

The Distribution Coefficient of Atrazine with Illinois Soils W

A Laboratory Exercise in Environmental Chemistry

Eric Dolan, Yan Zhang, and Doug Klarup*

Department of Chemistry, Eastern Illinois University, Charleston, IL 61920

Background and Rationale

The fate of organic chemical contaminants in ground-water is an important issue in environmental chemistry and of concern to most students. One of the factors that control the movement of an organic chemical to and through ground-water is the extent of interaction between the chemical and the specific soil matrix. This interaction can be quantified through measurement of the soil–water distribution coefficient, K_d :

$$S = K_d C \quad (1)$$

where S is the amount of compound sorbed to the soil and C is the concentration in the water. K_d , in turn, usually is dependent upon the fraction of organic material in the soil matrix because organic sorption can be viewed as a “partitioning” between the water and the organic material in the soil (f). An equation that shows this dependence is

$$K_d = K_{oc} \times f_{oc} \quad (2)$$

where K_{oc} is the organic carbon–water distribution coefficient and f_{oc} the fraction of organic carbon in the soil. This equation suggests that a plot of K_d vs f_{oc} should be linear, with a slope equal to K_{oc} and an intercept equal to zero. A nonzero intercept would suggest significant contribution to K_d from nonorganic phases of soil.

In this laboratory experiment students (i) measure the distribution coefficient of a corn herbicide, atrazine, for soil samples they have collected, (ii) measure the fraction of organic carbon, f_{oc} , for each soil, (iii) employ appropriate error estimation techniques to their data and (iv) collectively explore the correlation between f_{oc} and K_d using linear regression algorithms that take into account uncertainty in both the x and y data. The level of the experiment is suitable for an environmental chemistry course or instrumental analysis course.

The experiment is designed to help the students learn several things. It gives them good insight into how sorption controls the migration of organic contaminants through soils and groundwater. Each student sees how his or her “organic” soil is able to sorb more atrazine than the “nonorganic” soil. By combining all of their data, the students see where “their” soil falls in relation to others and can judge for themselves the relationship between the amount of organic carbon in soil and the soil’s ability to sorb atrazine.

The data treatment also shows students that, as long as appropriate data treatment methods are applied and reasonable

uncertainty estimations are included, it is still possible to extract relevant information even when the data accumulated are quite variable. They learn that the use of a regression algorithm that accommodates significant uncertainty in x and y data can be very important, particularly when the data are scattered over a wide range.

Procedural Summary

The required equipment should be found in most undergraduate chemistry laboratories. Almost any detectable organic chemical with low water solubility could be used in this exercise. We chose atrazine because it has been used extensively in Illinois and therefore is of interest to Illinois students.

The students collected >100 g of two different soils for testing, one an organic soil (containing significant amounts of organic matter) and the other a sandy, or nonorganic, soil. The soil samples were sealed in plastic bags and used within three days of collection. Approximately 10 g of each soil was used to determine f_{oc} via a simple loss-on-ignition technique. The K_d values for atrazine were determined by combining 10 g of the organic soil or 50 g of the nonorganic soil with a standard 40-ppm atrazine solution for approximately 24 hours. Intermittent mixing was done by hand. After 24 hours the mixture was centrifuged for 4 minutes (Sorval Superspeed SS-1) and the supernatant was filtered first through #42 Whatman filter paper and then through a 0.2- μ m syringe membrane filter (Gelman Supor-200). Runs done without soil showed no loss of atrazine through this procedure.

The filtered atrazine solutions were analyzed with a Beckman HPLC apparatus consisting of a model 112 HPLC pump equipped with a 20- μ L sample loop, a model 153 fixed-wavelength (254 nm) UV detector, and a Shimadzu Chromatopac C-RIB Data Processor. The column used was a 4.6 \times 250-mm reverse-phase Whatman PARTISPHERE C-18 column, equipped with a removable guard cartridge assembly. The mobile phase used was degassed 1:1 water–acetonitrile (HPLC grade, Fisher Scientific). Each student performed four HPLC analyses: one from a run made without soil, one from the organic soil mixture, one from the nonorganic soil mixture, and then another from the run made without soil. The two no-soil measurements were used to help determine the atrazine concentrations in the other solutions and the uncertainty associated with the HPLC measurements.

Uncertainty Estimation

With the variability of these environmental samples, it was desirable to provide appropriate error estimates for measured and calculated values. The uncertainty in f_{oc} was quite high (based on analyses on the same soil done by different students) and we decided upon a (conservative) relative standard deviation of 13% for each soil sample.

^WSupplementary materials for this article are available on JCE Online at <http://jchemed.chem.wisc.edu/Journal/issues/1998/Dec/abs1609.html>.

*Corresponding author. Email: cfdgk@eiu.edu.

The determination of the uncertainty in K_d , since it is a calculated value, was more complicated. First, uncertainties in C were determined by calculating the pooled standard deviation for all the duplicate no-soil analyses made and using this value to determine an overall percent relative uncertainty in all C values of 5.36% ($\epsilon_C = 0.0536 \times C$). Then the resulting ϵ_C values were used to determine appropriate ϵ_{K_d} values, where ϵ_{K_d} and ϵ_C are the absolute uncertainties in K_d and C , respectively, via this numerically determined equation:

$$\epsilon_{K_d} = 0.1135 \times K_d \times \epsilon_C \quad (3)$$

The regression analyses for our combined data needed to accommodate the fact that large uncertainties existed in both the x (f_{oc}) and y (K_d) data. Conventional linear regression algorithms assume little uncertainty in the x data, so we chose to follow the method suggested by Irvin and Quickenden (2) using a Microsoft EXCEL spreadsheet program to determine appropriate linear regression values for the slope, intercept, and associated uncertainties.

Results

When the class plotted K_d vs f_{oc} , the linear correlation was evident (see Fig. 1). The regression equation used to fit the data was $K_d = 57.2 (\pm 4.9) \times f_{oc} - 0.06 (\pm 0.04)$, $R^2 = .85$. The K_{oc} value determined (57.2 ± 4.9) was at the low end of those reported in the literature, but not unreasonable. The

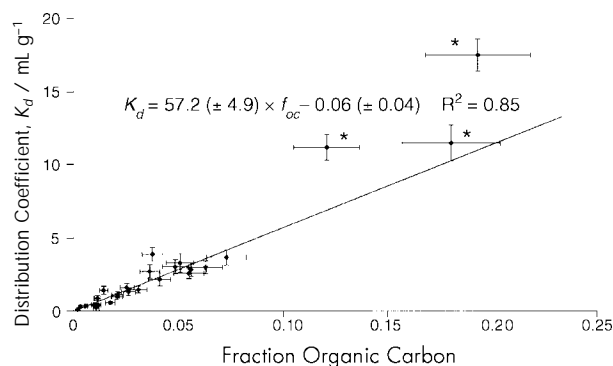


Figure 1. The relationship between f_{oc} and K_d with all usable data collected by the students. The * indicates sample partially or wholly made of commercial potting soil. The regression equation obtained using a conventional regression algorithm (Microsoft Excel) is $K_d = 80.5 (\pm 4.5) \times f_{oc} - 0.62 (\pm 0.30)$, $R^2 = .93$.

proximity of the intercept to zero suggested that nonorganic sorption of atrazine played little role in our soil samples.

Literature Cited

1. Chiou, C. T.; Porter, P. E.; Schmedding, D. W. *Environ. Sci. Technol.* **1983**, *17*, 227–231.
2. Irvin, J. A.; Quickenden, T. I. *J. Chem. Educ.* **1983**, *60*, 711–712.