

# PSUEDOKINETICS ARISING FROM THE UPSCALING OF EQUILIBRIUM

PHILIP J. BINNING<sup>1</sup>, MICHAEL A. CELIA<sup>2</sup>, LI LI<sup>2</sup>

<sup>1</sup>Institute of Environment and Resources, Technical University of Denmark, Bygningstorvet, Building 115, DK-2800 Kgs. Lyngby, Denmark.

<sup>2</sup>Department of Civil and Environmental Engineering, Princeton University, Princeton, NJ 08544, USA.

## ABSTRACT

Multicomponent contaminant transport models in groundwater are typically based on assumptions of local geochemical equilibrium on the grid scale. In heterogenous systems there may be significant coupling between transport processes and geochemical equilibrium at smaller than grid block scale. When these processes are upscaled to grid scale, geochemical evolution may take on a kinetic character. We have termed this upscaled kinetic behaviour as pseudo-kinetics and illustrate it through some examples at the pore and aquifer scales.

## 1. INTRODUCTION

When modelling multicomponent contaminant transport in groundwater, it is common to assume geochemical equilibrium. Widely used models making this assumption include PHREEQC [Parkhurst and Appelo, 1999] and its two-dimensional relative PHAST. Most users unquestioningly accept the equilibrium assumption - but does it really apply? This paper addresses this question and shows that when equilibrium geochemical and transport processes are coupled at the small scale, then a macroscopic concentration is often not at equilibrium, where the large scale concentration is defined as an average of smaller scale values.

When we write the contaminant transport equation, there is an implicitly assumed averaging scale in the governing equation because concentration is a macroscopic variable that is defined over a control volume. That control volume can be defined by the pore scale, some geological length scale, or a grid block for a regional model. All these possibilities assume that a representative elementary volume can be defined in a way that ensures that concentration is a well behaved and smooth variable. Typically when defining such a concentration, it is assumed that geochemical processes occurring at the small scale are reproduced at the larger scale, or that geochemical processes scale up in the simplest way. This paper will show that this is not always true. Examples will be used to illustrate when it is reasonable to assume that geochemical equilibrium processes are scale invariant.

Examples where conservative tracers appear to be non-conservative in upscaling systems can be found in the literature. For example, Martin-Hayden and Robbins [1997] showed that if concentrations are measured using monitoring wells with long well screens, an

averaging takes place where clean and contaminated water are mixed to produce lower concentration values. If these average concentrations are analysed with a contaminant transport model, the modeller may erroneously conclude that biodegradation processes are taking place.

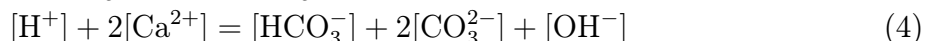
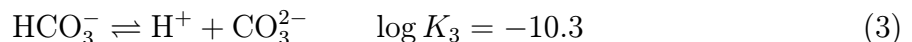
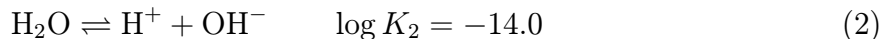
Geochemists have long recognised the need to carefully evaluate the equilibrium assumption. For example, Lichtner [1996] showed that there is some length and time scale above which reaction kinetics can be ignored and geochemical equilibrium assumed. These scales can be determined by the requirement that the Damköhler number be greater than 1 for local equilibrium, where the Damköhler number is defined to be the ratio between a first order reaction rate, a length scale and the velocity  $Da = \frac{kL}{v}$ .

Finally, macrokinetic behaviour is well known to occur in upscaled systems where equilibrium sorption processes occur. For example, Miralles-Wilhelm and Gelhar [1996] show how kinetic reaction terms arise in upscaled equations for heterogeneous systems.

None of the previous authors have considered the possibility that similar pseudokinetic behaviour occurs when upscaling groundwater systems where geochemical equilibrium is known to occur at the small scale. This paper provides two examples to illustrate the occurrence of pseudokinetics. In both examples, the length scales are determined over which pseudokinetic behaviour is observed.

## 2. RESULTS

The first example is at the pore scale, while the other considers an aquifer scale system. Both examples consider calcite dissolution. A calcite and water system can be described by the geochemical equilibrium and mass balance expressions:



The system is characterised by 5 variables ( $[\text{Ca}^{2+}]$ ,  $[\text{CO}_3^{2-}]$ ,  $[\text{HCO}_3^-]$ ,  $[\text{H}^+]$ ,  $[\text{OH}^-]$ ) and 5 equations. If the mineral calcite is present, then all five species are determined. In porous media where calcite is not present, the calcite equilibrium equation (1) does not apply and the system has one degree of freedom. In that case, transport processes determine the concentrations of the five species. To fully describe the system it is therefore necessary to describe the transport of only one of the 5 species as the others follow from the 4 remaining equilibrium expressions.

**2.1. Pore scale pseudokinetics.** The first example considers water flowing into a pore of radius  $R$ . The pore walls are non-reactive at the upstream end and pure water flows in the pore. At a certain point ( $z \geq 0$ ), the walls of the pore become calcite. Here the concentration of the equilibrium species is determined downstream of the transition ( $z \geq 0$ ). The distribution of the the five species can be determined using the Graetz-Nusselt solution (see page 381 Bird et al. [2002]). This analytical solution was originally developed to describe heat transfer in pipes, but can also be applied to the dissolution problem described here as it is governed by the same equations. The Graetz-Nusselt

solution employs the water continuity and water flow equations to describe the steady state velocity distribution in the pipe:

$$(\nabla \cdot \mathbf{v}) = 0 \quad (6)$$

$$\rho[\mathbf{v} \cdot \nabla \mathbf{v}] = \mu \nabla^2 \mathbf{v} - \nabla \mathcal{P} \quad (7)$$

where  $\mathbf{v}$  is the velocity,  $\rho$  the density and  $\mu$  the viscosity and  $\mathcal{P} = p + \rho gh$  the modified pressure. The velocity is then given in cylindrical coordinates by (equation 2.3-18, Bird et al. [2002]):

$$v_z = \frac{(\mathcal{P}_o - \mathcal{P}_L)R^2}{4\mu L} \left[ 1 - \left( \frac{r}{R} \right)^2 \right] \quad (8)$$

where  $\mathcal{P}_o$  is the characteristic pressure and  $\mathcal{P}_L$  is the modified pressure at some distance  $z = L$ . The maximum velocity occurs in the center of the pore and is given by:

$$v_{z,max} = \frac{(\mathcal{P}_o - \mathcal{P}_L)R^2}{4\mu L} \quad (9)$$

and the radially averaged velocity is defined to be

$$\langle v_z \rangle = \frac{1}{A} \int_0^{2\pi} \int_0^R v r dr d\theta = \frac{1}{2} v_{z,max} \quad (10)$$

where  $A$  is the cross sectional area of the pore. The steady state distribution of contaminant mass is governed by the advection diffusion equation:

$$\mathbf{v} \cdot \nabla c - D_o \nabla^2 c = 0 \quad (11)$$

where  $D_o$  is the diffusion coefficient, subject to

$$c(z=0) = c_1 \quad c(z=\infty) = c_o \quad c(r=R) = c_o \quad \frac{\partial c}{\partial r}(r=0) = 0 \quad (12)$$

The solution is obtained after introduction of the following dimensionless variables:

$$\Theta = \frac{c - c_o}{c_1 - c_o} \quad \phi = \frac{v_z}{\langle v_z \rangle} \quad \xi = \frac{r}{R} \quad \zeta = \frac{D_o z}{\langle v_z \rangle R^2} \quad (13)$$

Here  $c_1$  is the entrance concentration and  $c_o$  is the wall concentration. Neglecting diffusion in the  $z$ -direction (it is much smaller than the advection), the equation can be written

$$\phi \frac{\partial \Theta}{\partial \zeta} - \frac{1}{\xi} \frac{\partial}{\partial \xi} \left( \xi \frac{\partial \Theta}{\partial \xi} \right) = 0 \quad (14)$$

where

$$\phi = 2[1 - \xi^2] \quad (15)$$

Separation of variables then gives:

$$\Theta(\xi, \zeta) = X(\xi)Z(\zeta) \quad (16)$$

$$\frac{\partial Z}{\partial \zeta} = -c^2 Z \quad (17)$$

$$\frac{1}{\xi} \frac{\partial}{\partial \xi} \left( \xi \frac{\partial X}{\partial \xi} \right) + c^2 \phi X = 0 \quad (18)$$

Subject to

$$Z(0) = 1 \quad Z(\infty) = 0 \quad X(1) = 0 \quad X'(0) = 0 \quad (19)$$

The solution is:

$$Z = e^{-c^2\zeta} \quad (20)$$

$$X(\xi) = \sum_{i=1}^{i=\infty} A_i X_i(\xi) \quad (21)$$

where  $X_i(\xi)$  is an eigenfunction satisfying (18). The eigenfunctions satisfy the orthogonality condition

$$\int_0^1 \xi \phi X_i X_j d\xi = 0 \quad i \neq j \quad (22)$$

By applying the boundary condition at  $\zeta = 0$  we know that

$$\sum_{i=1}^{i=\infty} A_i X_i(\xi) = 1 \quad (23)$$

Multiplying this by  $X_i \xi \phi$  and applying the orthogonality condition (22), the unknown coefficients can be determined as

$$A_i = \frac{\int_0^1 X_i \xi \phi d\xi}{\int_0^1 X_i^2 \xi \phi d\xi} \quad (24)$$

The solution is shown in Figure 1 for a pore of radius 0.005 m,  $c_o = 1.1 \times 10^{-4}$  mol/L (the equilibrium concentration of  $\text{Ca}^{2+}$  in water in the presence of calcite),  $D_o = 0.792 \times 10^{-9}$  m<sup>2</sup>/s ( $\text{Ca}^{2+}$  in water),  $\frac{\mathcal{P}_o - \mathcal{P}_L}{L} = 0.001$  Pa/m and  $\mu = 1.0019 \times 10^{-3}$  PaS. The radially averaged concentration can be calculated directly from the solution and is shown in Figure 2. For a pore of radius 0.005 m, the average velocity is 98m/yr and the average concentration in the water reaches equilibrium after approximately 0.1 m. For distances less than 0.1 m, the water within the pore is not at equilibrium. At the large (pore averaged) scale, the solution takes time to reach equilibrium concentrations and this time can be interpreted as "psuedo-kinetics", or kinetics that are not present in the actual problem, but are artefacts of the averaging process.

The analytical solution can be used to calculate an equilibrium length scale for a given pore radius  $R$ , where the equilibrium length scale is defined to be the distance a contaminant must be transported before geochemical equilibrium occurs in the macroscopically averaged variable. When

$$\zeta = \frac{D_o z}{\langle v \rangle R^2} = 1 \quad (25)$$

in (16), then  $\frac{\langle c_z \rangle}{c_o} = 0.99$ . Substituting the expression for  $\langle v_z \rangle$  given by (10) into (25), then it can be seen that

$$L_{eq} = \frac{(\mathcal{P}_o - \mathcal{P}_L) R^4}{8\mu L D_o} \quad (26)$$

Calculations of  $L_{eq}$  are shown in Figure 3 for various pore radii. It can be seen that psuedo-kinetic effects are only significant for large pores. For example, for pore radii of 1 mm the equilibrium length scale is 0.16 mm.

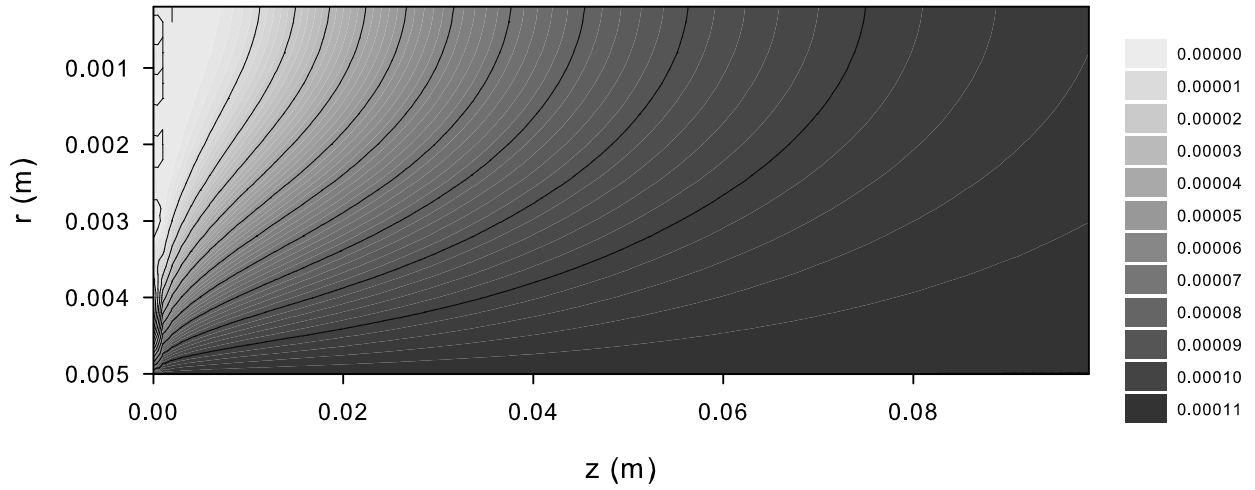


FIGURE 1. Concentration distribution of  $[Ca^{2+}]$  in a pore as a function of radial distance from the centre of the pore. Calcite is present on the pore walls for  $z \geq 0$  where  $z$  is the distance along the main axis of the pore and pure water enters the pore at  $z = 0$

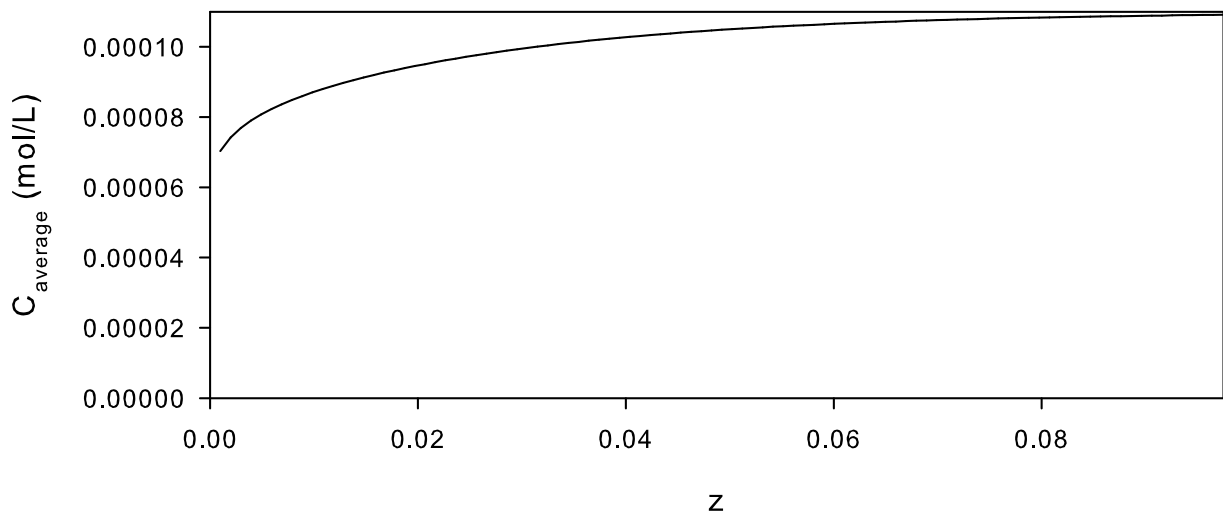


FIGURE 2. Average pore concentration (over  $r$  at a given cross section) of the concentration distribution shown in figure 1.

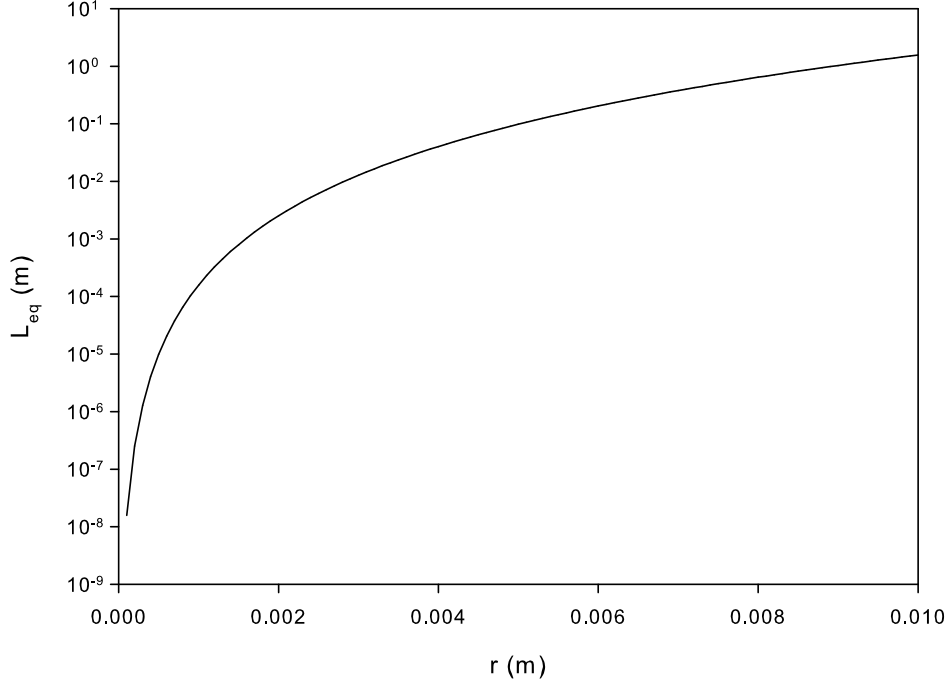


FIGURE 3. Distance that pore water must travel down a pore of radius  $R$  before the average concentration reaches 99% of the equilibrium concentration for a pressure gradient  $\frac{\mathcal{P}_o - \mathcal{P}_L}{L} = 0.001$  Pa/m.

**2.2. Aquifer scale psuedo kinetics.** A similar approach can be used to obtain an analytical solution on the aquifer scale. In that case, groundwater flows into an aquifer with velocity  $v$ . At a point ( $z \geq 0$ ) the upper and lower aquifer boundaries change to calcite. If these boundaries are separated by a distance  $B$ , then the concentration in the aquifer at steady state can be determined by the solution of the equation:

$$v \frac{dc}{dx} - D_x \frac{d^2c}{dx^2} - D_z \frac{d^2c}{dz^2} = 0 \quad (27)$$

where  $D_x$  and  $D_z$  are the dispersion coefficients in the  $x$  and  $z$  directions, subject to

$$c(0, z) = 0, c(\infty, z) = c_{eq}, c(x, 0) = c_{eq}, \frac{dc}{dx}(x, B) = 0 \quad (28)$$

The solution can be obtained by separation of variables and is given by

$$c(x, z) = \sum_{n=0}^{\infty} A_n \sin(c_n z) e^{mx} \quad (29)$$

where  $A_n = \frac{4}{(2n+1)\pi}$ ,  $c_n = \frac{(2n+1)\pi}{2B}$ ,  $m = \frac{Pe_x}{2B} \left[ 1 - \sqrt{1 + \frac{(2n+1)^2 \pi^2}{Pe_x Pe_z}} \right]$ ,  $Pe_x = \frac{vB}{D_x}$ ,  $Pe_z = \frac{vB}{D_z}$ . Equilibrium length scales can be obtained in the same way as for the pore scale example. If parameters similar to those of the Cape Cod Field experiment are used ( $v = 0.341$  m/day,  $\alpha_L = 0.96$  m and  $\alpha_T = 0.018$  m, where  $D_x = \alpha_L v$  and  $D_z = \alpha_z v$ ) [Garabedian et al, 1991],

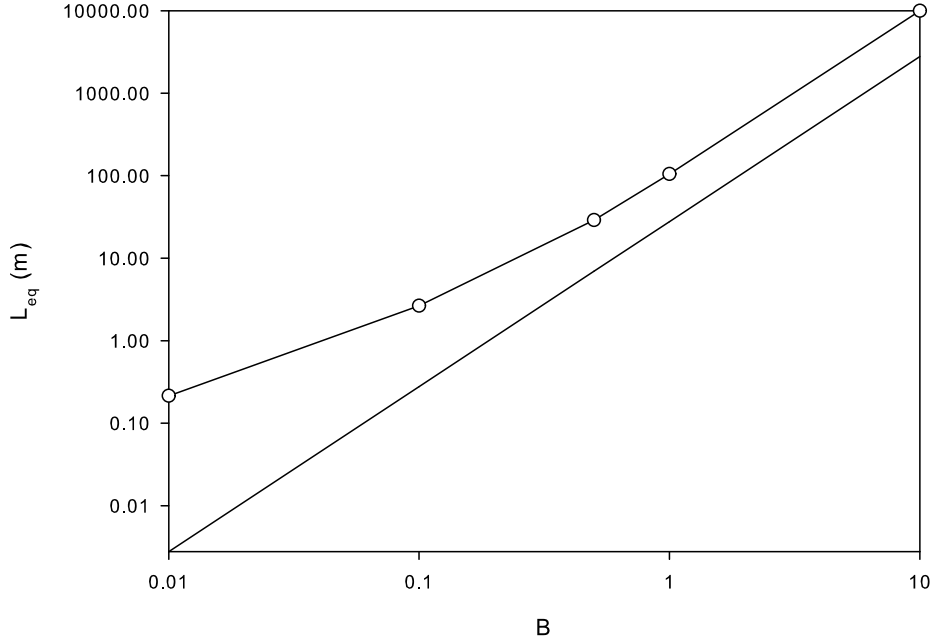


FIGURE 4. Distance that ground water must travel between calcite deposits separated by  $2B$  before the average concentration is 99% of equilibrium (Symbols). Also shown is a "mixing length" (no markers).

then the equilibrium length scales are shown for various aquifer thicknesses  $B$  in Figure 4. The figure shows that if calcite layers are separated by a distance of 1m, then the system does not come to equilibrium for 103m. For layers separated by 10m, the length scales are approximately 10,000m. These calculations indicate that if calcite intrusions in an aquifer are separated by any appreciable distance, then the aquifer cannot in practice be regarded as being at equilibrium with calcite. To model this system a small scale equilibrium model or an upscaled psuedo-kinetic model is required.

The equilibrium length scales are related to mixing lengths. The mixing length can be derived by noting that the dimensions of a contaminant plume are related to its variance  $\sqrt{2D_z t}$ . If  $B = L_{mix} = \sqrt{2D_z t}$  and the time is given by the velocity and mixing length as  $t = \frac{L_{mix}}{v}$ , then  $L_{mix} = \frac{B^2}{2\alpha_T}$ . As can be seen in Figure 4, the mixing length is approximately equivalent to the equilibrium length.

### 3. CONCLUSIONS

Some simple analytical solutions have been used to show that upscaling can lead to the appearance of psuedo-kinetic reactions in the macroscale variables and that psuedo kinetic behaviour will occur at all scales. Equilibrium length scales are significant for large pores and for aquifers where there is an appreciable distance between calcite inclusions. For instance, an aquifer with transport parameters similar to those observed in the Cape Cod field experiment and calcite intrusions separated by 10m, cannot be expected to come to

equilibrium for many kilometers. Equilibrium length scales are related to mixing lengths that have been discussed for many decades in the literature.

Pseudo kinetic reactions can be expected to occur whenever there is geological heterogeneity or concentration gradients. Modelling such systems is challenging because we usually do not know the exact geometry of the geology. Without having a precise description of that geology it is not reasonable to assume geochemical equilibrium in contaminant transport. Future work must focus on the statistical description of geochemical heterogeneity and the definition of upscaled equations. An approach similar to that employed by Miralles-Wilhelm and Gelhar [1996] to upscale equilibrium sorption processes might be fruitful.

#### REFERENCES

- Bird, R.B., Stewart, W.E. and Lightfoot, E.N. (2002) *Transport phenomena*, 2nd ed., 895pp., John Wiley and Sons Inc, New York.
- Garabedian, S.P., LeBlanc, D.R., Gelhar, L.W. and Celia, M.A. (1991) Large scale natural gradient tracer test in sand and gravel, Cape Cod Massachusetts. 2. Analysis of spatial moments for a nonreactive tracer. *Water Resources Research* 27(5), 911-924.
- Lichtner, P.C. (1996) Continuum formulation of multicomponent-multiphase reactive transport, in *Reactive transport in porous media*, Lichtner, P.C., Steefel, C.I. and Oelkers, E.H. (eds), Mineralogical Society of America.
- Martin-Hayden, J.M. and Robbins, G.A. (1997) Plume distortion and apparent attenuation due to concentration averaging in monitoring wells. *Ground Water* 35(2), 339-346.
- Miralles-Wilhelm, F. and Gelhar, L.W. (1996) Stochastic analysis of sorption macrokinetics in heterogeneous aquifers. *Water Resources Research* 32(6), 1541-1549.
- Parkhurst, D.L. and Appelo, C.A.J. (1999) User's guide to PHREEQC (Version 2)—a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, *U.S. Geological Survey Water-Resources Investigations Report 99-4259* 312pp., US Geological Survey.