Reducing Variance in Batch Partitioning Measurements

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Introduction

Abstract

The partitioning experiment is commonly performed with little or no attention to reducing measurement variance. Batch test procedures such as those used to measure K_d values (e.g., ASTM D 4646 and EPA402 -R-99-004A) do not explain how to evaluate measurement uncertainty nor how to minimize measurement variance. In fact, ASTM D 4646 prescribes a sorbent:water ratio that prevents variance minimization. Consequently, the variance of a set of partitioning measurements can be extreme and even absurd. Such data sets, which are commonplace, hamper probabilistic modeling efforts.

An error-savvy design requires adjustment of the solution:sorbent ratio so that approximately half of the sorbate partitions to the sorbent. Results of Monte Carlo simulations indicate that this simple step can markedly improve the precision and statistical characterization of partitioning uncertainty.

Standard Batch Test

ASTM D 4646

1. Combine 20 mL of water containing sorbate with 1 gram of sorbent
2. Measure decrease in aqueous concentration of sorbent
3. Calculate K_d using following equation:

$$K_d = \frac{(C_i - C_f)}{C_f} \cdot \frac{20\text{mL}}{1.0\text{g}}$$

C_i = initial aqueous conc.
C_f = final equilibrated conc.

K_d Sensitivity to Fraction Sorbed

Alternate equation:

$$K_d = \frac{f}{1-f} r_{ws}$$

f = fraction partitioned (sorbed)
r_{ws} = ratio of solution to sorbent (mL/g)

Too Little Sorption | Ideal Sorption | Too Much Sorption

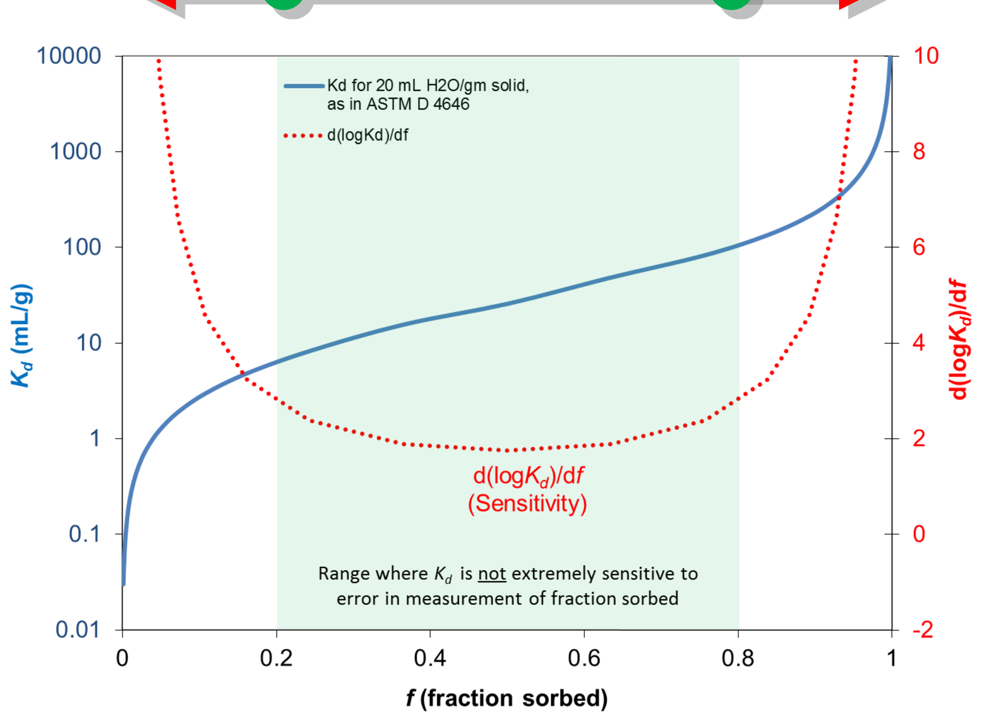


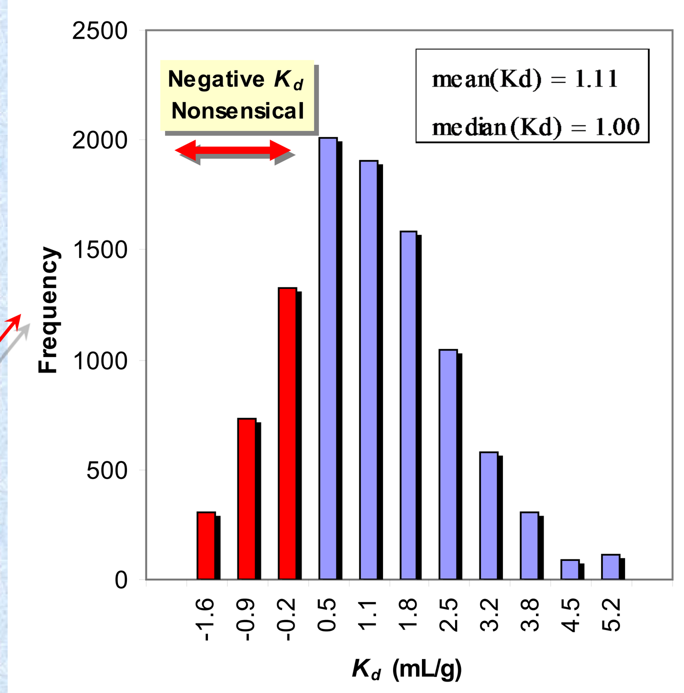
Figure 1. K_d sensitivity to fraction sorbed (r_{ws} = 20 mL/g).

Analysis

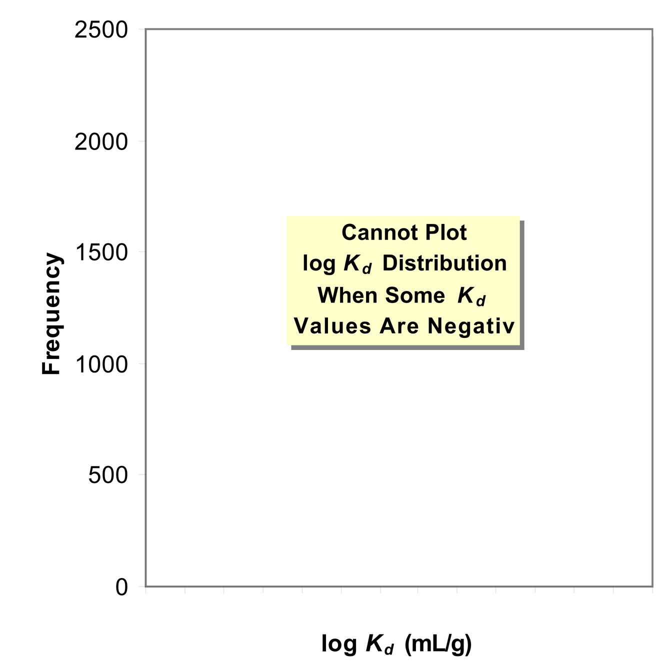
Monte Carlo Simulations

- Simulate ASTM D 4646 for three different K_d values: 1, 20, and 100 mL/g (C_f/C_i = 0.95, 0.50, and 0.16)
- Apply normal standard deviation of $0.06C_i$ to the measurement of the final concentration, C_f
- Perform 10,000 realizations
  - Simulations performed using Mathcad 2001
  - Normal distribution discretized into 100 equally probable slices represented by their midpoints

A. K_d = 1 mL/g



Log Transform



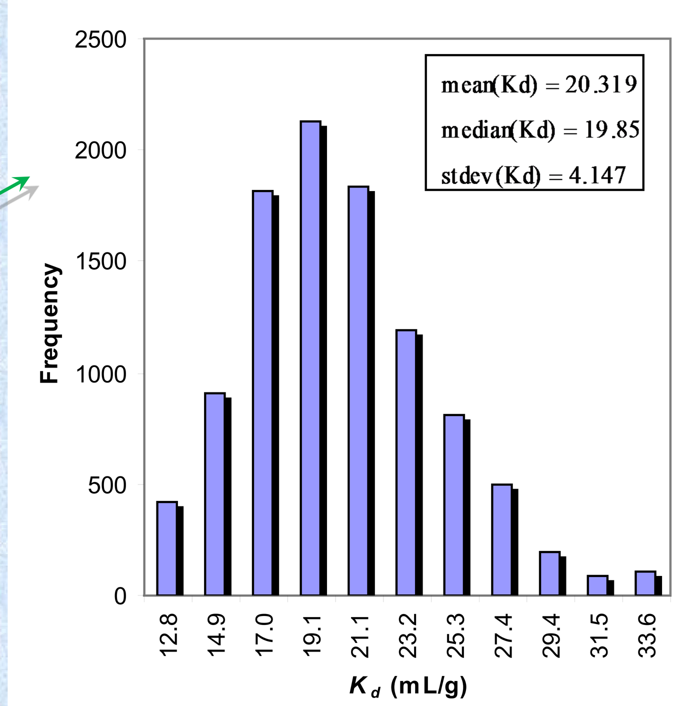
Too Little Sorption (f < 0.2)

95% Confidence Intervals
- $0.83 < C_f/C_i < 1.07$
- $-0.07 < f < 0.17$

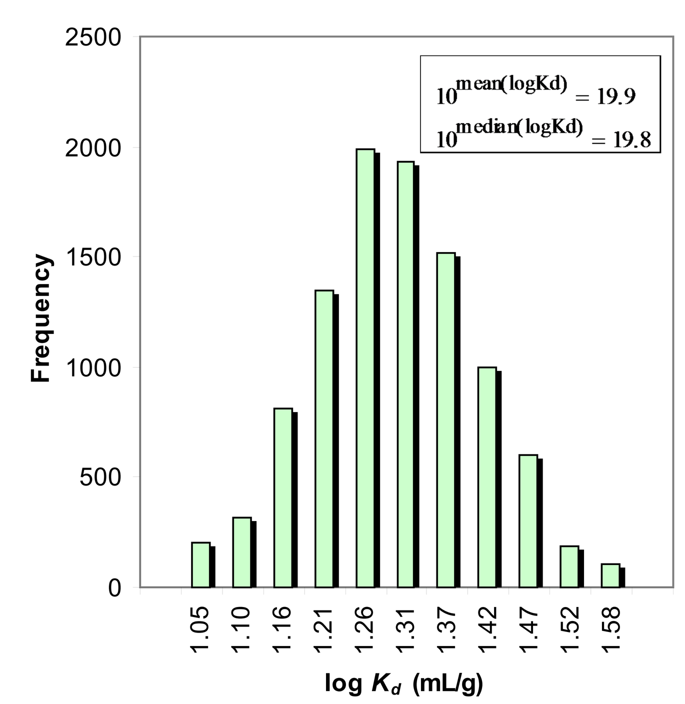
Problems
- Negative K_d values are nonsensical
- Cannot determine variance
- Cannot log transform

Solution
- Determine median K_d using all measurements (including negative)
- Decrease r_{ws} to median K_d and redo the experiments

B. K_d = 20 mL/g



Log Transform



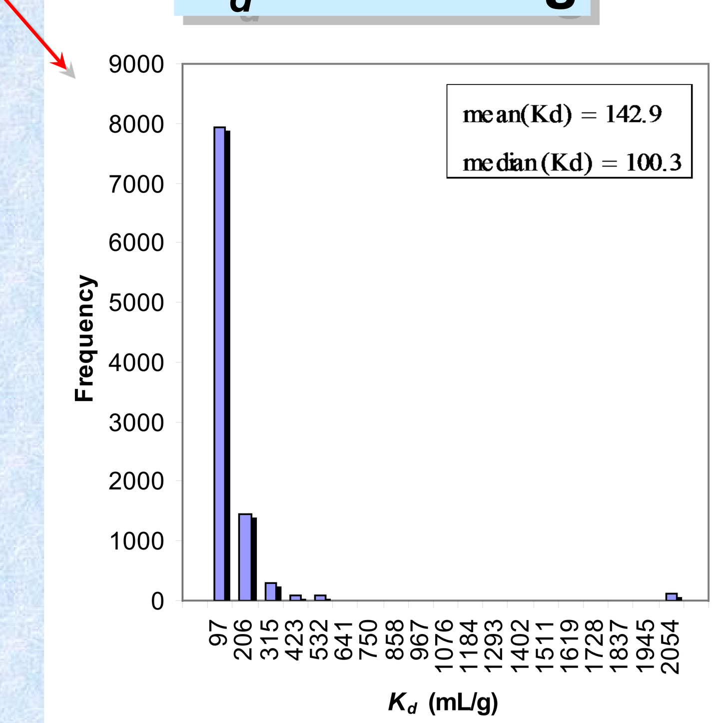
Ideal Sorption ($f \approx 0.5$)

95% Confidence Intervals
- $0.38 < C_f/C_i < 0.62$
- $0.62 < f < 0.38$

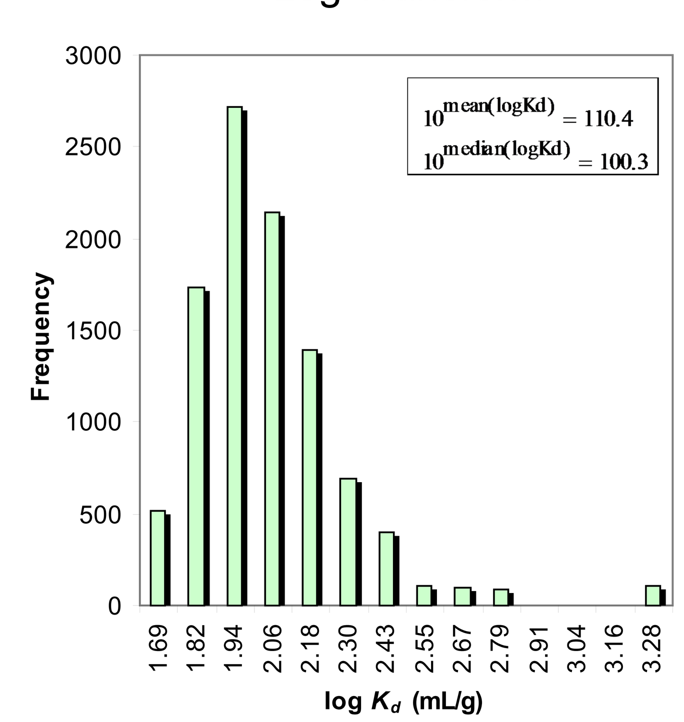
No Problems
- The ASTM D 4646 method has the perfect r_{ws} for a K_d of 20 mL/g

Lognormal Distribution
- Log transform of K_d generates a nearly normal distribution

C. K_d = 100 mL/g



Log Transform



Too Much Sorption (f > 0.8)

95% Confidence Intervals
- $0.05 < C_f/C_i < 0.29$
- $0.71 < f < 0.95$

Problems
- Huge variance due to high sensitivity of K_d to f at high f (Figure 1)
- Skewed distribution even after log transform
- Potential detection limit problems

Solution
- Determine median K_d
- Increase r_{ws} to median K_d and redo the experiments

Discussion

Optimal Design

A partitioning experiment can be optimized by adjusting the water:sorbent ratio (r_{ws}) to match the expected K_d. This idea is not new. The adjustment will cause approximately 50% of the sorbate to sorb. As shown in Figure 1, when 50% sorbs, K_d sensitivity to measurement variance is minimized.

$$r_{ws} = K_d$$

Uranium and Plutonium

Modeling the transport of uranium and plutonium in ground water generally requires the measurement and use of U and Pu K_d values. Unfortunately, the same problems that appear in the Monte Carlo simulations in this study are observed in sets of U and Pu K_d measurements (e.g., BSC 2004). Because the water:sorbent ratio (r_{ws}) is locked at 20 mL/g by ASTM D 4646, fractions adsorbed in these tests are typically below 5% for U and above 95% for Pu.

Numerous oxidation states and complexation reactions likely contribute to uncertainty in U and Pu K_d measurements. These complexities, however, should not trivialize application of the optimal design rule above.

Conclusions

Variance in partitioning measurements can be considerably reduced by setting the solution:sorbent ratio (r_{ws}) to the expected K_d value so that approximately half of the solute sorbs (f = 0.5).

Too Little Sorption (f < 0.2)
- High log K_d sensitivity to variance in f measurements (Figure 1)
- Frequent nonsensical negative K_d measurements due to C_f measurements that exceed C_i (Analysis A)
- K_d distributions that are difficult to characterize (Analysis A)

Too Much Sorption (f > 0.8)
- High K_d sensitivity to variance in f measurements (Figure 1)
- High variance in K_d measurements (Analysis C)
- Skewed distributions (Analysis C)
- Potential detection limit problems

The Monte Carlo simulations demonstrate that the error-savvy design advocated here minimizes variance in partitioning measurements and allows improved probabilistic characterization for transport modeling. This approach may not be feasible in every situation and should not preclude the use of other methods of measuring mobility such as column experiments and in situ partitioning measurements.

References

1. ASTM D 4646 - 03. Standard Test Method for 24-h Batch-Type Measurement of Contaminant Sorption by Soils and Sediments. ASTM International, West Conshohocken, PA.
2. BSC 2004. Radionuclide Transport Models Under Ambient Conditions. MDL-NBS-HS-000008 REV 02. Las Vegas, Nevada: Bechtel SAIC Company. Available at http://www.ocrwm.doe.gov.
3. EPA402-R-99-004A 1999. Understanding Variation in Partition Coefficient, K_d, Values. Volume I: The K_d Model of Measurement, and Application of Chemical Reaction Codes. U.S. Environmental Protection Agency, Washington, DC.

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