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DETERMINATION OF A CLAY–WATER DISTRIBUTION COEFFICIENT FOR COPPER

Purpose: To determine the distribution coefficient of a metal on a characterized soil

To learn to use a flame atomic absorption spectrometer

BACKGROUND

Perhaps the most important fate and transport parameter is the *distribution coefficient*, K_d, a measure of the adsorption phenomenon between the aqueous and solid phases and is fundamental to understanding the processes responsible for the distribution of pollutants in aquatic systems. (For its application to fate and transport modeling of groundwater, lakes, and riverine systems, refer to Chapters 24 through 27.) Mathematically, it can be represented as the ratio of the equilibrium pollutant concentration in the solid (sediment or soil) phase to the equilibrium pollutant concentration in the dissolved (aqueous) phase:

$$K_d = \frac{C_{\text{solid}}\ (\text{mg/kg})}{C_{\text{aqueous}}\ (\text{mg/L})} \tag{17-1}$$

The purpose of the distribution coefficient is to quantify which phase (solid or aqueous) the pollutant has a preference for and to determine the mass of pollutant present in each phase. The distribution coefficient 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 free aqueous-phase concentration is usually the most toxic form of pollutants. 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 can eventually settle out in quiescent regions of the natural water body or in estuaries and remove sufficient amounts of pollutant from the aquatic system.

Distribution coefficients are relatively easy to determine 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 by measuring (or knowing) the total mass of pollutant added to each sample (determined in a blank sample), measuring the pollutant in the dissolved phase after equilibration, and estimating the mass of pollutant on the solid phase by difference (total mass of pollutant in blank minus aqueous phase mass). The distribution coefficient is then calculated using equation (17-1).

The major problem with designing K_d experiments for the laboratory is the variability (and unpredictability) of results that are obtained given the variety of solid phases available, the nature of the pollutant used (ionic metals or hydrophobic organic compounds), and the experimental aqueous conditions used (pH values, ionic strengths, solids concentrations, and pollutant concentrations). Aqueous conditions are especially important when measuring K_d for ionic pollutants. Unless the lab instructor has conducted the experiment previously under the exact experimental conditions to be used in the lab, 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. In this chapter we present a procedure, using standardized materials and conditions, for the determination of a distribution coefficient for copper. The procedure is also environmentally friendly since no (or limited) hazardous waste is generated.

THEORY

The fate and transport of pollutants in aquatic systems and sorption phenomena of pollutants is often discussed in environmental chemistry lecture courses. How a pollutant interacts with its surroundings (solubility in water; sorption to soil and sediment particles) will greatly influence how it travels through the environment. *Sorption* is a generic term used to describe all processes in which a pollutant prefers a solid phase to the dissolved phase. Absorption and adsorption are used to describe this process for metals and polar (or ionizable) organics interacting with solid surfaces, while partitioning is used to describe this process for hydrophobic

compounds interacting with natural organic matter. The key parameter describing absorption and adsorption is the distribution coefficient (K_d). The key parameter for describing partitioning is the *partition coefficient* (K_p). Both are ratios of the concentration of pollutant in or on the solid phase to the concentration of pollutant dissolved in the aqueous phase. The goal of this lab is to learn how to determine a distribution coefficient for a water–solid suspension containing Cu^{2+} ions. Normally, heavy metals are used in K_d determinations, but these generate hazardous waste and raise health concerns. Copper will be used in this laboratory exercise as a surrogate for heavy metals.

Adsorption of metals to clay surfaces is usually due to cationic exchange reactions resulting from a pH-dependent charge on the clay or from isomorphic substitutions. The pH-dependent charge is fairly self-explanatory and is present primarily on the broken edges of clays. Isomorphic substitution is a permanent charge on the clay resulting from Al or Si in the clay sheets being replaced by an element of lesser positive charge; thus, a net negative charge is present on the clay. This net negative charge is usually neutralized by common cations (i.e., Na^+, K^+, Ca^{2+}, Mg^{2+}, etc.) in solution, but some metals will preferentially exchange with these cations and be strongly held (adsorbed) to the clay surface. The extent of this adsorption is determined by the magnitude of the K_d.

ACKNOWLEDGMENTS

REFERENCES

O'Connor, D. J. and J. P. Connolly, *Water Res.*, **14**, 1517–1523 (1980).

Stumm, W. and J. J. Morgan, *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*, 2nd ed., Wiley, New York, 1981.

IN THE LABORATORY

There are a number of ways to conduct this laboratory exercise; your instructor will decide which is best for your class. One option is to divide the class into three groups, one group for the determination of K_d as a function of Cu concentration, one group for the determination of K_d as a function of ionic strength, and one group for the determination of K_d as a function of suspended solids. Another option is to have the entire class determine K_d as a function of Cu concentration; in this case, the instructor may provide you with the results for the other experiments. Regardless of the approach being used, you must come to lab with a good understanding of K_d and how the experiments are designed.

Safety Precautions

- As in all laboratory exercises, safety glasses must be worn at all times.
- Avoid skin and eye contact with NaOH, HCl, and HNO_3 solutions. If contact occurs, rinse your hands and/or flush your eyes for several minutes. Seek immediate medical advice for eye contact.

Chemicals and Solutions

- Sorbents
  - *Ca-montmorillinite* (obtained from the Clay Minerals Society, Source Clays Repository. Product STx-1. The origin of the clay, chemical composition, cation exchange capacity, and surface area are given at `http://cms.land.gov` and in the supplemental material of this article. Ordering information is also available at this Web site. Mass requirements are about 0.100 ± 0.001 g per vial.)
  - *K-kaolinite* (obtained from the Clay Minerals Society, Source Clays Repository. Product KGa-1b. The origin of the clay, chemical composition, cation exchange capacity, and surface area are given at `http://cms.land.gov` and in the supplemental material of this article. Ordering information is also available at this Web site. Mass requirements are about 0.100 ± 0.001 g per vial.)
- *Stock copper solution*. Dissolve 0.268 g of $CuCl_2 \cdot 2H_2O$ (GMW 170.34) in 100.0 mL of deionized water (volumetric flask) to make a 1000-mg/L solution. Make a 1 : 100 dilution of this solution to obtain a 10.0-mg/L solution of Cu^{2+}.
- *Calcium nitrate solution*. Prepare two 100-mL portions of 2.00 M $Ca(NO_3)_2 \cdot 4H_2O$.
- *$Ca(NO_3)_2$ ionic strength adjustor*. 0.8469 M: Dissolve 11.808 g of $Ca(NO_3)_2 \cdot 4H_2O$ (GMW 236.16 g/mol) in 100.0 mL of deionized water to

make a $0.500\,M$ $Ca(NO_3)_2 \cdot 4H_2O$ solution. Make $10:100$ and $1:100$ dilutions of this solution to obtain $0.08469\,M$ and $0.008469\,M$ solutions, respectively.

- $1\,M$ HCl and $1\,M$ NaOH for adjusting pH.
- 1% nitric acid.
- Run blanks of each Cu solution in equilibrium vials.
- 1000 mg/L Cu standard in 5% HNO_3.

Equipment and Glassware

- Cu flame atomic absorption spectroscopy (FAAS) lamp
- FAAS unit
- New 50-mL plastic, sealable vials (24 vials per solid evaluated are needed) (blue max. disposable centrifuge tubes, polystyrene, conical bottom, sterile: Falcon, VWR Scientific Products Number 21008-939)
- 100- or 50-mL graduated cylinders
- Plastic filter holders and filters (polycarbonate filter holder, 25-mm filter,12 per pack; VWR Scientific Products Number 22001-800)
- 25-mL plastic syringes
- 25-mm Gelman-type A/E glass fiber filter (glass fiber filters, type A/E; Pall Gelman, VWR Scientific Products Number 28150-178)
- 0.2-μm membrane filter or similar brand (Spartan-13, Agilent Technologies, HP-5061-3366)
- Plastic beakers for holding filtered samples
- Test tube rotator (Glas-Col mini-rotator, 120 V, VWR Scientific Products Number 33725-042; test tube rockers will probably work just as well)

PROCEDURE

Week 1

Prerinse all plastic vials and caps with deionized water.

Team 1: K_d as a Function of Total Suspended Solids (TSS) and Clay Type

1. The mineral phases to be used as your adsorbent are kaolinite (KGa-1b) and Ca-montmorillinite (STx-1). Thus, you will have two sets of vials, or two experiments, one with each absorbent.
2. *Preparation of stock Cu solution* (from $CuCl_2 \cdot 2H_2O$). Make a 1000-mg/L solution by adding 2.683 g of $CuCl_2 \cdot 2H_2O$ to a 1-L volumetric flask and filling to the mark with deionized water. (Do not add acid yet.)
3. *Preparation of solutions for making suspensions*. The goal is to prepare solutions in which the ionic strength and pH are as close to identical as possible. There are probably several ways to do this, but we will use the following approach:
   - *$Ca(NO_3)_2 \cdot 4H_2O$ stock solution*. Transfer 29.54 g of $Ca(NO_3)_2 \cdot 4H_2O$ (GMW is 236.16 g/mol) to a 250-mL volumetric flask and fill to the mark. This will yield a 0.500 M solution.
4. Your goal is to measure K_d as a function of TSS and mineral phase. Prepare two vials for each TSS concentration of each clay type. You will use four different TSS concentrations of each clay: 500 mg/L, 1000 mg/L, 5000 mg/L, and 10,000 mg/L. You will be using a total volume in each sample vial of 40.0 mL. Weigh 0.020 g (for the 500-mg/L vials), 0.0400 g (for the 1000-mg/L vials), 0.200 g (for the 5000-mg/L vials), and 0.400 g (for the 10,000-mg/L vials). Be as close as you can to these weights, and record your significant figures to four decimal places. All vials in this experiment will use a copper concentration of 5.00 mg/L. You will also need to have two blanks containing ionic strength adjustor, Cu, and water (see step 5), but no mineral phase. Label each with masking tape and a number (e.g., "T1-1" represents "team 1 vial 1," "T1-B1," "team 1, blank 1"). In all, you will have at least two blanks (no mineral phase) and two vials for each TSS of each mineral phase.
5. Prepare the following solution in a 100-mL (or better yet, 50-mL) graduated cylinder:
   - 2.00 mL of 0.50 M $Ca(NO_3)_2 \cdot 4H_2O$ stock solution.
   - Add the appropriate amount of Cu solution (for this experiment, consult the 5.00-ppm row in Table 17-1).
   - Fill to 40.0 mL with deionized water.
6. Add the solution to each vial prepared in step 5, cap, and mix well. The pH should be between 5.0 and 5.5 for the kaolinite and between 6.5 and 7.0 for the montmorillinite. Adjust as needed with 1M HCl or NaOH.

TABLE 17-1. Cu Solution Table for Team 1

Desired Cu Solution Concentration in a Vial (ppm)	Addition Volume (mL) of the Cu Solution to the Right to Yield the Desired Cu Concentration to the Left	Standard Cu Solution[a] (mg/L)
50.0	2.00	1000.
25.0	1.00	1000.
10.0	4.00	100.
5.00	**2.00**	**100.**
1.00	4.00	10.0
0.500	2.00	10.0

[a]To prepare a 1000-ppm Cu^{2+} solution, add 2.683 g of $CuCl_2 \cdot 2H_2O$ to a 1000–mL volumetric flask and fill to the mark. To prepare the 100-ppm Cu solution, make a 10 : 100 dilution of the 1000-ppm solution. To prepare the 10-ppm Cu solution, make a 1 : 100 dilution of the 1000-ppm solution.

7. Again, be sure to prepare at least two blanks for each Cu concentration (containing everything, including Cu standard, but no solid phase). These will be necessary to determine if any Cu adsorbs to the container walls.

8. Place the vials on the mixer for at least three days.

Team 2: K_d as a Function of Cu Concentration (Kaolinite)

1. The mineral phase to be used as your adsorbent is kaolinite (KGa-1b).

2. *Preparation of stock Cu solution* (from $CuCl_2 \cdot 2H_2O$). Make a 1000-mg/L solution by adding 2.683 g of $CuCl_2 \cdot 2H_2O$ to a 1-L volumetric flask and filling to the mark with deionized water. (Do not add acid yet.)

3. *Preparation of solutions for making suspensions*. The goal is to prepare solutions where the mass of solid phase, the ionic strength, and the pH are as close to identical as possible. There are probably several ways to do this, but we will use the following approach:

   ○ $Ca(NO_3)_2 \cdot 4H_2O$ stock solution. Transfer 29.54 g of $Ca(NO_3)_2 \cdot 4H_2O$ (GMW is 236.16 g/mol) to a 250-mL volumetric flask and fill to the mark. This will yield a 0.500 M solution.

   Your goal is to measure the K_d as a function of Cu concentration for a kaolinite clay. Prepare two vials for each Cu concentration. You will use a TSS concentration of 5000 mg/L. You will be using a total volume in each sample vial of 40.0 mL. Weigh 0.200 g (for the 5000 mg/L TSS) into each vial (except your blank vials). Be as close as you can to this mass, and record your significant figures to four decimal places. You will also need to have two blanks for each Cu concentration. These blank vials will contain ionic strength adjustor, Cu, and water (see step 4), but no mineral phase. Label each with masking tape and a number (e.g., "T2-1" represents "team 2, vial 1"; "T2-B1," "team 2, blank 1").

TABLE 17-2. Cu Solution Table for Team 2

Desired Cu Solution Concentration in a Vial (ppm)	Addition Volume (mL) of the Cu Solution to the Right to Yield the Desired Cu Concentration to the Left	Standard Cu Solution[a] (mg/L)
50.0	2.00	1000.
25.0	1.00	1000.
10.0	4.00	100.
5.00	2.00	100.
1.00	4.00	10.0
0.500	2.00	10.0

[a] To prepare a 1000-ppm Cu^{2+} solution, add 2.683 g of $CuCl_2 \cdot 2H_2O$ to a 1000-mL volumetric flask and fill to the mark. To prepare the 100-ppm Cu solution, make a 10 : 100 dilution of the 1000-ppm solution. To prepare the 10-ppm Cu solution, make a 1 : 100 dilution of the 1000-ppm solution.

4. Prepare the following solutions to fill the sediment-containing vials and blanks in a 100-mL (or better yet, 50-mL) graduated cylinder, using Cu^{2+} solutions of 1000 ppm, 100 ppm, and 10 ppm, made as described in Table 17-2.
   ○ 2.00 mL of 0.50 M $Ca(NO_3)_2 \cdot 4H_2O$ stock solution.
   ○ Add the appropriate amount of Cu solution for each concentration (Table 17-2).
   ○ Fill to 40.0 mL with deionized water.
5. Add each solution to the appropriate vials, cap, and mix well.
6. Again, be sure to prepare two blanks for each Cu concentration (containing everything, including Cu standard, but no solid phase). These will be necessary to determine if any Cu adsorbs to the container walls.
7. Place the vials on the mixer for at least three days.

Team 3: K_d as a Function of Cu Concentration (Montmorillinite (STx-1)

1. The mineral phase to be used as your adsorbent is montmorillinite (STx-1).
2. *Preparation of stock Cu solution* (from $CuCl_2 \cdot 2H_2O$). Make a 1000-mg/L solution by adding 2.683 g of $CuCl_2 \cdot 2H_2O$ to a 1-L volumetric flask and filling to the mark with deionized water. (Do not add acid yet.)
3. *Preparation of solutions for making suspensions.* The goal is to prepare solutions where the mass of solid phase, ionic strength, and pH are as close to identical as possible. There are probably several ways that we can do this, but we will use the following approach.
   ○ *$Ca(NO_3)_2 \cdot 4H_2O$ stock solution.* Transfer 29.54 g of $Ca(NO_3)_2 \cdot 4H_2O$ (GMW is 236.16 g/mol) to a 250-mL volumetric flask and fill to the mark. This will yield a 0.500 M solution.

TABLE 17-3. Cu Solution Table for Team 3

Desired Cu Solution Concentration in a Vial (ppm)	Addition Volume (mL) of the Cu Solution to the Right to Yield the Desired Cu Concentration to the Left	Standard Cu Solution[a] (mg/L)
50.0	2.00	1000.
25.0	1.00	1000.
10.0	4.00	100.
5.00	2.00	100.
1.00	4.00	10.0
0.500	2.00	10.0

[a] To prepare a 1000-ppm Cu^{2+} solution, add 2.683 g of $CuCl_2 \cdot 2H_2O$ to a 1000-mL volumetric flask and fill to the mark. To prepare the 100-ppm Cu solution, make a 10 : 100 dilution of the 1000-ppm solution. To prepare the 10-ppm Cu solution, make a 1 : 100 dilution of the 1000-ppm solution.

Your goal is to measure K_d as a function of Cu concentration for a montmorillinite clay. Prepare two vials for each Cu concentration. You will use a TSS concentration of 5000 mg/L. You will be using a total volume in each sample vial of 40.0 mL. Weigh 0.200 g (for the 5000-mg/L TSS vials) in each vial (except your blank vials). Be as close as you can to this mass, and record your significant figures to four decimal places. You will also need to have two blanks for each Cu concentration. These blank vials will contain ionic strength adjustor, Cu, and water (see step 4), but no mineral phase. Label each with masking tape and a number (e.g., "T3-1" represents "team 3, vial 1"; "T3-B1" "team 3, blank 1").

4. Prepare the following solutions in a 100-mL (or better yet, 50-mL) graduated cylinder:

   o 2 mL of 0.50 *M* $Ca(NO_3)_2 \cdot 4H_2O$ stock solution.

   o Add the appropriate amount of Cu solution from Table 17-3.

   o Fill to 40.0 mL with deionized water.

5. Add each solution to the appropriate vial, cap, and mix well.

6. Again, be sure to prepare two blanks for each Cu concentration (containing everything, including Cu standard, but no solid phase). These will be necessary to determine if any Cu adsorbs to the container walls.

7. Place the vials on the mixer for at least three days.

Team 4: K_d as a Function of Ionic Strength (I) and Mineral Phase

1. The mineral phases to be used as your adsorbent are kaolinite and montmorillinite.

2. *Preparation of stock Cu solution* (from $CuCl_2 \cdot 2H_2O$). Make a 1000-mg/L solution by adding 2.683 g of $CuCl_2 \cdot 2H_2O$ to a 1-L volumetric flask and filling to the mark with deionized water. (Do not add acid yet.)

TABLE 17-4. Cu Solution Table for Team 4

Desired Cu Solution Concentration in a Vial (ppm)	Addition Volume (mL) of the Cu Solution to the Right to Yield the Desired Cu Concentraction to the Left	Standard Cu Solution[a] (mg/L)
50.0	2.00	1000.
25.0	1.00	1000.
10.0	4.00	100.
5.00	2.00	100.
1.00	4.00	10.0
0.500	2.00	10.0

[a] To prepare a 1000-ppm Cu^{2+} solution, add 2.683 g of $CuCl_2 \cdot 2H_2O$ to a 1000-mL volumetric flask and fill to the mark. To prepare the 100-ppm Cu solution make a 10 : 100 dilution of the 1000-ppm solution. To prepare the 10-ppm Cu solution, make a 1 : 100 dilution of the 1000-ppm solution.

3. *Preparation of solutions for making suspensions.* The goal of this is to prepare solutions where the mass of solid phase and that of Cu concentration are identical while the ionic strength changes systematically. There are probably several ways to do this, but we will use the following approach:

   ○ *$Ca(NO_3)_2 \cdot 4H_2O$ stock solution.* Transfer 29.54 g of $Ca(NO_3)_2 \cdot 4H_2O$ (GMW is 236.16 g/mol) to a 250-mL volumetric flask and fill to the mark. This will yield a 0.500 M solution.

   Your goal is to measure K_d as a function of ionic strength (I) for a kaolinite and montmorillinite clay. Prepare two vials for each ionic strength and clay type. You will use a TSS concentration of 5000 mg/L and a total volume in each sample vial of 40.0 mL. Weigh 0.200 g (for 5000 mg/L TSS) into each vial (except your blank vials). Be as close as you can to this weight, and record your significant figures to four decimal places. You will also need to have two blanks. These blank vials will contain ionic strength adjustor, Cu, and water (see step 4), but no mineral phase. Label each with masking tape and a number (e.g., "T4-1" represents "team 4, vial 1"; "T4-B1," "team 4, blank 1").

4. Prepare the following solution in a 100-mL (or better yet, 50-mL) graduated cylinder:

   ○ Use the appropriate amount of Cu solution (for you, this will be 5.00 ppm in Table 17-4).

   ○ Add $Ca(NO_3)_2 \cdot 4H_2O$ stock solution. (Determine the appropriate amount from Table 17-5. You will need to have the appropriate dilutions shown in the second column.)

   ○ Fill to 40.0 mL with deionized water.

5. Add each solution to the appropriate vials, cap, and mix well.

TABLE 17-5. Table for Determining the Ionic Strength of the Solution for Team 4

Addition (mL)	of a Molar Ca(NO$_3$)$_2$ Solution (mol/L) to 100 mL	to Obtain a Final Ca(NO$_3$)$_2$ (mg/L) Concentration of:	Final Ionic Strength (mg/L)
2.00	0.008469	100	9,600
1.00	0.08469	500	10,900
2.00	0.08469	1,000	12,400
1.00	0.8469	5,000	24,400
2.00	0.8469	10,000	39,400
3.00	0.8469	15,000	54,400
4.00	0.8469	20,000	69,400

6. Again, be sure to prepare two blanks (containing everything, including Cu standard, but no solid phase). These will be necessary to determine if any Cu adsorbs to the container wall.
7. Place the vials on the mixer for at least three days.

Week 2

There will be several demonstrations at the beginning of lab to illustrate use of the filter apparatus and mixing system.

1. Turn on the AAS to warm up the lamp.
2. Prepare calibration standards at concentrations of 0.100, 0.500, 1.00, 5.00, 10.0, 25.0, and 50.0 ppm Cu^{2+}. Prepare these in 1% HCl.
3. Filter the solutions that you prepared last week. First, filter them through the Gelman-type A/E glass-fiber filter, then through a 0.2-µm HPLC nylon filter with a syringe. Filter both the blanks and the actual samples.
4. Analyze the samples using AAS as demonstrated.
5. Turn in your data in tabular form and as a graph.

Waste Disposal

After neutralization, all solutions can be disposed of down the drain with water.

ASSIGNMENT

For your lab report, compile all of the data for each solid, estimate K_d for each solid phase, and write a short answer to each of the following issues.

1. Contrast the differences in K_d between the solid phases.
2. Contrast the results for the variation of TSS.
3. Contrast the results for the variation of ionic strength.
4. Explain why the dilution water contained $Ca(NO_3)_2$.

ADVANCED STUDY ASSIGNMENT

1. Prepare a list of things to do when you arrive in the laboratory.
2. Prepare a dilution table showing how you will make your calibration standards for the flame atomic absorption spectroscopy unit.
3. Research the clay mineralogy and structure of kaolinite and montmorillinite. Turn in chemical formulas and a figure of the structures. Show how montmorillinite can undergo isomorphic substitution.
4. Draw and label the major components of a flame atomic absorption spectrometer. Describe each major component in two to three sentences.