

$$C(x,t) = \frac{M}{A\sqrt{4\pi \frac{D_x}{R} t}} e^{\frac{(x-\frac{v}{R}t)^2}{4\frac{D_x}{R}t} - kt} \qquad (2)$$

where C = the pollution concentration (g/m^3), x = distance from the source (m), t = time (d), M = the mass of contaminant added to the aquifer (g), A = cross-sectional void volume contaminated by the pollution (m^2), D_x= dispersion coefficient (m^2/d), R = retardation factor (unitless), v = velocity (m/d), and k = first-order reaction rate for degradable pollutants (1/day).

Similar, with a bit more complexity, the equation for a step input of a pollutant to a one-dimensional groundwater system is given by (Dunnivant and Anders, 2005)

$$C(x,t) = \left(\frac{C_0}{2}\right)\left\{e^{\left(\frac{x}{2D_x}\right)\left(1-\left(1+\frac{R4kD_x}{v}\right)^{\frac{1}{2}}\right)}\right\}\left\{erfc\left[\frac{x-\left(\frac{v}{R}\right)(t)\left(1+4k\frac{RD_x}{v}\right)^{\frac{1}{2}}}{2\left(D_x\left(\frac{v}{R}\right)t\right)^{\frac{1}{2}}}\right]\right\}$$

where C_o = initial concentration of the contaminant (g/m^3), x = distance from the source (m), D_x= longitudinal dispersivity (dispersion coefficient, m^2/d), k = first-order reaction rate (1/day), v = velocity (m/day), R = retardation factor (unitless), t = time (days), and erfc is the complementary error function, which is a mathematical correction accounting for migration of the pollutant outside of the model's one-dimensional boundary condition.

Note the relationship between K_d and R in Equation 1 and the relationship of R to down-gradient pollutant concentrations in Equations 2 and 3. High K_d values yield high R values, which delay the transport of pollutants, and result in the spreading out of pollutant breakthrough curve. These equations are typically covered in the lecture portion of a contaminant hydrogeology class, and their inclusion in the laboratory setting strengthens the connection between the lab and lecture.

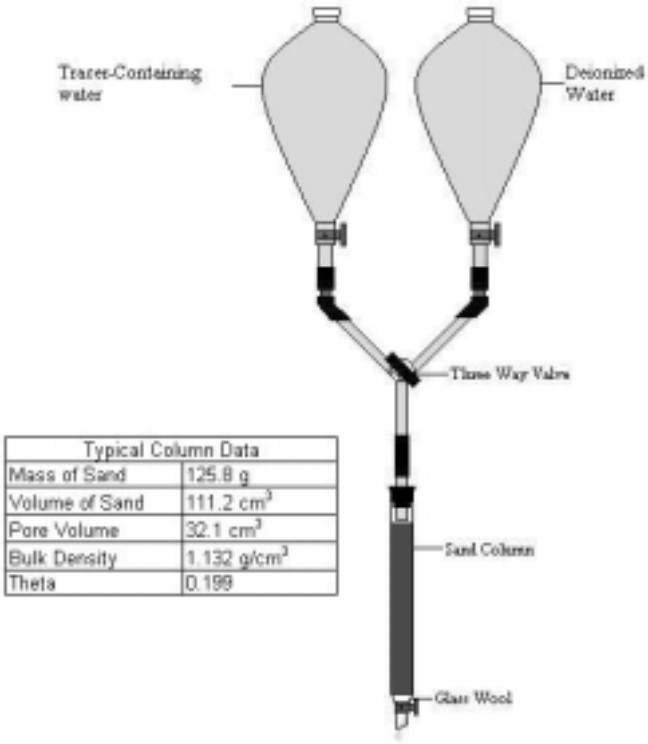

Figure 1. Experimental apparatus for a step input of tracers.

EXPERIMENT OVERVIEW

This experiment is divided into two, three-hour laboratory periods. At the beginning of the first lab period the instructor introduces the students to the purpose of the experiment, illustrates the various components of the experimental apparatus (shown in Figure 1, and described in the online instructions; http://people.whitman.edu/~dunnivfm/OnlineMaterials.doc.zip), notes important points of the procedure, and explains terminology such as pore volume, pulse input, step input, reduced concentration or absorbance, and breakthrough curves. These terms are crucial in understanding pollutant fate and transport in groundwater systems.

Definitions - The pore volume is simply the total volume of water contained between the sand grains in the column. Column-specific pore volumes are measured by the student simply by taking the absolute weight difference of the column apparatus filled with dry sand and the same apparatus filled with water. This value, typically around 30 percent of the total volume of the column, is given in mL for laboratory columns. This term can be expanded for use on the x-axis of a breakthrough curve to essentially give us a time measurement (the more water that has passed through the column at a constant flow rate then the greater the time that has passed.) The use of pore volume measurements gives us a way to compare breakthrough curves from columns of different sizes since each column will be normalized to its own pore volume. The number of pore volumes identified on the x-axis and associated with a given chemical expresses how much water has to be pushed through the column to make each tracer move through the column. One pore volume is necessary to move most conservative tracers through the column, while retained (absorbed) chemicals require addition pore volumes. Again, pore volume measurements on the x-axis are more useful, as opposed to actual mL of water, since each column will have a different volume (mL) of water in the mobile phase, whereas one pore volume always means a unit mobile phase in any given column.

There are typically two simple types of pollutant input scenarios, the step and pulse input functions. A step input is characterized by a change in pollution input from zero to a continuous input concentration (e.g. from 0.0 mg/L to 25 mg Cd^{2+}/L). In this input scenario, the effluent Cd^{2+} concentration begins at zero and increases until it reaches the input concentration (25 mg Cd^{2+}/L in our example). The resulting breakthrough curve will occur later and have a more gradual slope than that for a step input of conservative tracer. Real world examples of a step input would be a leaky underground storage tank or transfer pipe.

In contrast, a pulse input is a one-time, finite input of pollutant (e.g. 0.5 mL of a 25 mg/L Cd^{2+} solution), and elutes as a bell-shaped peak which is shifted later in the experiment relative to the conservative tracer. We originally designed this experiment to include both a step and pulse input of pollutants, but the step input is more easily preformed and the data are easier for the student to interpret. The magnitude of the peak for a realistic pollutant pulse input is extremely small (since the peak is broader due to its longer time in the column and increased dispersion) as compared to the magnitude of the fluorescein tracer peak, and students tend to incorrectly think the Cd^{2+} peak is unimportant. Thus, we have not included the procedure or results for a pulse input experiment.

Plots of the data resulting from a step column experiment consist of the concentration of pollutant exiting the column as a function of number of pore volumes eluted (note in this case the pore volume is actually a measure of time since column volume and porosity are constant, and we are using a constant flow rate). In most cases, we plot reduced concentrations, which express the concentration (or absorbance) of pollutant in a given sample divided by the concentration (or absorbance) of pollutant added to the system. The overall plot is referred to as a breakthrough curve (BTC) since it shows at any given pore volume (or time) the distribution of pollutant in the column, and thus clearly shows "breakthrough" of pollutants from the column. Examples of step BTCs obtained by students are given in Figure 2.

After the technical terms have been explained to the students, each group of students assembles the sand column and flow apparatus, and takes several physical measurements of the column (weight measurements for pore volume calculations, bulk density, and water content of the column). After testing the setup and upon the approval of the instructor, the student conducts a conservative tracer experiment in which a step input is applied to the column. Samples are collected, and the absorbance of fluorescein (the conservative, or non-reactive and non-absorbed, tracer) in each sample is measured on a standard visible spectrophotometer. After the complete breakthrough of the conservative tracer, the column is rinsed with distilled water and kept intact (with water covering the sand) for use the following week. During the second week, the student adds a similar step input of cadmium solution to the

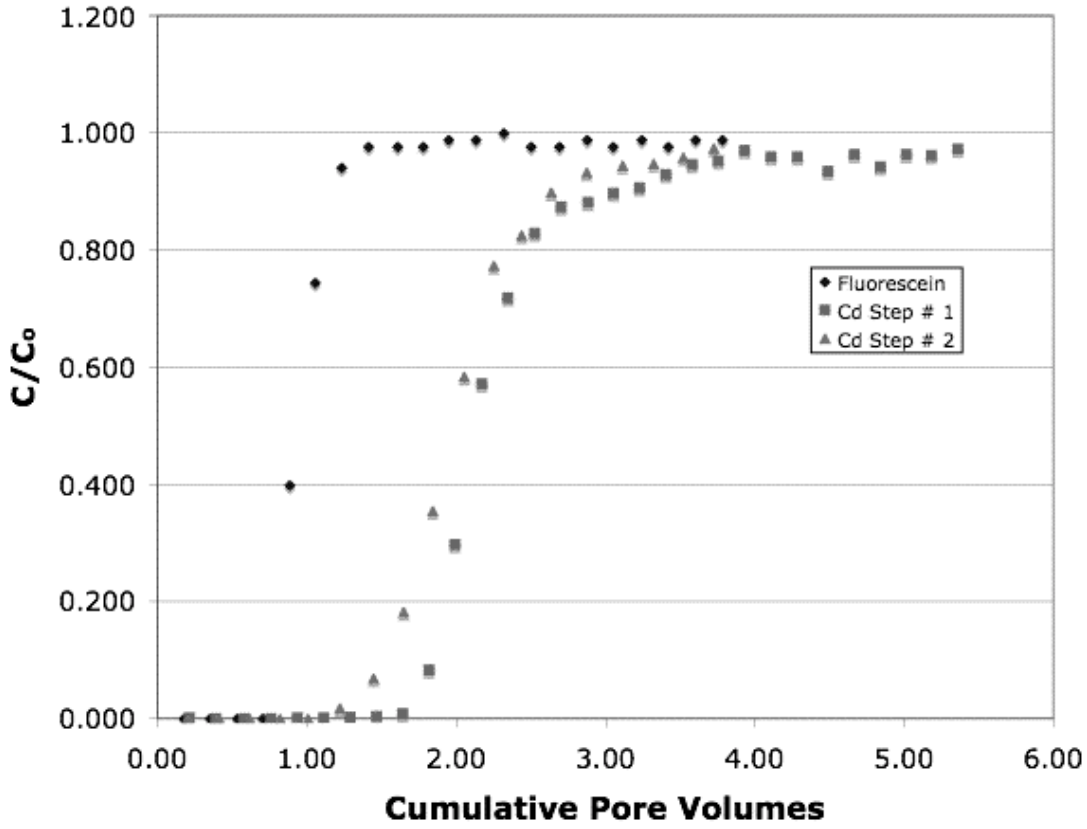

Figure 2. Example breakthrough curves.

column. Samples from the column are collected and analyzed on a flame atomic adsorption spectrophotometer (FAAS) (ICP may also be used) until complete cadmium breakthrough has occurred (where the effluent Cd^{2+} concentration equals the inlet Cd^{2+} concentration).

The chemistry behind the retention or lack of retention of the tracers is fairly simple. The conservative tracer, fluorescein, does not have functional groups that are readily attracted to the surface of the sand, so fluorescein moves unhindered through the sand matrix. On the other hand, the cadmium ion, has a strong positive charge which is attracted to the negative surface charge of the sand (the surface charge of sand is negative in DI). The cadmium ions are repeatedly exchanged with naturally present Group I ions in the sand, such as Na^{+}, and allow the cadmium ions to slowly migrate through the column.

After the experiment, the students construct the conservative (fluorescein) and non-conservative (Cd^{2+}) breakthrough curves (fractional pore volume of each sample versus analyte concentration or reduced concentration) on the same spreadsheet plot. The retention of cadmium, relative to the conservative tracer, is very evident. Sample data sheets are given in the supplement online instructions. These data are discussed in the following section.

EXPERIMENTAL RESULTS

Typical student results for the conservative tracer are plotted here in Figure 2. This figure shows the expected shape of a step breakthrough curve. Note that the conservative tracer elutes from the column first and its transport represents the rate of transport of water through the column. The width or spread of the conservative tracer profile is indicative of the dispersion in the column. Research-grade, well-packed columns will produce very narrow profiles, while more poorly packed columns (such as the ones resulting from our experimental design) will produce broader curves. The Cd^{2+} elution shows considerable delay relative to that of the conservative tracer, and its excess retention time in the column is indicative of the extra time the Cd^{2+} is attached to the sand. In general, if a chemical elutes from a column 2.5 pore volumes after the conservative tracer in a laboratory column experiment, we assume that it will take 2.5 times as long for it to be transported to the monitoring point of interest in a real groundwater system, with comparable mineralogy and chemistry.

Column studies much like the ones described here, but using soil from a specific site rather than pure sand, are used to predict the relative flow or retention of pollutants in real-world groundwater systems. They are also necessary components of laboratory-based remedial investigation-feasibility studies (RI-FS), which are

conducted as part of a Superfund site remediation. Once the site-specific velocity of water has been measured or predicted for the groundwater system, the retention results (R and K_d) from the column study can be extrapolated to estimate the transport of pollutants in the real-world system.

LEARNING OUTCOMES

We feel this is an experiment of mid-level difficulty that can be used in an advanced undergraduate or graduate laboratory. We have used it successfully in an undergraduate environmental chemistry course and a geochemistry course at a small liberal arts college.

The main outcome from conducting this experiment is that the students gain a practical understanding of pollutant hydrology terminology and laboratory techniques through experiential learning. Specifically, students have a first-hand working knowledge of conservative/non-conservative tracers, the important but complicated concept of pore volume, and are exposed to a very common experimental set-up for conducting pollutant fate and transport investigations in groundwater systems.

The most difficult part of the experiment for the student is setting up the apparatus and adjusting the flow and water level in the sand columns, but we feel it is necessary for the student to complete these steps as it enforces the concepts of pore volume and the measurements that go into setting up and constraining such a system. This experience also gives them a small appreciation of the detail required for research-grade experiments. The most difficulty arises during the first lab, when the students are (conveniently) only using the non-retained tracer (conservative fluorescein), and we have found that more than adequate time is available to pack the column at least twice. In fact, the students can probably complete the entire experiment twice during a three-hour lab period. By the second week, the students have gained the needed proficiency to repeat the column setup and complete the retained Cd^{2+} tracer experiment.

The calculations required in this experiment are relatively straightforward and most questions from the students concern the initial calculation of pore volume. Thus, we have included a sample data set in the supplemental online file for illustration and practice. The pore volume seems to be the most difficult concept in the lab, and it should be carefully explained in the pre-lab lecture. Again, pore volumes are normalized quantities representing the amount of water passing through the column, relative to the total amount it can hold. Another was of stating this is: a "pore volume" is the total volume of water residing in the pores of the soil media, while "pore volumes" refers to the total volume of water that has passed through the column divided by the volume of one column pore volume. This term is valuable because different columns have difference absolute volumes of water, and this allows data (BTCs) from different columns to be overlain and compared when both data sets are presented in pore volumes.

Of course we suggest covering the theory of contaminant hydrology in lecture prior to attempting this laboratory exercise. Students always "think" they understand the concepts of pore volume, breakthrough curves, and fate and transport in groundwater systems after lecture, but they gain a much higher level of understanding from these laboratory exercises.

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