Modeling of the Sorption Process

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Accurately modeling of the sorption process is critical to understanding the long-range impacts of PCBs, especially at this site. Wu and Gschwend[1] have developed a practical theory for the sorption process based on reversible transient diffusion. Wu and Gschwend approximate the media as a probabilistic distribution of variable sized spheres. Wu and Gschwend[2] have demonstrated that the theory is both practical and accurate based on laboratory experiments with a variety of organics and sediments. Application of the method to this site will provide a superior quantitative prediction of the migration of PCBs and provide a better means of evaluating remediation and containment strategies than the simplistic classical approach. It is therefore recommended that this approach or its equivalent be required.

Wu and Gschwend begin with Fick's Law for transient diffusion in spherical coordinates, Equation 1.

$$\frac{\partial S(r)}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2 D_{eff} \frac{\partial S(r)}{\partial r} \right] \qquad 1$$

Where $\boldsymbol{S}$ is local concentration in the solid. They define an effective diffusion coefficient, $\boldsymbol{D_{eff}}$, by Equation 2.

$$D_{eff} = \frac{D_m n^2}{(1-n)\rho_s K_p + n} \qquad 2$$

Where $\boldsymbol{D_m}$ is the aqueous solution molecular diffusivity, $\boldsymbol{K_p}$ is the equilibrium partition coefficient, $\boldsymbol{\rho_s}$ is the dry solid density, and $\boldsymbol{n}$ is the inter-aggregate porosity. The average concentration for a single spherical particle is given by Equation 3.

$$\overline{S} = \frac{3}{4\pi R^3}\int_0^R 4\pi r^2 S(r)dr \qquad 3$$

The rate of change of the concentration in the aqueous phase is given by Equation 4.

$$\frac{dC}{dt} = -\frac{V_s}{V}\frac{d}{dt}\left[\frac{3}{R^3}\int_0^R r^2 S(r)dr \right] \qquad 4$$

Where $\boldsymbol{C}$ is the concentration in the aqueous phase, $\boldsymbol{V}$ is the volume of the solution, and $\boldsymbol{V_s}$ is volume of the solid phase. The concentration in the aqueous phase over time can then be computed by integrating Equation 4 with respect to time, yielding Equation 5.

$$C(t) = C_0 - \int_0^t \left\{ \frac{V_s}{V} \frac{d}{dt} \left[\frac{3}{R^3} \int_0^R r^2 S(r) dr \right] \right\} \qquad 5$$

No closed-form solution exists for Equation 5; therefore, it must be solved using numerical means. Several numerical methods are available for solving such integro-differential equations. Wu and Gschwend used the Explicit Euler Method implemented in BASIC code in their ***Water Resources Research*** paper. This formulation incorporates the physical properties of the contaminant and the solid media as indicated by the previously defined parameters in Equations 1 through 4.

In their ***Environmental Science Technology*** paper, Wu and Gschwend compare their computed results with laboratory measurements. They tested dichlorobenzene, trichlorobenzene, tetrachlorobenzene, and pentachlorobenzene with Charles River sediments, Iowa Soils, and North River sediments. The agreement between computed and observed concentrations over time was quite good for these combinations of organics and sediments. These experiments provide some level of validation for the accuracy of the method.

In order to apply this method for computing the transient concentration of PCBs in the aqueous phase at this site, the physical organic parameters (i.e., the aqueous molecular diffusivity, $\boldsymbol{D_m}$, the equilibrium partition coefficient, $\boldsymbol{K_p}$, the dry solid density, $\boldsymbol{\rho_s}$, the inter-aggregate porosity, $\boldsymbol{n}$, and the volume of the solid phase, $\boldsymbol{V_s}$) and the physical sediment parameters (i.e., particle size distribution) are required. The estimated concentration is then computed by numerically solving Equation 5 with these parameters. As this calculation would also be of use at other sites, a simple-to-use computer program could be developed to provide these calculations on a more general basis.

References

[1]Wu, S. C. and P. M. Gschwend, 1988, "Numerical Modeling of Sorption Kinetics of Organic Compounds to Soil and Sediment Particles," ***Water Resources Research***, Vol. 24, No. 8, pp. 1373-1383.

[2]Wu, S. C. and P. M. Gschwend, 1986, "Sorption Kinetics of Hydrophobic Organic Compounds to Natural Sediments," ***Environmental Science Technology***, Vol. 20, No. 7, pp. 717-725.