

An Environmental Chemistry Laboratory for the Determination of a Distribution Coefficient

Frank M. Dunnivant* and Jason Kettel

Department of Chemistry, Whitman College, Walla Walla, WA 99362; *dunnivfm@whitman.edu

Background

Environmental chemistry is a new field of study in many chemistry departments and only three published summaries of environmental laboratory experiments are available (1–3). While these laboratory manuals contain excellent experiments for the training of students in environmental monitoring, relatively few standardized procedures have been published for broader issues such as the measuring of fate and transport parameters. Perhaps the most important fate and transport parameter is the distribution coefficient, K_d .

The distribution (or partition) coefficient is a measure of absorption phenomena between the aqueous and solid phases. It is fundamental to understanding processes responsible for the distribution of pollutants in aquatic systems (groundwater, lakes, rivers, and estuaries). Mathematically it can be represented as the ratio of the equilibrium pollutant concentration in the solid (sediment or soil) phase to the pollutant concentration in the dissolved (aqueous) phase

$$K_d = \frac{C_{\text{solid}}}{C_{\text{aqueous}}} \quad (1)$$

where C_{solid} is conventionally expressed in units of mg/kg and C_{aqueous} is in units of mg/L.

The purpose of the distribution coefficient is to determine which phase the pollutant has a preference for and to quantify the mass of pollutant in each phase. It is used in virtually every fate and transport model for the estimation of pollutant concentrations in aqueous systems. The aqueous phase concentration is important because the most toxic form of a pollutant is usually in the free aqueous phase. Inorganic and organic colloids and suspended solids in natural waters will increase the apparent water-phase concentration, but pollutants adsorbed to these particles are usually not available for biological uptake. These particles eventually settle out in quiescent regions of the natural water body or in estuaries; in this way pollutants are removed from the aquatic system.

Distribution coefficients are relatively easy to obtain by allowing a pollutant–soil–water mixture of known composition to equilibrate, separating the mixture into solid and aqueous phases, and determining the pollutant concentration in each phase. This technique can be simplified further by measuring (or knowing) the total mass of pollutant added to each sample, measuring the pollutant in the dissolved phase after equilibration, and estimating the mass of pollutant on the solid phase by difference (total pollutant added minus aqueous phase mass). The distribution coefficient is then calculated using eq 1 for both experimental techniques.

The major problem in designing K_d experiments for the laboratory is the variability (and unpredictability) of results that are obtained. This is due to the variety of solid phases available, the nature of the pollutant used (ionic metals or hydrophobic organic compounds), and the experimental

aqueous conditions (pH values, ionic strengths, and concentrations of solids and pollutants) (4, 5). The aqueous conditions are especially important when the K_d for ionic pollutants is being measured. Unless the instructor has previously conducted the experiment under the exact experimental conditions to be used by the students, aqueous solutions may not contain sufficient pollutant in the aqueous phase to be measured or all of the pollutant may be present in the aqueous phase. Given these experimental design problems, it is not surprising that this vital experimental parameter (K_d) is not typically taught in environmental chemistry lab courses, but is usually covered in lecture material.

This article describes a procedure that uses standardized materials and conditions to determine a distribution coefficient for copper. The procedure will allow instructors to easily design experiments for upper-level undergraduate and graduate environmental chemistry laboratories. It is also environmentally friendly, since no (or limited) hazardous waste is generated.

Materials and Supplies

Chemicals

Kaolin. Kaolin was obtained from The Clay Minerals Society, Source Clays Repository, product KGa-1b. The origin of the clay and its chemical composition, cation exchange capacity, and surface area are given at <http://web.missouri.edu/~geoscjy/SourceClay/> and in the supplemental material.^W Ordering information is also available at this Web site. Mass requirements are 0.100 ± 0.001 g per vial.

Montmorillinite. Montmorillinite was obtained from The Clay Minerals Society, Source Clays Repository, product STx-1. The origin of the clay and its chemical composition, cation exchange capacity, and surface area are given at <http://web.missouri.edu/~geoscjy/SourceClay/> and in the supplemental material.^W Ordering information is also available at this Web site. Mass requirements are 0.100 ± 0.001 g per vial.

Stock Copper Solution. The stock Cu solution (1000 mg/L) was made by dissolving 0.268 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ($M_r = 170.34$ g/mol) in 100.0 mL of deionized water (volumetric flask) to make a solution containing 1000 mg/L of Cu. Make 1:10 and 1:100 dilutions of this solution to obtain a 100 and 10.0 mg/L solutions of Cu^{2+} , respectively. All three of these solutions are used in preparing the Cu–water–soil suspensions.

$\text{Ca}(\text{NO}_3)_2$, 0.500 M. Dissolve 11.808 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ($M_r = 236.16$ g/mol) in 100.0 mL of deionized water to make a 0.500 M $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution.

HEPES, 0.80 M. Dissolve 47.66 g of *N*-2-hydroxyethylpiperazine-*N'*-2-ethanesulfonic acid (HEPES, $M_r = 238.30$) in ~200 mL deionized water in a beaker. Adjust the pH of this solution to approximately 7.5 using 1.0 M NaOH. Quantitatively transfer this solution to a 250.0-mL volumetric flask and fill to the mark.

NaOH, 1 M, and HCl, 1 M. These are used to adjust the pH of buffer solutions.

Equipment

50-mL centrifuge tubes with caps. We used Blue Max disposable centrifuge tubes made of polystyrene, with a conical bottom. These were manufactured by Falcon and distributed by VWR Scientific; No. 21008-939.

25-mm diameter polycarbonate filter cartridge. We used a 25-mm polycarbonate filter holder distributed by VWR Scientific; No. 22001-800 (12 per pack).

25-mm Gelman-type A/E glass fiber filter. These were manufactured by Pall Gelman and distributed by VWR Scientific; No. 28150-178.

0.2- μ m membrane filter. We used a filter manufactured by Spartan-13 and distributed by Agilent Technologies; No. HP-5061-3366.

Any 25-mL disposable plastic/polycarbonate syringes.

Test tube rotator. We used a Glas-Col Mini-Rotator, 120 V, VWR Scientific; No. 33725-042. (Test tube rockers will probably work just as well.)

A flame atomic absorption spectrophotometer (FAAS) unit capable of analyzing aqueous copper solutions. We used a Perkin-Elmer 1100B in this investigation.

Student procedures and handouts.^W

Experimental Procedures

Each of the experiments is designed as a two-week lab. In the first week, the students divide into teams, plan their experiment, and set up solutions to be equilibrated during the next 3 to 4 days. This involves carefully weighing out the reference clay materials, making dilution water containing the appropriate copper concentration(s), buffer(s), and ionic strength adjuster(s), and mixing the suspensions. In week two, the students filter the suspensions, analyze the aqueous-phase copper concentration on an atomic absorption spectrophotometer, calculate their K_d using the spreadsheet template provided, and compile the results.^W

Hazards

Although these experiments present no unusual hazards, standard precautions should be used in handling solutions and in disposing of copper wastes.

Example Results

K_d versus Cu Concentration

Without question, the most important experiment is the determination of K_d as a function of copper concentration (Fig. 1). In theory, one can determine the distribution coefficient at one pollutant concentration, represented by any single point in Figure 1. However, this is only a one-point estimate of the K_d and will not reflect a good statistical average of the experimental conditions; moreover, the K_d does not always show a linear relationship with concentration. The best estimate of K_d is an average of all of the data points in Figure 1, which is also the slope of the line.

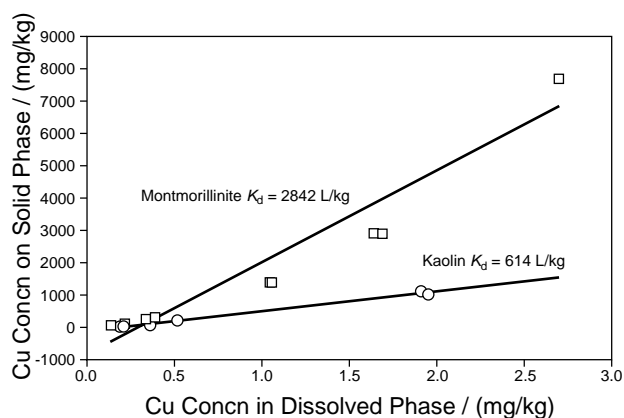


Figure 1. K_d as a function of Cu concentration; 0.050 M HEPES buffer at pH 7.3, 0.025 M $\text{Ca}(\text{NO}_3)_2$, and 2500 mg/L TSS for montmorillinite and kaolin.

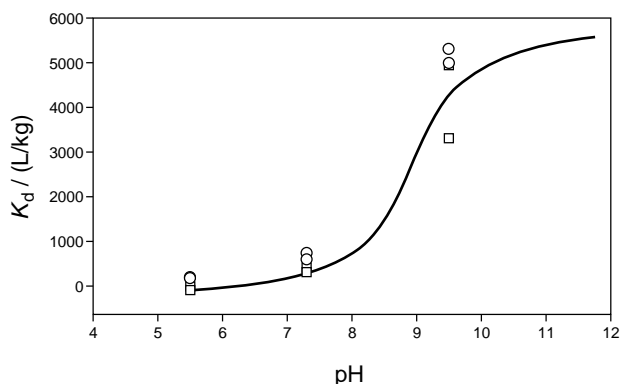


Figure 2. K_d as a function of solution pH; 0.050 M pH buffers, 0.025 M $\text{Ca}(\text{NO}_3)_2$, 2500 mg/L TSS, and 1.00 mg/L total Cu concentration. The curve represents the expected trend.

Readers and students will undoubtedly notice the error present in Figure 1. This error, represented by the deviation between the individual data points and the line, is not only due to inexperienced students' lab technique but also reflects the difficulty in experimentally measuring distribution coefficients. Rarely do all of the individual data points and the slope of the line agree. It is also useful for the students to speculate on which experimental variables are responsible for this error, including the possibility that the higher concentrations are outside of the linear relationship. The students should also note that montmorillinite yields a higher K_d than kaolin owing to its greater surface area, expandable nature, and surface charge.

K_d versus pH

The distribution coefficient for metal pollutants is usually highly dependent on the pH of the suspension. Although this would be an important experiment for the students to conduct, it is perhaps the most difficult. In our lab, we conducted this experiment using sulfonic acid-based buffers (MES for a pH of 5.5, HEPES for a pH of 7.2, TAPS for a pH of 8.3, and CHES for a pH of 9.2). In general, our data followed the expected trend (Fig. 2, excluding the data for pH 8.5, TAPS buffer). The K_d data point for the TAPS buffer was

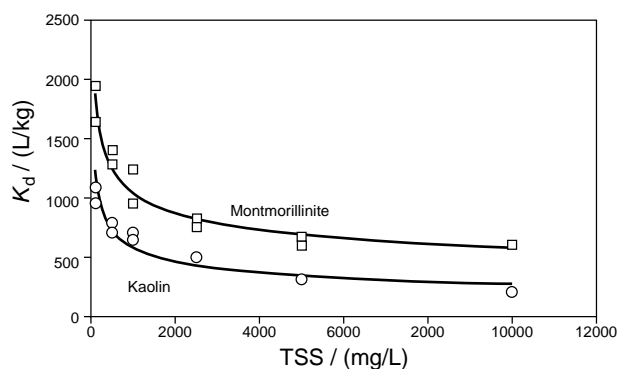


Figure 3. K_d as a function of TSS; 0.050 M HEPES buffer at pH 7.3, 0.025 M $\text{Ca}(\text{NO}_3)_2$, and 1.00 mg/L total Cu concentration.

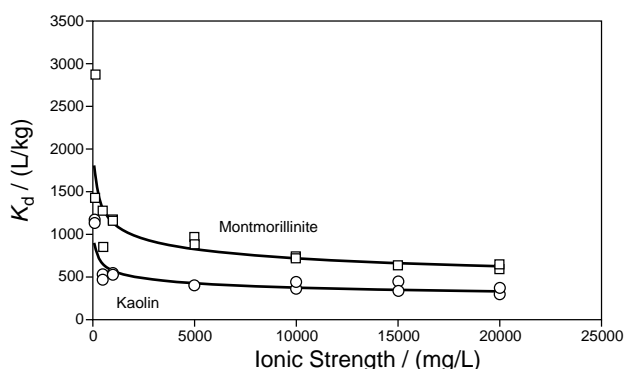


Figure 4. K_d as a function of ionic strength; 0.050 M HEPES buffer at pH 7.3, 1.00 mg/L total Cu concentration, and 2500 mg/L TSS for montmorillinite and kaolin.

unexpectedly low. The varying complexation ability of the buffers resulted in inconsistent aqueous copper concentrations and this interfered in the calculation of K_d (particularly with the TAPS buffer). If the dependence of K_d on pH is to be evaluated, we suggest that the students adjust the pH of each suspension with 1 M NaOH or HCl and avoid the use of pH buffers. In general, the K_d for Cu should be lower at low pH values and slowly increase between the pH values of 4 and 7.

K_d versus Total Suspended Solids (TSS)

Another interesting experiment is to measure K_d as a function of the amount of clay added to each vial (TSS). In theory, there should be no difference in the observed K_d , but numerous investigations have found that K_d decreases with increasing TSS (4). Results from our experiments are shown in Figure 3 and show the expected power law relationship.

K_d versus I

Since this laboratory exercise deals with ionic pollutants it is important to consider ionic strength as an experimental parameter. We measured K_d as a function of $\text{Ca}(\text{NO}_3)_2$ concentration (Fig. 4). As the figure shows, an increase in ionic strength results in lower K_d values. This can be explained by

a collapse of the ionic double layer around the clay particles and a charge neutralization of the Cu^{2+} ion by the nitrate ion (6). As the charge of the $\text{Cu}^{2+}-\text{NO}_3^-$ complex is decreased it has less affinity for the clay particles and adsorption decreases (a lower K_d). In addition, the Ca^{2+} ions can compete for sorption sites with the Cu^{2+} ions. The lowering of K_d with increasing ionic strength is observed for both the kaolin and the montmorillinite suspensions.

Evaluation of the Experiments

When these experiments are used in conjunction with lecture material on sorption phenomena and fate and transport modeling, students make an easy and direct link between the laboratory exercise and theory. It is recommended that the K_d experiments be used in a class after the students have completed instrumental methods of analysis. Students learn new techniques in sample preparation and microfiltration and they repeat FAAS procedures.

The response to this lab has been very positive; it is the favorite environmental chemistry lab conducted at Whitman College. To paraphrase the students, "we feel we are applying classic chemical techniques [FAAS] to a real world problem."

In total, this article describes experiments that could take up to eight lab periods to complete, but we do not suggest that all students necessarily complete all of them. The most important is the experiment presented in Figure 1 (K_d versus Cu concentration), but if the class enrollment is sufficient, you could divide the class into teams and complete all of the experiments in two weeks.

Acknowledgments

We would like to thank the students from Environmental Chemistry (classes of 2000 and 2001) for help in developing these procedures and collecting the experimental data. We are also indebted to Fred Girod of the Collegium Budapest–Institute of Advanced Study for the use of computers and Internet services during the preparation of this manuscript.

Supplemental Material

Detailed procedures for students are available in this issue of *JCE Online*.

Literature Cited

- Boebnke, N. D.; Del Delumyea, R. *Laboratory Experiments in Environmental Chemistry*; Prentice-Hall: Upper Saddle River, NJ, 2000.
- Ondrus, M. G. *Environmental Chemistry: Experiments and Demonstrations*, 2nd ed.; Wuerz: Winnipeg, MB, Canada, 1996.
- Sawyer, C. N.; McCarty, P. L.; Parkin, G. F. *Chemistry for Environmental Engineers*; McGraw-Hill: New York, 1994.
- O'Connor, D. J.; Connolly, J. P. *Water Res.* **1980**, *14*, 1517–1523.
- Stumm, W.; Morgan, J. J. *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*, 2nd ed.; Wiley: New York, 1981.
- Sposito, G. *The Surface Chemistry of Soils*; Oxford University Press: New York, 1984.