Review of Uncertainty Analysis in Geochemical Speciation

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Introduction

Human activities inevitably involve the use of harmful, dangerous chemicals. Geochemical computer models predict how such chemicals move through and interact with the environment; they can also suggest how to reduce or manage the resulting dangers to the environment, crops, animals, and humans. Although these models are believed to be true, they are, on average, a simplification of the system being studied.

Background

Although a computer simulation may have an answer for every question, it is necessary to estimate how reliable or uncertain these answers are.

We can categorize uncertainty into three types:

- **Model uncertainty**–we know that the computer simulation uses some mathematical and chemical models of the process being studied.
- **Parameter/database uncertainty**–the simulation relies on a database of parameters such as thermodynamic constants that determine chemical reaction rates.
- **Input uncertainty**–the model is fed input data that is surely subject to various kinds of measurement error and bias.

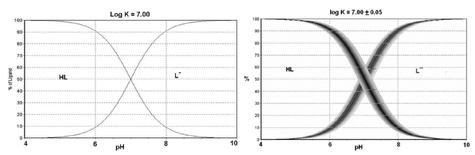

Figure 1: "Typical speciation curves: (a) as normally drawn, (b) proposed format" from a study describing techniques for demonstrating the effect of errors on parameters (Pettit and Pettit, 2009).

Any geochemical computer simulation result should therefore be accompanied by some estimate of the magnitudes of the uncertainties and their influence on the accuracy of the result. The purpose of this review to present an overview of those results.

Model Uncertainty

Model uncertainty considers the differences in how certain underlying processes, such as site densities and metal ion binding, are quantified, and what reaction equations are considered.

In a study by Unsworth (2000), PHREEQCI and WHAM (Model V), two chemical speciation programs were compared. First, a uranium speciation simulation was ran with the programs' default datasets (with the FA data addition for PHREEQCI).

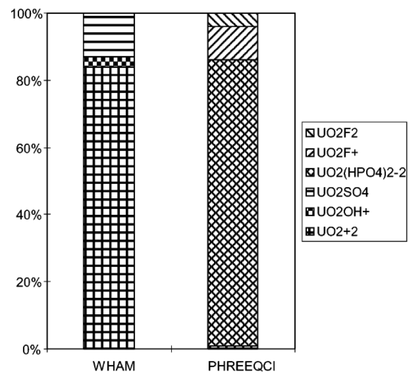

Figure 2: "Predicted uranium speciation using two different (WATEQ4F and MINTEQ) thermodynamic databases with the same program (PHREEQCI)" (Unsworth et al. 2002).

Then two different databases, MINTEQ and WATEQ4F, were used for the same uranium speciation problem using PHREEQCI. Analogously, the same simulation was repeated with both software but with data imported from a database from the Nuclear Energy Agency (NEA) database.

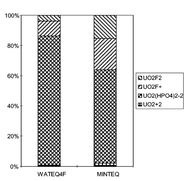

Figure 3: "Predicted uranium speciation using the WHAM and PHREEQCI programs" (Unsworth et al. 2002).

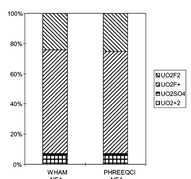

Figure 4: "Predicted uranium speciation using WHAM and PHREEQCI with the NEA-TDB dataset" (Unsworth et al. 2002).

Parameter Uncertainty

Sometimes called database uncertainty, parameter uncertainty may come from inconsistent or unreliable thermodynamic constants for the model being studied. These constants are often collected into large databases that contain data for several thousand chemical species.

In Schecher and Driscoll's study (1987), the focus was to evaluate the effect of error on database parameters on speciation calculations of aluminum also using MC methods. It was found that uncertainty of the thermodynamic constants varied with pH. In addition, uncertainty in specific complexes (AlF and AlSO4) affected the overall uncertainty of all aqueous complexes in the solution.

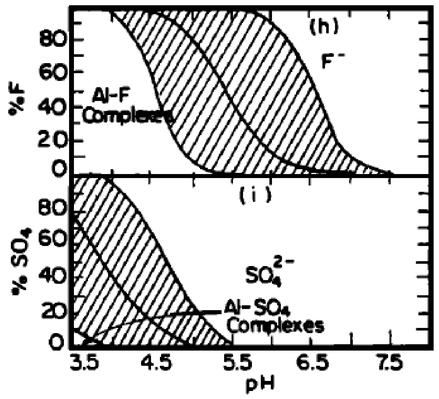

Figure 5: "Confidence limits (98%) for mean model output due to variations in equilibrium constants obtained from literature" (Schecher and Driscoll, 1987).

Input Uncertainty

Input uncertainty may come from an incomplete characterization or lack of information of the solution being studied. Groenenberg et al (2010), considered dissolved organic matter (DOM) characterization consisting of fulvic acid (FA) as an input variable that has large variability; FA makes up anywhere between 40-100% of DOM. Using MC, the output uncertainty is predicted to be high with increasing pH and FA fraction.

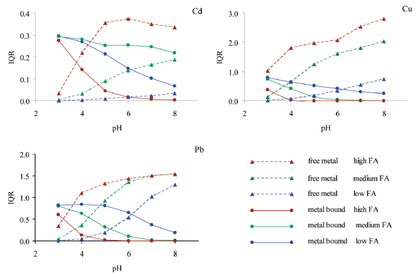

Figure 6: "Interquantile ranges (between 25-75%-iles) of the model predictions from MC simulations for log concentrations of metal bound to FA and the free metal ion as a function of pH for various concentrations of FA (high=200, medium=20, low=2mg$\dot{L}^{-1}$ for Cd, Cu, and Pb" (Groenenberg et al, 2010).

Closing Remarks

The model, parameters chosen, and input variables all affect the accuracy of geochemical equilibrium calculations. Careful consideration is required when choosing a model, thermodynamic database, and input variables when modeling geochemical systems.

References

[Groenenberg et al., 2010] Groenenberg, J. E., Koopmans, G. F., and Comans, R. N. J. (2010). Uncertainty analysis of the nonideal competitive adsorption–donnan model: effects of dissolved organic matter variability on predicted metal speciation in soil solution. *Environ. Sci. Technol*, 44:1340–1346.

[Pettit and Pettit, 2009] Pettit, L. and Pettit, G. (2009). A more realistic approach to speciation using the iupac stability constants database. *Pure Appl. Chem.*, 81:1585–1590.

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[Unsworth et al., 2002] Unsworth, E. B., Jones, P., and Hill, S. J. (2002). The effect of thermodynamic data on computer model predictions of uranium speciation in natural water systems. *J. Environ. Monit.*, 4:528–532.