EXPERIMENTS ILLUSTRATING PHASE PARTITIONING AND TRANSPORT OF ENVIRONMENTAL CONTAMINANTS

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Historically, chemical engineers have been primarily concerned with maximizing the efficiency of individual processes while designing chemical production facilities. Current regulatory pressures to minimize risks associated with the production of chemicals, however, require chemical engineers to understand the fate of these chemicals in the environment. The fundamental mass transfer processes controlling the migration of contaminants in environmental systems are similar to those in chemical engineering processes. There are distinct differences, though, that have implications in how individual processes are analyzed. For example, contaminant concentration in the environment is generally very low (on the order of parts per million (ppm)), and the number of compounds present in a given environmental system is very large and unknown compared with typically well-controlled chemical engineering processes. The complexity of these systems needs to be simplified in order to describe mass transfer process environmental systems.

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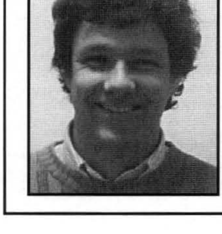

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At Clarkson University, the fate of hazardous organic pollutants in the environment is covered in the class "Hazardous Waste Management Engineering." Senior-level students from the departments of civil and environmental engineering, chemical engineering, and industrial hygiene typically enroll in this class. Fundamental processes governing the environmental fate and transport of organic contaminants are covered during introductory lectures and are used throughout the semester to support more advanced material related to human exposure levels, risk assessment, and design of treatment strategies. Throughout the semester, the relationships between chemical behavior and molecular structure (*i.e.*, size and polarity) are emphasized.

After this class was taught for two years, it became apparent that students had difficulty grasping the concepts of partitioning of solutes between phases. Thus, the experiments described here were developed to help students understand the partitioning and transport of organic compounds in environmental systems. Constraints of class length (50 minutes), size (30-40 students per section), and budget, however, limited the scope of possible experiments. A creative solution of using nontoxic, colored solutes, allowing strikingly visual detection as the solutes partitioned between phases, effectively illustrated the concepts of phase partitioning and enabled all students to be active participants in both the qualitative and quantitative components of this laboratory.

BACKGROUND AND THEORY

A significant fraction of groundwater contamination in the United States is the result of spills and disposal of organic liquids in the ground. The organic phases, referred to as nonaqueous phase liquids (NAPLs), are typically considered to be "immiscible" with water, although their solubilities are high enough to contaminate groundwater at levels higher than drinking-water quality standards.[1] Figure 1 illustrates the partitioning and transport processes affecting a NAPL such as gasoline. Since gasoline is less dense than water, it accumulates at the water table. Subsequent partitioning of contaminants into both the groundwater and soil gases will occur.

The equilibrium dissolution of solute from a NAPL and subsequent sorption of the aqueous-phase solute to sand are considered in this laboratory. Because of the low concentrations involved in these processes, it is assumed that the density and molecular weight of the phases, and activity coefficients of each species in the aqueous phase, remain essentially constant. For many NAPLs, it is reasonable to also assume that the organic phase is an ideal solution and, thus, that activity coefficients in this phase are close to one. With these simplifications, phase equilibria governing the partitioning of solutes between these environmental compartments is often approximated with linear relationships describing the concentrations of a species between phases[2]

NAPL-water systems: $$C = C^* X \tag{1}$$

Soil-water systems: $$q = K_d C \tag{2}$$

where

C concentration (mg/L) of a compound in the aqueous phase
C^* solubility of the pure liquid chemical in water (mg/L)
X mole fraction of this compound in the NAPL
q concentration sorbed on the soil (mg/kg)
K_d soil-water distribution coefficient (L/kg)

Equation (1) is Raoult's Law for liquid-liquid equilibria and has been shown to be fairly accurate for even complex NAPL mixtures comprised of chemicals with low solubilities.[1]

Both C^* and K_d are partition coefficients describing the linear equilibrium relationship between phase concentrations. Their values are highly dependent on the molecular structure of the compound.[3] Nonpolar organics are hydrophobic, exhibiting trends of generally decreasing solubilities and increasing soil-water distribution coefficients with increasing molecular weight. The presence of polar functional groups, especially those with O, N, or S atoms, decreases the aqueous-phase activity coefficient, thereby greatly increasing the aqueous-phase solubility and decreasing the soil-water distribution coefficient of organic compounds.

Following the partitioning of organic compounds from the NAPL to the aqueous phase, the contaminant molecules are transported with flowing groundwater, potentially polluting downgradient sources of drinking water. Convection (also called advection by environmental engineers) and dispersion are the predominant transport mechanisms, although the sorption of solutes to soil effectively retards the transport rate. Assuming equilibrium between solid and the liquid phases, the standard transport equation with a linear sorption term added can be written in one dimension as

$$\frac{\partial C}{\partial t} = D_l \frac{\partial^2 C}{\partial x^2} - \upsilon_x \frac{\partial C}{\partial x} - \frac{\rho_b}{n} K_d \frac{\partial C}{\partial t} \tag{3a}$$

or

$$\frac{\partial C}{\partial t} = \frac{D_l}{R} \frac{\partial^2 C}{\partial x^2} - \frac{\upsilon_x}{R} \frac{\partial C}{\partial x} \tag{3b}$$

where

D_l hydrodynamic dispersion coefficient in the longitudinal direction
υ_x average linear interstitial velocity of the aqueous phase
R retardation coefficient $(R = 1 + \rho_b K_d / n)$
n porosity of the porous medium
ρ_b bulk density of the porous medium

The retardation coefficient can also be described as the ratio of the mean velocity of water (υ_x) to the mean velocity of the solute $(\upsilon_{x_{sol}})$

$$R = \frac{\upsilon_x}{\upsilon_{x_{sol}}} \tag{4}$$

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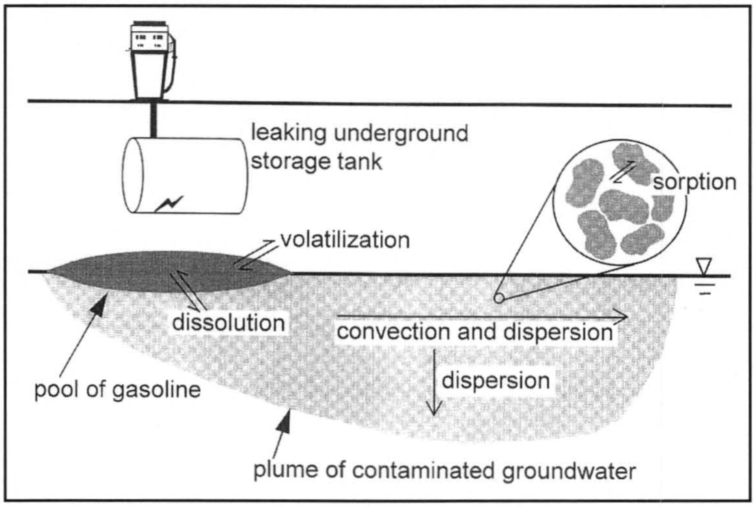

Figure 1. *Processes affecting the fate of a NAPL such as gasoline in the subsurface.*

A solute with a low retardation coefficient (R~1) will be relatively mobile within an aquifer system, potentially resulting in higher human exposure levels than a solute that sorbs strongly.

EXPERIMENTAL DESIGN AND RESULTS

A laboratory experiment was developed to reinforce the concepts of phase partitioning and its relationship to molecular structure and the mobility of a solute in a groundwater system. Three NAPLs with different colors and hydrophobicities were mixed with water, and then the contaminated water infiltrated through sand to observe the partitioning of the colored solutes. This experiment was included in the hazardous waste management class during the fall semester of 1995.

An assessment of the effectiveness of this laboratory indicated that the students perceived an increase in their comprehension of these concepts. Results of their homework assignments, however, showed that they still struggled with quantitative homework problems. Thus, an additional experiment was designed for the 1996 class that involved a more quantitative measure of retardation coefficients as contaminated water samples were pumped through a soil column and the velocity of the contaminant was measured relative to the velocity of water.

Materials • Adding dye to nontoxic organic phases created three NAPLs with different colors and a range of partitioning behaviors. Table 1 describes the composition of the "red," "blue," and "green" NAPLs. The polarity (or hydrophobicity) of these dyes is the property critical to their partitioning behavior and the success of the experiment. The overall polarity of a molecule depends on contributions of polar atoms (O, S, N, Cl) and nonpolar atoms (C, H). Qualitatively, oil-red-o is more hydrophobic than methylene blue because a greater fraction of the oil-red-o molecule is comprised of carbon (see Table 1). Similarly, green food color is more polar than methylene blue since the number of polar atoms in green food color is higher than in methylene blue (Table 1). In order for the observed partitioning of the color to be representative of the overall bulk NAPL partitioning, the polarity of the dye has to mimic the polarity of the NAPL. The polarity of the bulk organic liquids used increased from mineral oil to ethanol. Thus the polarity of the selected colors represent the polarity of the NAPL.

Other materials included tap water as the aqueous phase and clean quartz sand, suitable for a child's sandbox, for the soil.

Laboratory 1
A Qualitative Understanding of the Partitioning of Solutes Between NAPL-Water and Water-Sand Systems

The first laboratory allows a qualitative assessment of the

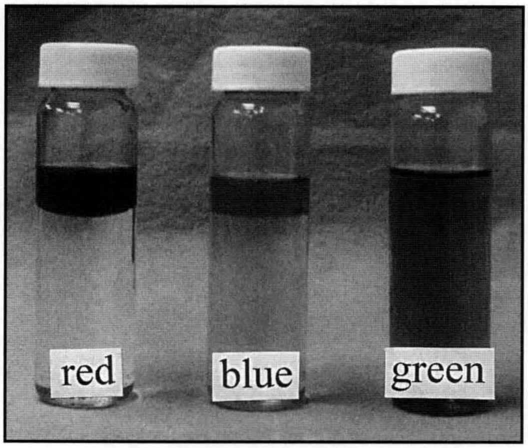

Figure 2. *Photograph illustrating the partitioning of red, blue, and green solutes (left to right) from a NAPL to water.*

TABLE 1
Composition of Colored NAPLs

NAPL	*Bulk Organic Phase*	*Solute*[1]	*Chemical Formula*	*Characteristics*
red	mineral oil	oil-red-o[2]	$C_{26}H_{24}N_4O$	very hydrophobic
blue	5% (by vol.) octanol in mineral oil	methylene blue[3]	$C_{16}H_{18}N_3SCl$	slightly hydrophobic
green	ethanol	green food color[4]	$C_{16}H_{10}O_7Cl_2Na_2S_2$[5] $C_{16}H_8O_8N_2Na_2S_2$[6]	hydrophilic

[1] Only a small amount of dye required for each to provide vivid color

[2] Available through Fisher Scientific (biotechnology reagent)

[3] Dissolved in octanol prior to mixing with mineral oil

[4] Mixture of FD&C Yellow 5 and FD&C Blue 1; available through McCormick & Co. Inc., Maryland

[5] FD&C Yellow 5 (5)

[6] FD&C Blue 1 (5)

partitioning behavior of the red, blue, and green solutes as well as the bulk organic phases. Teams of 3-4 students each were provided with bottles containing each of the three NAPLs, three 40-mL screw-cap vials about 75% full of water, two filtering crucibles about 50% full of dry sand, two 50-mL beakers, and several disposable capillary pipettes.

In the first phase of the experiment, students observed the range of possible partitioning behaviors between the NAPLs and aqueous phase. The steps simply involved adding approximately 1 mL of NAPL to each of the three water vials, gently shaking them to equilibrate, and then observing the distribution of color and the bulk organic fluid between phases. Results range from no observable partitioning of the hydrophobic red solute in mineral oil to the complete dissolution of the very polar green solute in ethanol (see Figure 2). The blue solute illustrates the concept of having a partially soluble solute in an essentially insoluble bulk organic phase. In this case, much of the blue color transferred to the aqueous phase, although most of the volume of NAPL remained as a separate immiscible phase. This case is most representative of environmentally significant NAPLs such as gasoline.

TABLE 2
Questions Posed to Increase Conceptual Understanding

Questions for NAPL-water partitioning

- Classify the solubility (soluble, partially soluble, insoluble) of three colored solutes and the bulk organic phases
- Discuss the implications of these differences on the fate of NAPLs in the subsurface
- What differences in the chemical structures would you expect based on the observed solubilities?

Questions for aqueous phase-soil partitioning

- Rank the solutes in order of increasing potential for sorption; explain your answer
- Discuss the implications of these differences on the mobility of these solutes in the environment
- What differences in the chemical structures would you expect based on the observed sorption behavior?

Summary questions

- Are the observations and conclusions drawn from the solubility experiment consistent with the results of the sorption experiment? Explain.
- Describe the overall fate of each of the three NAPLs following a spill to the environment

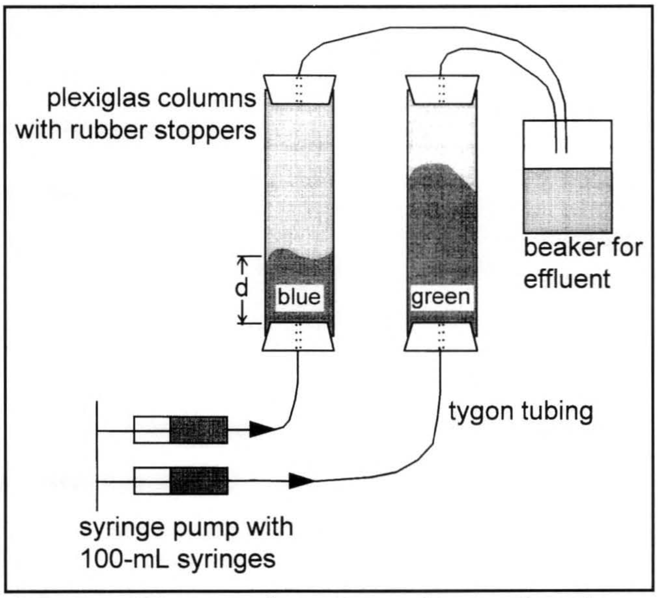

Figure 3. *Schematic of experimental system for column retardation experiment.*

The second phase of the first laboratory provided a greater understanding of the partitioning of solutes between aqueous and soil phases. As described above, the mixing of NAPLs and water generated blue and green contaminated water. Each of these aqueous phases was then poured through sand in the filtering crucibles that were held over 50-mL beakers. The very polar green solute was not retarded, as evidenced by the lack of change in color of either the sand or water. With the less polar blue solute, however, the sand turned blue and the effluent became clear, illustrating that slightly soluble solutes can be strongly sorbed, greatly decreasing contaminant concentrations in the aqueous phase.

In order to help students increase their understanding of partitioning behavior, we posed several questions to promote their ability to connect experimental observations to fundamental concepts (see Table 2). These questions focused primarily on the relationship between chemical structure and mobility of chemicals in the environment.

Laboratory 2
A Quantitative Measure of Solute Retardation

The second laboratory was developed to quantify the extent of solute sorption. The equipment required for this laboratory (see Figure 3) was more extensive and, thus, the laboratory was conducted as a demonstration, with students taking turns making the measurements over time. Colored aqueous phases for this experiment were prepared by the direct addition of dyes into the aqueous phase (0.05 g/L methylene blue for the "blue" aqueous phase and 10 mL/L green food color for the "green" aqueous phase).

Two Plexiglas columns (3.8-cm diameter by 25-cm long) were carefully packed with a uniform sand (30-40 mesh; $d_{50} = 0.5$ mm) to provide a relatively homogeneous sand to help minimize solute dispersion within the column. Several pore volumes of degassed water were then pumped through each column to displace and dissolve all of the air. At t=0, pumping of the blue and green aqueous phases through the columns at rates typical of groundwater flow (Q=0.1 mL/min) was initiated.

Using colored solutes allowed visual assessment of the migration of these solutes. The interface between clean and colored water was marked on each column over time and the average distance traveled by the colored water was recorded. Assuming that convection is the predominant transport mechanism, the position of the sharp front marked by the colored water was used to estimate the interstitial solute velocity. Thus, the retardation coefficient (Eq. 4) was calculated as

$$R = \frac{Q / An}{L / t} \qquad (5)$$

where

Q volumetric flow rate of water
A column cross-sectional area
L distance traveled by the colored water in time t
n porosity, included to convert to an interstitial aqueous phase velocity

Equation (5) can be rearranged to calculate the retardation coefficient by linear regression of the L-versus-t data.

Figure 4 illustrates differences in the travel time of the solutes through the soil columns. As expected from the qualitative experiment described above, the greater distance traveled by the very-polar green solute indicates that it is much more mobile than the less-polar blue solute. The observed variability in the position of the front around the column perimeter at any point in time (Figure 4) is attributed to column-scale heterogeneities in soil permeability that affect local rates of convection. To accommodate for this variability, the experimental analysis was completed using the average of four measured travel distances at each time. These average travel distances with error bars representing ± one standard deviation are included in Figure 5.

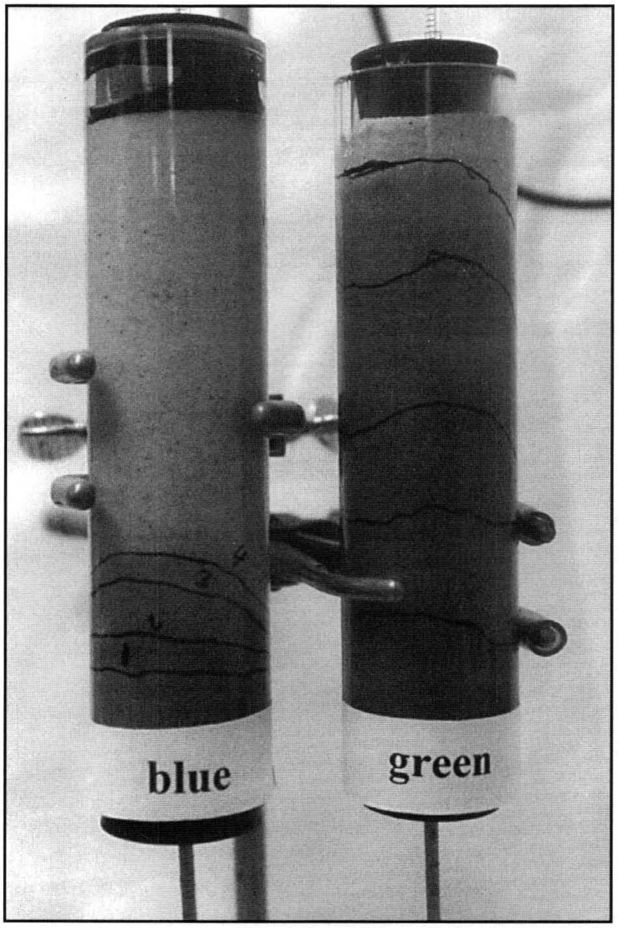

Figure 4. *Photograph of the column retardation experiment after twelve hours. The polar green solute clearly travels at a higher velocity than the blue.*

Linear regression of the data was used to estimate the retardation coefficients for each solute. Regression coefficients greater than 0.99 were obtained in both cases. The low retardation of the green solute (R=1.4±0.1) confirms the fact that this solute would be highly mobile in an aquifer system, while the higher retardation coefficient for the blue solute (R=4.4±0.2) provides quantitative evidence of the greater extent of sorption of this solute. With both visual and quantitative interpretation of this experiment, students grasped the impact of sorption and the connection between this partitioning process and the potential for exposure to contaminants through drinking water downgradient of a pollution source.

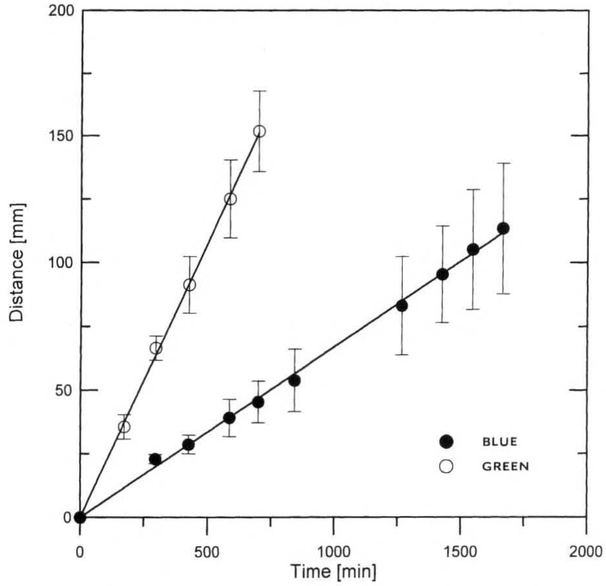

Figure 5. *Calculation of retardation coefficients from measured average distance of solute travel as a function of time. Solid lines represent the linear regressions and error bars illustrate ± one standard deviation of the four individual measurements of distance at each time.*

DISCUSSION AND CONCLUSIONS

Students completing these experiments observed the wide variability in the behavior of organic pollutants in the environment. They concluded that the mobile green solute and the bulk organic liquid that comprised this NAPL were hydrophilic and very mobile in the environment. The solute and bulk organic liquid that comprised the red NAPL, on the other hand, were very hydrophobic and relatively immobile in an aquifer system.

From a pedagogical standpoint, providing students with an active learning experience and very visual observation of these phenomena effectively improved their overall understanding of the fate and transport of organic contaminants in an environmental system. In terms of Bloom's hierarchy of learning,[4] the first laboratory increased the students' *comprehension,* while the second laboratory addressed the *application* of these ideas in engineering calculations. Both comprehension and application are critical steps for the students to achieve prior to advancing to the more challenging tasks of analysis and synthesis. Thus, by completing these laboratories early in the semester, students were better prepared for tackling more complex issues associated with formulating engineering decisions with respect to the potential for environmental contamination.

ACKNOWLEDGMENTS

Support from a National Science Foundation CAREER grant (BES-9501567) was used in developing these laboratories.

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COMET Project

Continued from page 23.

for introducing these topics.

As the instructor, I should have made more clear to the students the connections between the project and the course material. I also should have explained why the project is of value to a beginning engineer. Clearly stated instructional objectives are known to facilitate student learning.[10] The project might have been more closely linked to the main course content if, for example, it had permitted chemical energy sources and involved more energy balance calculations in the COMET design. But this would have been difficult since the project had to be safe and relatively short and simple for sophomore students. The COMET project is therefore a compromise that achieves the primary goal of introducing ideas not found in traditional pencil-and-paper projects, but does so in a non-chemical engineering-specific format.

Logistical Improvements

> *"I think this project would have been better at the beginning of the quarter."*
>
> *"Give the groups an extra week or so to think about the project."*
>
> *"Make the project worth more than 5%."*

A number of students would have preferred different logistical arrangements for the project. Because it involved a lot of work, students wanted the project assigned earlier in the quarter when it would not conflict with midterms, wanted more time to work on the project, and wanted it to be worth a larger fraction of their grade. All of these changes can be easily made and will be implemented next time.

CONCLUSIONS

The COMET project provided a relatively simple assignment that introduced sophomore chemical engineers to a number of important engineering concepts that are often not addressed until later in the curriculum: teamwork, open-ended problems, design, hands-on experimentation, technical writing, and estimation based on limited data. Most students enjoyed the project and recommended its use in future classes.

ACKNOWLEDGMENTS

Thanks to Melissa Bradley, Richard Felder, and David McGill for helpful discussions and to Dayton Funk for photography. This work was supported in part by a CAREER Young Investigator Award from the National Science Foundation (BES-9624832).

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