Remediation of contaminated sediments is one of the most challenging problems in environmental engineering today. One of the few effective means of reducing exposure and risk to contaminated sediments is through the use of capping with clean media. The primary purposes of a cap over contaminated sediments include:

1. armor contaminated sediments to ensure they are not re-suspended in high flow conditions
2. physically isolate contaminated sediments from benthic organisms that typically populate only the upper few cm of sediments
3. provide a mass transfer resistance to advective and diffusive processes that encourage chemical release from the sediments

Because most sediment contaminants are highly sorptive, their migration through a cap is retarded due to transient accumulation on the clean cap material. Thus the time for typical sediment contaminants to migrate through a cap can be hundreds or thousands of years if the cap is designed and maintained to retain its integrity throughout that period. Effective design of a cap to isolate contaminated sediments requires a model capable of describing the chemical fate and transport processes that take place within the cap.

The standard method of estimating chemical migration in a cap is via a transient advection-diffusion model as described in Palermo et al. (1998). Normally, an analytical solution to the mass conservation equation, assuming the cap is semi-infinite, is employed in such an analysis. Such a model is, in general, not applicable after the conditions at the top of the cap (such as benthic activity or changing organic carbon content) influence contaminant behavior. This is a serious limitation in that the protectiveness of a cap is largely defined by the contaminant behavior in the biologically active zone. This zone is subject to significantly different transport processes and rates than in the underlying cap layer and may exhibit significantly different physical and chemical characteristics, such as increased organic carbon content and sharp gradients in redox conditions.

An alternative approach is to consider only steady state conditions, in which it is possible to consider the complexities of the upper boundary and still employ relatively simple analytical solutions to the chemical transport equations. The estimation of flux through a cap at steady state is conservative as the contaminant flux is a maximum at steady state. To further ensure conservatism, the concentration beneath the cap layer (that is, in the underlying contaminated sediment) is assumed to maintain a constant concentration with no depletion due to chemical reactivity or migration into the cap. This maximum flux can then be used to estimate concentrations in the biologically active layer. Chemical reactivity in the cap or biologically active layer can be incorporated for appropriate compounds by employing either measured rates of degradation or by considering conservative estimates from the literature. Through use of the steady state design approach, it is possible to estimate the maximum contaminant concentration that may ever be achieved within the biologically active zone. The
presumption is if predicted contaminant concentrations under steady state conditions do not exceed levels of concern or excessive risk, then a cap would be effective management approach for the contaminated sediments. The goal of this paper is to develop a simple and easy to use steady state model based upon this framework that can be used to make conservative estimates of a cap’s protectiveness over long times.

For the purposes of this model, the sediment cap/water column was divided into five layers: the underlying sediment, the containment layer, the bioturbation layer, the boundary layer, and the overlying water column. The overall flux of contaminant to the overlying water column was assumed to be dictated by transport through the containment layer. Figure 1 shows a chart of the sediment cap system along with some of the model parameters.

\[
\begin{align*}
\text{Underlying Sediment} & : C = C_0 \text{ (constant)} \\
\text{Cap Layer, } C & : \text{Advection, Diffusion, Decay} \\
\text{Bioturbation Layer, } C_{\text{bio}} & : \text{Advection, Bioturbation (Pore Water and Particle)} \\
\text{Boundary Layer, } C_{\text{bl}} & : \text{Mass Transfer} \\
\text{Overlying Water} & : C_w \approx 0
\end{align*}
\]

**Figure 1. Sediment Cap System.**

Different transport processes influence the different layers. The transport processes considered in the cap layer were advection, diffusion, and first-order decay. Transport through the bioturbation layer was assumed to be dictated by advection and bioturbation of both the pore water and the sediment particles. Transport through the boundary layer was assumed to be dictated by advection and mass transfer (modeled with a boundary layer mass transfer coefficient). The underlying sediment and overlying water concentrations were assumed to be constant.

Using a mass balance approach, the steady-state flux through the cap layer was:

\[
J = \frac{D_{\text{eff}}}{h_{\text{cap}} \sinh \alpha} \left\{ \alpha e^{\frac{Pe}{2}} C_0 - \left[ \frac{Pe}{2} \sinh \alpha + \alpha \cosh \alpha \right] C_{\text{bio}} \right\} + UC_{\text{bio}}
\]
(2) \[ \alpha = \sqrt{\frac{Pe^2}{4} + Da} \]

Where:

\( J \) = flux
\( C_0 \) = aqueous-phase concentration at cap-sediment interface
\( C_{bio} \) = aqueous-phase concentration in bioturbation layer
\( C \) = aqueous-phase concentration
\( z \) = depth
\( D_{eff} \) = effective diffusivity
\( U \) = Darcy velocity
\( \lambda \) = first-order decay rate
\( \varepsilon \) = porosity

\( Pe = \) the Peclet Number = \( \frac{Uh_{cap}}{D_{eff}} \) = the relative importance of advection to diffusion

\( Da = \) the Damkohler Number = \( \frac{\varepsilon \lambda h_{cap}^2}{D_{eff}} \) = the relative importance of decay to diffusion

The flux through the bioturbation and boundary layers can be related through mass transfer coefficients. The flux through the bioturbation layer is comprised of the advective flux, the bioturbation of particles flux, and the bioturbation of pore water flux. The flux in the boundary layer is comprised of the advective flux and the mass transfer flux. Quantitatively:

(3) \[ J = (k_{bio}^p \varepsilon R_f + k_{bio}^{pw})(C_{bio} - C_{bl}) + UC_{bio} = k_{bl}(C_{bl} - C_w) + UC_{bl} \]

Where:

\( k_{bio}^p \) = particle bioturbation coefficient
\( k_{bio}^{pw} \) = pore water bioturbation coefficient
\( k_{bl} \) = boundary layer mass transfer coefficient
\( C_{bl} \) = boundary layer concentration
\( C_w \) = overlying water concentration (assumed zero)
\( R_f \) = retardation factor

The retardation factor is the ratio of the solid-phase concentration to the mobile (aqueous) phase concentration. Quantitatively:

(4) \[ R_f = 1 + \frac{\rho_{sfeKoc}}{\varepsilon} \]

Where:

\( \rho_b \) = sediment bulk density
The flux, $J$, can be determined from Equation (3). However, Equation (3) is also a function of $C_{bio}$. Combining Equations (1) and (3) and solving for the concentration in the bioturbation layer results in the following expressions:

\[ C_{bio} = \frac{\alpha e^{Pe/2}}{\left( \frac{R_{bio}}{U} - \frac{1}{2} \right) Pe \sinh \alpha + \alpha \cosh \alpha} C_0 \quad (5) \]

\[ R_{bio} = \frac{(k_{bio} p e R_f + k_{bio} p e + U)(k_{bio} + U)}{(k_{bio} p e R_f + k_{bio} p e + k_{bio} + U)}; \quad \alpha = \sqrt{\frac{Pe^2}{4} + Da} \quad (6) \]

Using a similar approach for an advectively- or diffusively- dominated system, the mathematics simplify with the following results:

\[ C_{bio} = \frac{U}{R_{bio}} \exp \left( -\frac{Da}{Pe} \right) C_0 \quad \text{(advectively-dominated system)} \quad (7) \]

\[ C_{bio} = \frac{D_{eff}}{h_{capi} R_{bio}} \frac{\sqrt{Da}}{\sinh \sqrt{Da}} C_0 \quad \text{(diffusively-dominated system)} \quad (8) \]

Equation (5) should converge to Equation (7) for large seepage rates (advectively-dominated systems) and Equation (8) for small seepage rates (diffusively-dominated systems). Figure 2 presents a plot of Equations 1, 7, and 8 versus seepage rate for typical values of the other model parameters. It also shows the convergence of the model presented here with these simpler models.
Figure 2. Convergence of Model with Simpler Models: (a) convergence with typical values for all parameters; (b) convergence with long half-life (no biodegradation); (c) convergence with short half-life (all parameters are zero).
In summary, the proposed steady state model provides a useful and conservative predictor of long-term cap flux through the cap. As such the model, although simple in form, can be used to evaluate the long-term effectiveness of a cap and provides a conservative indicator of long-term cap performance. The model can quickly determine whether a given cap is capable of achieving flux and sediment concentration targets at all times. If a cap is found to be a feasible means of achieving these risk based targets, a more complete design can be undertaken to evaluate any geotechnical issues associated with placement and stability to ensure the long-term physical integrity of the cap.

References