Parsons Engineering Department

Certificate of Software Validation

User Discipline HYDROGEOLOGY

Certification No. HY-009

Software Title. Active Capping Transport Model

Date of Validation 01/06/09

Software Supplier REIBLE(1)

Validated Version Version 2.0

Software Description and Use 1-Dimensional, solute transport model through a sediment cap, also see attached documentation.

System Requirements:

	Operating System	Windows XP/Vistas
	RAM	512K
	Hard Disk	yes
	Math Coprocessor	yes
	Windows	yes
	Other	Matlab version 7.7 or later

Restrictions/Limitations see attached documentation

The above-named software is certified as a validated software. The scope of this validation is as follows:

a. The software has demonstrated satisfactory function for its intended tasks, through the following verification methods (check all pertinent items):

- (2) By independent verification testing.
- ___ By extensive use on active projects.
- ___ Industry tested and proven.
- ___ NRC/other agency approved (list agency and number if possible).________
- (1) Supplier-performed verification.
- ___ Other (describe)________

b. All users have received/will receive suitable instructions/sufficient documentation to use the software.

Submitted: Software Custodian________ Date________

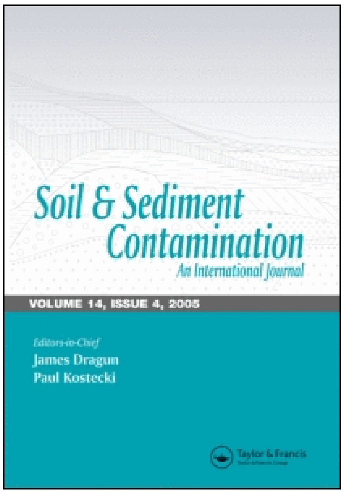
Approved: Section Manager________ Date________

(1) Danny Reible, Ph.D., Bettie Margaret Smith Professor of Environmental Health Engineering, Department of Civil, Architectural, Environmental Engineering, The University of Texas at Austin, 1 University Station C1786, Austin, TX 78712-0273.

(2) Model results were compared with well-documented 1-D solute transport equations by Charles Andrews. See attached memorandum.

Printed copies of this document are uncontrolled copies.

This article was downloaded by: *[reible@mail.utexas.edu]*
On: *24 June 2009*
Access details: *Access Details: [subscription number 912623667]*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Soil and Sediment Contamination: An International Journal
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713401148

An Analytical Modeling Approach for Evaluation of Capping of Contaminated Sediments

David J. Lampert [a]; Danny Reible [a]
[a] Department of Civil, Architectural, Environmental Engineering, The University of Texas at Austin, Austin, TX, USA

Online Publication Date: 01 July 2009

To cite this Article Lampert, David J. and Reible, Danny(2009)'An Analytical Modeling Approach for Evaluation of Capping of Contaminated Sediments',Soil and Sediment Contamination: An International Journal,18:4,470 — 488

To link to this Article: DOI: 10.1080/15320380902962387

URL: http://dx.doi.org/10.1080/15320380902962387

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Soil and Sediment Contamination, 18:470–488, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1532-0383 print / 1549-7887 online
DOI: 10.1080/15320380902962387

Taylor & Francis
Taylor & Francis Group

An Analytical Modeling Approach for Evaluation of Capping of Contaminated Sediments

DAVID J. LAMPERT AND DANNY REIBLE

Department of Civil, Architectural, Environmental Engineering,
The University of Texas at Austin, Austin, TX, USA

Downloaded By: [reible@mail.utexas.edu] At: 00:03 24 June 2009

An analytical design tool is developed to predict performance of a cap for containment of contaminated sediments. Transient conditions within a cap can be modeled by advection, diffusion, and reaction within the typically homogeneous chemical isolation layer for which analytical models exist. After contaminant penetration of the chemical isolation layer, a steady state model is proposed that incorporates pore water advection and diffusion, sediment erosion and deposition, sediment re-working and pore water pumping via bioturbation, and reaction. The steady state model allows the complexities of the biologically active layer to be considered while maintaining an analytical form for convenient and rapid evaluation. In this paper, the model framework, behavior, and limitations are presented.

Keywords Capping, contaminated sediments, modeling

Introduction

Remediation of contaminated sediments is one of the most challenging problems in environmental engineering today. One of the primary risks associated with contaminated sediments is bioaccumulation in benthic organisms, which is a route of entry into the food chain. Thus an important goal of sediment remediation is reducing concentrations to these organisms.

Few alternatives exist for management of contaminated sediments. One promising technology for reducing exposure and risk to contaminated sediments *in situ* is through the use of capping with clean media. Capping with clean media has been shown to reduce surficial sediment concentrations in the lab and to agree well with traditional mass transport models (Thoma et al., 1991). In a field study, Azcue et al. (1998) found that the flux of metals was reduced significantly one year after capping. Zeman and Patterson (1997) discuss the successful implementation of a sand cap in Hamilton Harbor, Ontario, Canada. A capping project in the St. Paul Waterway near Tacoma, Washington, successfully demonstrated habitat restoration (Parametrix, 1998). Ten years of monitoring showed minimal cap disturbance and the ability of capping to contain contaminants. As an added benefit, sand capping restored shallow-water habitat that had been reduced by 90% over the past

Address correspondence to Danny Reible, Bettie Margaret Smith Professor of Environmental Health Engineering, Department of Civil, Architectural, Environmental Engineering, The University of Texas at Austin, 1 University Station C1786, Austin, TX 78712-0273, USA. E-mail: reible@mail.utexas.edu

100 years. Simpson et al. (2002) found that capping was successful at reducing metal fluxes, particularly due to organism-induced mixing (bioturbation) in the clean cap material rather than in the sediments.

The primary purposes of a cap over contaminated sediments are:

1. Armoring contaminated sediments to ensure they are not re-suspended in high flow conditions.
2. Physically isolating contaminated sediments from benthic organisms that typically populate only the upper few cm of sediment.
3. Providing resistance to transport processes that result in chemical release from the sediments.

Because many sediment contaminants are highly sorptive, their migration through a cap can be retarded due to accumulation on the clean cap material. A portion of the cap is typically compromised by the following processes: intermixing between sediment and the lower layer of the cap, expression of contaminated pore water by consolidation of underlying sediment, and bioturbation (organism-related mixing) of the near surface layer. The remaining layer is termed the chemical isolation layer. It has been estimated that the time for typical sediment contaminants to migrate through strongly sorbing chemical isolation layers may be hundreds or thousands of years (Murphy et al., 2006). For other less sorbing caps where the breakthrough time is shorter, capping can serve as a mass transport resistance to reduce the steady state flux and surficial concentrations near the sediment-water interface.

Evaluation and design of sediment caps require a model to predict the relationship of design parameters to chemical fate and transport processes that take place within the contaminated sediment cap containment system. Chemical migration in porous containment layers can be estimated using a transient advection-diffusion model as described by Bear (1972). For example, numerous approaches to the transport of contaminants through soil containment layers have been presented (e.g. Rowe and Booker, 1985; Rubin and Rabideau, 2000; Malusis and Shackelford, 2002). The majority of this work has been applied to soil slurry liners, which differ from sediment caps in several important ways.

The top of the sediment cap (hereafter referred to as the bioturbation layer) 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. The organisms that reside in this zone also re-work sediment particles; this process significantly affects chemical transport. It is also within this zone that chemical reactivity is highest due to the exchange of nutrients, labile organic matter, and electron acceptors with the overlying water. The thickness of the cap may increase due to deposition or decrease due to erosion. Finally, mass transport at the sediment-water interface requires different boundary conditions than those used in soil slurries due to the presence of turbulent motion in the overlying surface water.

The EPA has provided guidance for *in situ* cap design (Palermo et al., 1998). The important considerations for cap design are minimizing erosion, reducing contaminant flux to biological receptors, and providing appropriate thickness to account for consolidation of the surficial sediments. The EPA guidance document presents a simplistic approach for evaluating contaminant fluxes and concentrations in a sediment cap. In this approach, the transient migration and flux through the cap system is assumed to be controlled by the chemical isolation layer and estimated by advection or diffusion. This approach does not include

Downloaded By: [reible@mail.utexas.edu] At: 00:03 24 June 2009

important processes such as degradation and cannot predict contaminant concentrations or fluxes in the biologically active zone that is often of primary importance.

In this paper, an approach is presented to address these limitations. The result is a set of analytical models that can be used for initial screening and evaluation of sediment capping. Because the models are analytical, they can be used for rapid evaluation across a range of parameter values and can be used as a check for more complex numerical models, which may be applied to situations where no exact solution to the governing equations exists.

The models developed here enable an assessment of the concentration within the chemical isolation layer of a cap at any time, the time over which a cap is effective, and the potential exposure in the biologically active zone after contaminant penetration of the chemical isolation layer. The recommended approach is to employ a one-layer analytical transient model under the assumption of a semi-infinite domain until penetration of the chemical isolation layer occurs (i.e. while the assumption is valid). Upon penetration of the chemical isolation layer, the relatively rapid transport processes in the surface layer will subsequently quickly lead to steady state conditions. Under steady state conditions it is possible to consider the complexities of the upper boundary and still employ relatively simple analytical solutions to the chemical transport equations. Through use of a steady state model, it is possible to estimate the maximum contaminant concentration and flux that may ever be achieved within the biologically active zone. Thus the model can be used to determine a conservative cap design through estimation of the maximum concentrations and fluxes in the biologically active zone. The transient model presented here is equivalent to the one presented in the EPA guidance document (Palermo et al., 1998) but is included for completeness and discussion of how to adapt the model to evaluate other processes such as burial by sediment deposition. The combination of the transient model for the chemical isolation layer and the steady state model for the chemical isolation and bioturbation layers presented here provide:

1. the concentration profiles during contaminant migration through the chemical isolation layer;
2. the time of complete separation of the benthos from the contaminants;
3. the maximum concentration and flux that will be achieved after penetration of the cap assuming constant concentration in the underlying sediment.

Downloaded By: [reible@mail.utexas.edu] At: 00:03 24 June 2009

Conceptual Model

The conceptual model divides the system into five different parts: the underlying sediment, the chemical isolation layer, the biologically active or bioturbation layer, the sediment-water interface (benthic boundary) layer, and the overlying water column. The placed cap layer, with thickness h_{cap}, consists of both the chemical isolation layer, with thickness h_{eff}, and the bioturbation layer, with thickness h_{bio}. The underlying sediment layer also includes the zone in which cap and sediment have intermixed during placement as the pore water concentrations in this region are essentially indistinguishable from those in the underlying sediment. In transient calculations any portion of the cap compromised by chemical migration due to consolidation should also be considered part of the underlying sediment (Palermo et al., 1998). Under steady state conditions, however, pore water expression and consolidation do not influence contaminant behavior.

The underlying sediment concentration is assumed constant. In a real sediment capping system, as contaminants are transported from the former sediment-water interface to the clean cap material the concentrations in the underlying sediment would change. The

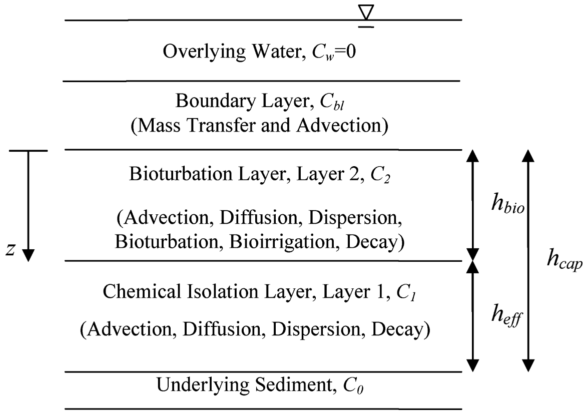


Figure 1. Sediment cap system and parameter definition.

Downloaded By: [reible@mail.utexas.edu] At: 00:03 24 June 2009

concentration at the bottom of the cap would likely decrease with depletion of mass to the capping materials. However, as shown by Rabideau and Kandelwahl (1998), the most conservative boundary condition for the underlying contaminated material in a containment system is constant concentration. Any change in the actual concentration would likely be a decrease as mass is lost to the cap material, which provides further conservatism to this assumption. An alternative to constant concentration in the sediment would be to model the entire sediment layer; this approach is more robust but would require numerical simulation to describe behavior in the sediment column and capping layer.

The transport processes in the chemical isolation layer are advection, diffusion/ dispersion, and decay. For the bioturbation layer, bioturbation-induced movement of particles and bioirrigation of pore water are also considered. Bioturbation-related processes are considered quasi-diffusive and hence are assumed to increase the effective diffusion/ dispersion coefficient. Transport through the aqueous boundary layer is dictated by the benthic boundary layer mass transfer coefficient (Boudreau and Jorgensen, 2001). Benthic boundary layer mass transfer is controlled by the turbulence in the overlying water. For river systems, this process is controlled by parameters such as current and water depth. In lake systems, this coefficient is typically controlled by lake mixing processes. Imberger and Hamblin (1982) provide an excellent overview of mechanisms of mixing processes in lakes; mechanisms of lake mixing including wind, wave and buoyancy-driven circulation. Figure 1 shows the conceptual model of the sediment cap system along with the model coordinate system.

Due to the low solubility of most sediment contaminants, the bulk sediment loading, W (mass of contaminant on solid phase per mass of solid phase), is the parameter that is typically used for quantifying contaminant levels in sediments instead of the pore water (mobile phase) concentration. W depends upon the sorption properties of the sediment or cap layer, however, and is potentially discontinuous while the pore water concentration is both continuous across interfaces and directly represents the mobile phase contaminants. Under the assumption of linear partitioning, the bulk sediment loading can be related to the pore water concentration, C, through the following relationship, assuming local equilibrium:

$$W = K_d C \tag{1}$$

Downloaded By: [reible@mail.utexas.edu] At: 00:03 24 June 2009

Where K_d represents the effective sediment-water partition coefficient in the cap material. It is generally reasonable to assume local equilibrium with the pore water at some effective (measured) partition coefficient due to the relatively slow contaminant migration rates within the sediment bed. Of critical importance to the rate of migration of contaminants in the cap material is the ratio of the total concentration (mass per unit volume) in the porous cap matrix to that of the mobile phase concentration, or the retardation factor, R_1 (defined in terms of model parameters subsequently).

For organic contaminants, the contaminant partition coefficient is often estimated as the product of the fraction organic carbon f_{oc} and the organic carbon partition coefficient, K_{oc}. This is likely a crude assumption in the underlying sediment that has been shown to exhibit a different relationship due to desorption resistance (McGroddy and Farrington, 1995) but may be a good assumption for the cap material and the new (clean) sediment. For typical sand, the organic carbon fraction tends to be less than 0.1%. At these low organic carbon contents, mineral sorption tends to become important even for organic compounds; so the assumption of 0.01–0.1% organic carbon is likely a lower bound to the effective sorption of organic contaminants on sandy cap materials (Schwarzenbach et al., 2003).

Due to the limited sorptive capacity of sand caps, permeable adsorptive caps, sometimes referred to as active caps, have been proposed (Reible et al., 2007; McDonough et al., 2007). These caps may contain organic sorbents such as activated carbon, organo-modified clays, coke, or metal sorbents such as apatite. These could be incorporated in the modeling approach herein by using the appropriate effective partition coefficient, although for sorbents exhibiting nonlinear sorption behavior, such as activated carbon, the model results are only approximate. Permeable reactive caps with enhanced degradation characteristics have also been proposed, although their long-term efficacy has not been demonstrated.

The approach presented here is developed using pore water concentrations, which represent the mobile contaminant phase in a stable cap and may be more closely related to the contaminants available for bioaccumulation (e.g. Lu et al., 2006; Beckles et al., 2007). Based on the assumptions listed above, the domain of the model for the cap system consists of two layers: the chemical isolation layer and the bioturbation layer. The underlying sediment, benthic layer, and overlying water are utilized to develop boundary conditions.

Transient Model and Containment Breakthrough Time

The governing transport equation for the chemical isolation layer (Layer 1) is:

$$R_1 \frac{\partial C_1}{\partial t} - U \frac{\partial C_1}{\partial z} = D_1 \frac{\partial^2 C_1}{\partial z^2} - \varepsilon_1 \lambda_1 C_1 \tag{2}$$

Where C_1 is the pore water concentration in the isolation layer, z is the depth downward from the cap-water interface, t is the time, λ_1 is the decay rate constant, R_1 is the retardation factor in the layer (defined here as the ratio of the total concentration to that in the mobile phase), U is the effective advective velocity (assumed to be directed upward although a negative value is still appropriate), and ε_1 is the porosity in the layer. The decay of the contaminant is assumed to be first-order and to occur only in the pore water. Thus seemingly large decay rate constants may have only a minimal impact on mass degradation rate since only a small fraction of the contaminants resides in the pore water. The strong sorptive nature of most sediment contaminants limits the rate of degradation due to limited bioavailability (Hyun et al., 2006; Beckles et al., 2007).

Downloaded By: [reible@mail.utexas.edu] At: 00:03 24 June 2009

For an active capping system, the chemical isolation layer must be further subdivided into sand and active layer(s), which would require introduction of additional governing and appropriate boundary conditions (continuity of concentration and flux) for each layer. The transport equation for each layer would be essentially the same, with the primary difference arising from the retardation term. For sorbing cap materials such as organoclays and peats that obey linear partitioning relationships, the governing equations would differ only in the value of the retardation factor. For a nonlinear sorption model (such as activated carbon) the governing equations would be almost the same, although the retardation factor would no longer be constant but a function of concentration. Note that in either case at steady state the sorption term disappears and the steady state model developed herein still applies.

For the chemical isolation layer, the bottom boundary condition is assumed to be a first-type or Dirichlet boundary with a concentration of C_0:

$$C_1(z = h_{cap}) = C_0 \tag{4}$$

For modeling during the transient period, i.e. before significant penetration of the overlying biologically active layer, the chemical isolation layer may be approximated as semi-infinite, which produces the second boundary condition:

$$\lim_{z \to -\infty} \frac{\partial C_1}{\partial z} = 0 \tag{5}$$

For an initially clean cap, the initial condition is:

$$C_1(t = 0) = 0 \tag{6}$$

The transient behavior can be estimated using an analytical solution to Equation (2) subject to the conditions in (4), (5), and (6). The solution to this problem was presented by van Genuchten (1981):

$$C(z,t) = \frac{C_0}{2}\left\{\begin{array}{l}\exp\left[\frac{(U-u)(h_{cap}-z)}{2D_1}\right]\operatorname{erfc}\left[\frac{R_1(h_{cap}-z)-ut}{\sqrt{4D_1R_1t}}\right]+\\ \exp\left[\frac{(U+u)(h_{cap}-z)}{2D_1}\right]\operatorname{erfc}\left[\frac{R_1(h_{cap}-z)+ut}{\sqrt{4D_1R_1t}}\right]\end{array}\right\} \tag{7}$$

$$u = \sqrt{U^2 + 4\varepsilon\lambda_1 D_1}$$

The transient model (7) is appropriate until the time when the isolation layer is completely compromised by migration from below by the processes of advection, diffusion, and dispersion. For a diffusion-dominated problem with no decay, Equation (7) reduces to the well-known complementary error function solution:

$$C = C_0 erfc\left(\frac{R_1^{0.5}(h_{cap} - z)}{\sqrt{4D_1 t}}\right) \tag{8}$$

This equation can be assumed valid while the concentration at the boundary of the containment and bioturbation layers is small; the complementary error function is equal to about 0.01 when the argument is about two (i.e. when the concentration predicted at the top of the cap layer is 1% of the underlying sediment concentration). Therefore, a conservative

Downloaded By: [reible@mail.utexas.edu] At: 00:03 24 June 2009

estimate of penetration time for a diffusion-dominated system is:

$$t_{diff} = \frac{R_1 h_{eff}^2}{16 D_1} \tag{9}$$

For an advection-dominated system with no decay, Equation (7) reduces to a front or step function with velocity U/R_1 ; hence an appropriate time for penetration is:

$$t_{adv} = \frac{R_1 h_{eff}}{U} \tag{10}$$

Because advection and diffusion/dispersion act together to compromise the chemical isolation layer, the time for penetration of the layer can be estimated by assuming the processes act in parallel. Thus, a time scale characteristic of the advective-diffusive migration through the isolation layer can be written:

$$t_{adv/diff} \approx \frac{1}{1/t_{diff} + 1/t_{adv}} \approx \frac{1}{16D_1/(R_1 h_{eff}^2) + U/(R_1 h_{eff})} \approx \frac{R_1 h_{eff}^2}{16 D_1 + U h_{eff}} \tag{11}$$

For times long compared to $t_{adv/diff}$ a steady state model will describe concentrations and fluxes in the cap. The transient time through the biologically active layer is typically negligible compared to that in the chemical isolation layer due both to its small thickness (5–15 cm) and the rapid sediment reworking and contaminant migration rates in this layer. Thus for times long compared to $t_{adv/diff}$, a steady state model is applicable to both the chemical isolation layer and the overlying bioturbation layer.

To verify the applicability of the relatively simple approach in Equation (11), the time required to achieve a concentration at the top of the chemical isolation layer equal to 1% of the concentration at the sediment-cap interface ($C/C_0 = 0.01$) and the time required to achieve a flux at the top of the chemical isolation layer 1% of the flux at the sediment-cap interface, $F/F_0 = 0.01$, were calculated from a full advection-diffusion model and compared to the prediction of Equation (11). The ratio of the flux at the top of the chemical isolation layer to the flux at the sediment-cap interface was calculated by,

$$F/F_0 = \frac{F(z = h_{bio}, t)}{F(z = h_{cap}, t)} = \frac{UC(z = h_{bio}, t) + D_1 \frac{\partial C(z = h_{bio}, t)}{\partial z}}{UC(z = h_{cap}, t) + D_1 \frac{\partial C(z = h_{cap}, t)}{\partial z}} \tag{12}$$

The results were computed for dimensionless time, τ, in terms of the dimensionless Peclet number, *Pe*, which is defined as:

$$\tau = \frac{t D_1}{R_1 h_{eff}^2} \tag{13}$$

$$Pe = \frac{U h_{eff}}{D_1} \tag{14}$$

The times to concentration or flux equal to 1% of that at the bottom of the sediment were calculated for two solutions to Equation (2), a semi-infinite cap layer and a finite cap layer with a zero concentration at the cap-water interface ($z = 0$). The calculated times were identical for both boundary conditions, since the top boundary does not affect the solution until significant penetration of the complete chemical isolation layer has occurred. The results in Figure 2 show that the prediction of breakthrough based on Equation (11)

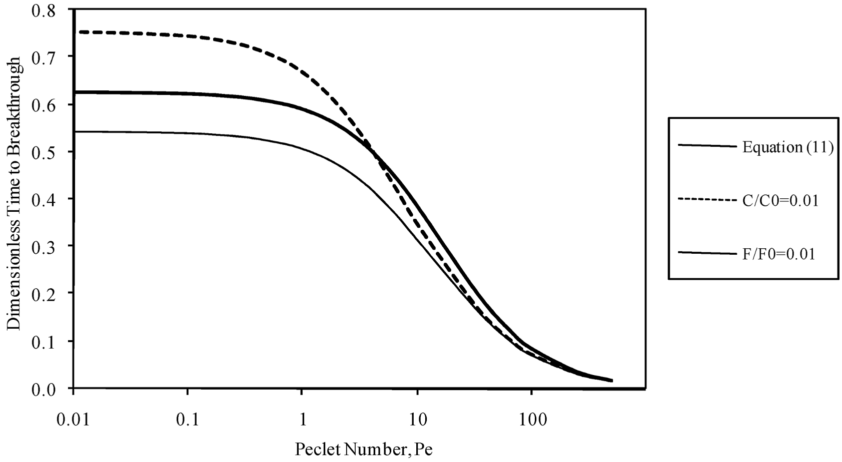


Figure 2. Comparison of breakthrough time approaches. Time required to achieve concentration (C) or flux (F) at top of the chemical isolation layer equal to 1% of the concentration (C_0) or flux (F_0) at the bottom of the layer from full solutions of Equation (2).

Downloaded By: [reible@mail.utexas.edu] At: 00:03 24 June 2009

fall between those based on flux and concentration at low *Pe*, while at high *Pe* Equation (11) slightly over-predicts breakthrough for both cases. The maximum over prediction compared with an F/F_0 value of 0.01 basis was 23%. It appears that Equation (11) provides a reasonable estimate for penetration time for a non-reactive solute over the entire range of *Pe* and, in particular, provides a good estimate of the time before conditions in the biologically active layer will begin to influence concentration profiles within the cap. Any decay would retard the breakthrough time and as a result the predictions from Equation (11) would be conservative.

The Bioturbation Layer and the Sediment-Water Interface

The transport equation for the bioturbation layer has the same general form as the chemical isolation layer; however, the processes of bioturbation are assumed to increase the effective diffusion/dispersion coefficient. The decay rate and retardation factor in the bioturbation layer may also be different than those observed in the chemical isolation layer. The Darcy velocity U must be the same for water (assumed incompressible). The transport equation for the bioturbation layer (Layer 2) is:

$$R_2 \frac{\partial C_2}{\partial t} - U \frac{\partial C_2}{\partial z} = D_2 \frac{\partial^2 C_2}{\partial z^2} - \varepsilon_2 \lambda_2 C_2 \tag{15}$$

Where C_2 is the concentration in the bioturbation layer, R_2 is the retardation factor in the bioturbation layer, D_2 is the effective diffusion/dispersion coefficient for the bioturbation layer, λ_2 is the decay rate for the bioturbation layer, and ε_2 is the porosity in the layer.

At the interface between the chemical isolation layer and the bioturbation layer, the concentrations and fluxes in the two layers must be equal. Recognizing that the advective flux is the same in each layer, the following represent appropriate boundary conditions at the interface between the bioturbation and underlying containment layers (here C_{bio} is

Downloaded By: [reible@mail.utexas.edu] At: 00:03 24 June 2009

defined as the concentration at the interface):

$$C_1(z = h_{bio}) = C_2(z = h_{bio}) = C_{bio} \tag{16}$$

$$-D_1 \frac{\partial C_1(z = h_{bio})}{\partial z} = -D_2 \frac{\partial C_2(z = h_{bio})}{\partial z} \tag{17}$$

The boundary condition at the cap-water interface is the most complex, as it essentially requires the effluent boundary condition from a porous medium, which has a long history and is the subject of many papers (Hulbert, 1944; Danckwerts, 1953; Wehner and Wilhelm, 1956). The concept of a benthic boundary layer mass transfer resistance composed of a laminar (diffusive) sublayer above the sediment-water interface has long been used for modeling mass transport from surficial sediments and is widely accepted in soil and marine science (see Boudreau, 1997). A complete mass balance on the interface results in the following expression (Boudreau and Jorgensen, 2001):

$$UC_2(z = 0^+) - D_2 \frac{\partial C_2(z = 0^+)}{\partial z} + R' = U_{bl} C_{bl}(z = 0^-) + k_{bl}(C_{bl} - C_w) \tag{18}$$

Where *R'* represents transport of contaminants from the exposed surficial sediment to the overlying water, and U_{bl}, $k_{bl,}$, and $C_{bl}(z)$ represent the effective advective velocity, effective mass transfer coefficient, and concentration in the benthic boundary layer, respectively. The value of R' has been shown to be small relative to the other processes (Boudreau and Jorgensen, 2001). The effective mass transfer coefficient in the benthic boundary layer can also be thought of as a diffusion in a laminar sublayer of thickness, δ, separating the cap-water interface from the bulk overlying water of concentration, C_w:

$$k_{bl}(C_{bl} - C_w) = D_{bl} \frac{C_{bl} - C_w}{\delta} \tag{19}$$

The value in the overlying surface water is taken to be zero without loss of generality (all other concentrations are taken relative to this surface water concentration). Combining these assumptions results in the following boundary condition of the third kind (Boudreau and Jorgensen, 2001):

$$D_2 \frac{\partial C_2(z = 0^+)}{\partial z} = k_{bl} C_{bl}(z = 0^-) = k_{bl} C_2(z = 0^+) \tag{20}$$

Steady State Model

To evaluate the concentrations in the combined containment and bioturbation layers, the relative importance of the different transport mechanisms can be evaluated with the following dimensionless numbers, which are defined as:

$$Pe_1 = \text{Peclet number in chemical isolation layer} = \frac{U h_{eff}}{D_1} = \frac{\text{Rate of advection}}{\text{Rate of diffusion}} \tag{21}$$

$$Da_1 = \text{Damkohler number in chemical isolation layer} = \frac{\varepsilon_1 \lambda_1 h_{eff}^2}{D_1} = \frac{\text{Rate of decay}}{\text{Rate of diffusion}} \tag{22}$$

$$Pe_2 = \text{Peclet number in bioturbation layer} = \frac{Uh_{bio}}{D_2} \tag{23}$$

$$Da_2 = \text{Damkohler number in bioturbation layer} = \frac{\varepsilon_2 \lambda_2 h_{bio}^2}{D_2} \tag{24}$$

$$Sh = \text{Sherwood number at cap-water interface} = \frac{k_{bl} h_{bio}}{D_2} = \frac{\text{Rate of mass transfer}}{\text{Rate of diffusion}} \tag{25}$$

Under steady state conditions the time derivatives in Equations (2) and (15) disappear. Equations (2) and (15) can be re-written in terms of the dimensionless parameters introduced above:

$$h_{eff}^2 \frac{\partial^2 C_1}{\partial z^2} + Pe_1 h_{eff} \frac{\partial C_1}{\partial z} - Da_1 C_1 = 0 \tag{26}$$

$$h_{bio}^2 \frac{\partial^2 C_2}{\partial z^2} + Pe_2 h_{bio} \frac{\partial C_2}{\partial z} - Da_2 C_2 = 0 \tag{27}$$

By assuming a solution of an exponential form, the general solution of (26) and (27) can be obtained. At steady state the concentrations at the boundaries of the domain are constant and assumed to have values of C_0 at the cap-sediment interface, C_{bio} at the boundary of the chemical isolation and bioturbation layers, and C_{bl} at the cap-water interface. The solutions to the governing ordinary differential equations are thus:

$$\begin{aligned} C_1 = {} & \frac{C_{bio} e^{-\frac{Pe_1}{2}} - C_0 e^{-\beta}}{2\sinh\beta} \exp\left[\left(\frac{Pe_1}{2} + \beta\right)\frac{h_{cap} - z}{h_{eff}}\right] + \frac{C_0 e^{\beta} - C_{bio} e^{-\frac{Pe_1}{2}}}{2\sinh\beta} \\ & \times \exp\left[\left(\frac{Pe_1}{2} - \beta\right)\frac{h_{cap} - z}{h_{eff}}\right] \end{aligned} \tag{28}$$

$$\beta = \sqrt{\frac{Pe_1^2}{4} + Da_1}$$

$$\begin{aligned} C_2 = {} & \frac{C_{bl} e^{-\frac{Pe_2}{2}} - C_{bio} e^{-\gamma}}{2\sinh\gamma} \exp\left[\left(\frac{Pe_2}{2} + \gamma\right)\frac{h_{bio} - z}{h_{bio}}\right] + \frac{C_{bio} e^{\gamma} - C_{bl} e^{-\frac{Pe_2}{2}}}{2\sinh\gamma} \\ & \times \exp\left[\left(\frac{Pe_2}{2} - \gamma\right)\frac{h_{bio} - z}{h_{bio}}\right] \end{aligned} \tag{29}$$

$$\gamma = \sqrt{\frac{Pe_2^2}{4} + Da_2}$$

The values of C_{bio} and C_{bl} can be determined by applying the boundary conditions (17) and (20) to Equations (28) and (29):

$$C_{bio} = \frac{C_o \frac{Pe_2}{Pe_1} e^{\frac{Pe_1}{2}} \beta \sinh\gamma}{\frac{Pe_2}{Pe_1}\beta\cosh\beta\sinh\gamma + \gamma\sinh\beta\cosh\gamma - \frac{\gamma^2\sinh\beta}{\left(Sh + \frac{Pe_2}{2}\right)\sinh\gamma + \gamma\cosh\gamma}} \tag{30}$$

Downloaded By: [reible@mail.utexas.edu] At: 00:03 24 June 2009

$$C_{bl} = \frac{C_0 e^{\frac{Pe_1+Pe_2}{2}}}{\left(\frac{Pe_1}{2} + \frac{Pe_1 Sh}{Pe_2}\right)\frac{\sinh\beta\cosh\gamma}{\beta} + \left(\frac{Pe_2}{2} + Sh\right)\frac{\cosh\beta\sinh\gamma}{\gamma} + \frac{Pe_1\gamma\sinh\gamma\sinh\beta}{Pe_2\beta} + \cosh\beta\cosh\gamma} \tag{31}$$

The concentration of contaminants in the bioturbation layer is of particular interest, as benthic organisms in the layer often provide the primary route of entry of contaminants into the food chain. Hence, another important parameter is the average concentration in the bioturbation layer. This concentration can be used to evaluate the potential long-term effectiveness of a sediment cap. Integrating Equation (29) over the bioturbation layer and dividing by the depth of the bioturbation layer provides the average value:

$$(C_{bio})_{avg} = \frac{C_{bl}e^{-\frac{Pe_2}{2}} - C_{bio}e^{-\gamma}}{2\sinh\gamma}\,\frac{e^{\frac{Pe_2}{2}+\gamma} - 1}{\frac{Pe_2}{2} + \gamma} + \frac{C_{bl}e^{\gamma} - C_{bio}e^{-\frac{Pe_2}{2}}}{2\sinh\gamma}\,\frac{e^{\frac{Pe_2}{2}-\gamma} - 1}{\frac{Pe_2}{2} - \gamma} \tag{32}$$

The average solids loading in the bioturbation layer, $(W_{bio})_{avg}$, can be determined from the partitioning relationship between the pore water and the sediment, where $(f_{oc})_{bio}$ is the expected fraction of organic carbon in the newly deposited sediment:

$$(W_{bio})_{avg} = (f_{oc})_{bio} K_{oc} (C_{bio})_{avg} \tag{33}$$

Additionally, the flux to the overlying water column, J, may be of interest. This can be evaluated by:

$$J = (k_{bl} + U)C_{bl} \tag{34}$$

Numerical Model Comparison

To check the validity of the analytical solutions for both the transient and steady state models, Equations (2) and (15) subject to boundary conditions (4), (16), (17), and (20) and initial condition (6) were solved independently by numerical analysis. A finite differencing scheme using the Crank-Nicolson method (Crank and Nicolson, 1947) with a forward difference for the advection term and central difference for the diffusion term was employed for the analysis. Reasonable estimates for the parameters were assumed for two cases using the methods described above. Simulations were performed for low and high values of Pe_1. Figure 3 shows that results of the simulations and the analytical solutions (7) and (28–31) are equivalent. Thus the analytical solutions can be used to predict concentrations within the chemical isolation layer during the transient period and to predict the steady state behavior. For estimation of cap behavior in the transition time between $\tau_{\text{adv/diff}}$ and steady state, a numerical model must be employed to approximate the solution to the governing equations.

Characterization of Transport Parameters

The factors R_1 and R_2 as defined here are the ratios of the total concentration in an elementary sediment volume (stationary phase) to that in the pore water (mobile phase) for the containment and bioturbation layers, respectively. A significant proportion of the total concentration in the pore water may be present in colloidal organic matter (Baker et al., 1985; Chin and Gschwend, 1992; Schlautman and Morgan, 1993). Chin and

Downloaded By: [reible@mail.utexas.edu] At: 00:03 24 June 2009

Downloaded By: [reible@mail.utexas.edu] At: 00:03 24 June 2009

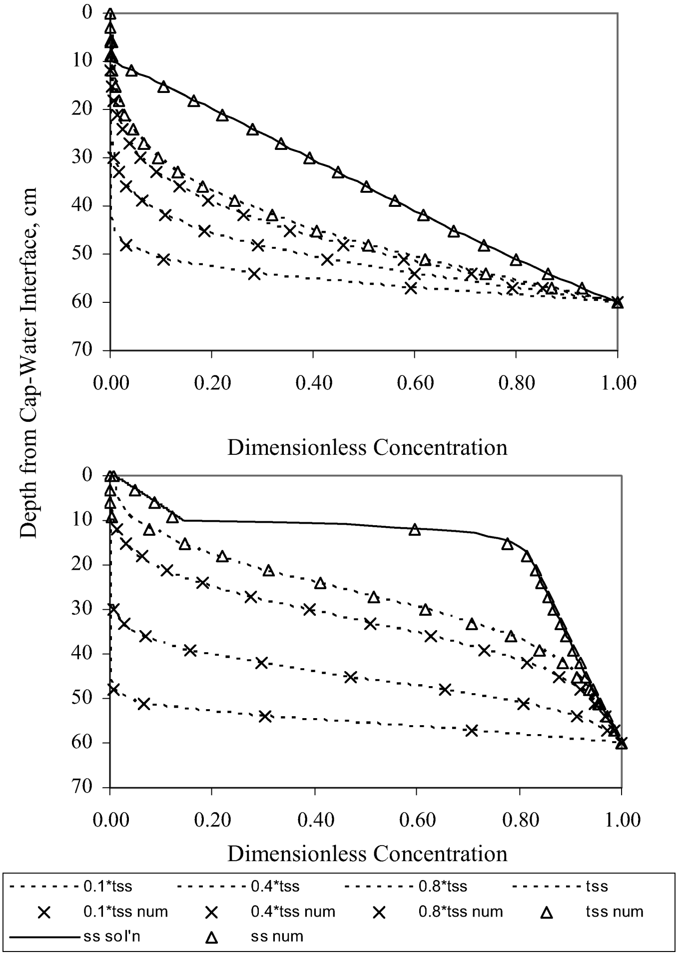


Figure 3. Transient and steady state concentration profiles throughout cap: comparison of analytical with numerical solution. Top: low flow ($Pe_1 = 0.66$); Bottom: high flow ($Pe_1 = 32.8$).

Gschwend (1992) found this relationship to be linear. Thus partitioning onto the total organic carbon in the pore water, ρ_{DOC}, with a colloidal organic carbon partition coefficient, K_{DOC}, serves to increase the effective solubility of the compounds. Coupling this assumption with the linear partitioning onto the cap material, and recognizing that the fractional organic carbon in the bioturbation layer, $(f_{oc})_{bio}$ will over time be different from that in the containment layer, $(f_{oc})_{eff}$, produces the following relationships for R_1 and R_2 in terms of ρ_{oc}, K_{DOC}, ε, the particle density ρ_P, and K_{oc}:

$$R_1 = \frac{\varepsilon_1 + \varepsilon_1 \rho_{DOC} K_{DOC} + (1 - \varepsilon_1)\rho_P (f_{oc})_{eff} K_{oc}}{1 + \rho_{DOC} K_{DOC}} \tag{35}$$

$$R_2 = \frac{\varepsilon_2 + \varepsilon_2 \rho_{DOC} K_{DOC} + (1 - \varepsilon_2)\rho_P (f_{oc})_{bio} K_{oc}}{1 + \rho_{DOC} K_{DOC}} \tag{36}$$

The Darcy velocity, U, here accounts for both groundwater upwelling and the effect of erosion/deposition. In a coordinate system fixed relative to the cap-water interface,

Downloaded By: [reible@mail.utexas.edu] At: 00:03 24 June 2009

deposition or erosion changes the net advective flux. Because particle deposition effectively buries both pore water and solid associated contaminants, the effective advective flux also encompasses both. The effective advective velocity associated with both the Darcy pore water upwelling, V, the velocity of sediment deposition, V_{dep}, and the retardation factor applicable to the cap-sediment layer, R, is:

$$U = V - RV_{dep} \tag{37}$$

Note that although new sediment is typically deposited at the cap–water interface, the mixing in this region is rapid and governed by bioturbation, or particle mixing processes that are not subject to retardation by pore water transport. Transient migration in the underlying cap containment layer is delayed by burial with new sediment and the apparent shifting of the sediment interface. For estimation of the time delay associated with burial, R in Equation (37) can be conservatively estimated by R_1 (the retardation in the underlying sand), despite the fact that typically more sorbing sediment is deposited at the cap-water interface (characterized by R_2). In the event of net erosion rather than deposition the value of V_{dep} is negative. For the purposes of conservative estimates and due to uncertainties over future deposition rates, it is often assumed that the deposition of new sediment is negligible despite the fact that contaminated sediments have typically accumulated in net depositional areas.

The advective flow is perhaps the most important parameter in this analysis, as it will dominate in many natural systems. The flow may be upward or downward, in which case the value is negative. In the absence of direct measurements, the flow may be modeled using Darcy's Law. This approach requires an understanding of the hydrogeology of the area, including the effective hydraulic conductivity of the sediment/groundwater system and the local groundwater elevation levels driving the flow rate. For direct measurement of groundwater flux, seepage meters such as the one described by Lee (1977) may be used to measure the groundwater seepage rate. Alternatively, Cook et al. (2003) describe methods for estimating flux using different kinds of tracers. The local effective hydraulic conductivity for the sediment-cap system is dictated by the layer with the lowest hydraulic conductivity. The hydraulic conductivity of the system is generally unaffected by the presence of a cap (since it is often composed of relatively coarse granular media) although the cap could be constructed to control permeability or may cause consolidation in the underlying sediment, reducing its permeability.

The value of D_1 is the sum of the diffusion and dispersion coefficients. Diffusion through granular porous media is often characterized by an effective diffusion coefficient D_{diff} given by the molecular diffusivity D_w times the porosity (the available diffusion area) and divided by a hindrance parameter (the lengthening of the diffusion path by the media). The model of Millington and Quirk (1961), where the hindrance parameter is taken to be the porosity to the negative one-third power, is widely used for diffusion in granular porous media such as a typical sand cap:

$$D_{diff} = \varepsilon_1^{\frac{4}{3}} D_w \tag{38}$$

Boudreau (1997) suggests an alternative that may be more applicable for fine-grained sediments:

$$D_{diff} = \frac{\varepsilon_1 D_w}{1 - \ln \varepsilon_1^2} \tag{39}$$

The molecular diffusivity is a function of temperature and molecular weight and can be estimated from the literature (e.g. Lyman et al., 1990). Mechanical dispersion characterized by D_{disp} of the contaminant through the cap can be modeled as the product of the velocity through the cap and some length scale defined as the dispersivity, α:

$$D_{disp} = \alpha U \tag{40}$$

Thus, the effective diffusion/dispersion coefficient in the containment layer can be determined by:

$$D_1 = \varepsilon_1^{\frac{4}{3}} D_w + \alpha U \tag{41}$$

After placement of a sediment cap, new sediment is deposited at the cap surface. As this deposition occurs, the top of the sediment cap is re-colonized by benthic organisms (worms and other macro invertebrates). These organisms blend the sediments at the top of cap, resulting in relatively rapid transport of contaminants from the bottom of the layer to the overlying water. Provided that the movement of particles and pore water by these organisms is essentially random, the length scale of the movement of the particles is smaller than that being studied (i.e. the cap thickness), and time scale between mixing events is smaller relative to other processes, the transport processes can be taken as quasi-diffusive (Boudreau, 1986). The diffusion-like mixing of particles is known as bioturbation, while the diffusion-like mixing of pore water is bioirrigation. These processes increase diffusion/dispersion coefficient from the containment layer, D_1, to that in the bioturbation layer, D_2. The flux of a chemical species, J_{bio}^{p}, associated with the diffusion of these particles associated with a bioturbation coefficient of D_{bio}^{p} and a solid-phase concentration (mass of chemical species per unit volume sediment particle) of M is:

$$J_{bio}^{p} = -D_{bio}^{p} \frac{\partial M}{\partial z} \tag{42}$$

If the time for movement of the sediment particles plus the time between particle movement events is large compared with that of desorption of contaminants, local equilibrium can be assumed, and the value of M can be re-written in terms of pore water concentration (noting that ε, ρ_p, $(f_{oc})_{bio}$, and K_{oc} are independent of depth):

$$J_{bio}^{p} = -D_{bio}^{p}(1-\varepsilon)\rho_P (f_{oc})_{bio} K_{oc} \frac{\partial C_2}{\partial z} \tag{43}$$

In addition to particle mixing, organisms also irrigate the surficial sediments through direct pore water exchange from the underlying sediments to the overlying water. The transport of contaminants associated with this process can be modeled by:

$$J_{bio}^{pw} = -D_{bio}^{pw} \frac{\partial C}{\partial z} \tag{44}$$

Thus the processes of bioturbation and bioirrigation serve to increase the effective diffusion/dispersion coefficient. The values of D_{bio}^{p} and D_{bio}^{pw} can be measured using radioactive tracers, such as described by McCafree et al. (1980). Thoms et al. (1995) provide an extensive review of measured biodiffusion coefficients at different locations in the United States. The effective diffusion coefficient for the bioturbation layer, D_2, can be determined

Downloaded By: [reible@mail.utexas.edu] At: 00:03 24 June 2009

Downloaded By: [reible@mail.utexas.edu] At: 00:03 24 June 2009

from the following:

$$D_2 = D_1 + D_{bio}^{pw} + D_{bio}^{p}(1-\varepsilon)\rho_P(f_{oc})_{bio}K_{oc} \tag{45}$$

The decay rates λ_1 and λ_2 are highly compound and site specific. The model taken here is based on first-order kinetics, which may not be appropriate as the degradation may depend on many factors other than the contaminant concentration but provides a relatively simple way of incorporating this important mechanism into a mathematical model. In the absence of a site-specific study, the literature may be used to estimate a degradation rates.

Transport at the cap-water interface is dictated by the benthic boundary layer mass transfer coefficient, which is a function of the turbulence and shear of the overlying water column. Boudreau and Jorgensen (2001) and Thibodeaux (1996) present empirical correlations for k_{bl} based on mixing conditions in the overlying water. The value of k_{bl} should be conservatively estimated, as its value directly affects the surficial sediment concentrations.

Steady State Model Behavior

The steady state model presented in (28–31) is a function of only the five parameters (21–25) and the depth of the two layers. To illustrate the behavior of the solution, consider a one-foot (30 cm) thick sand cap with an expected bioturbation depth of 10 cm. For Case I, consider a conservative ($Da_1 = Da_2 = 0$) contaminant, with $Sh = 10$ (minimal mass transfer limitations) and $D_2 = 10D_1$ ($Pe_2 = 0.05Pe_1$). Figure 4 shows the dimensionless concentration profiles for $0.1 < Pe_1 < 200$. For low Pe_1, the solution approaches a straight line in each layer, which is the expected result of a diffusion-dominated steady state profile. The increased diffusivity in the bioturbation layer results in lower concentrations in that layer. This behavior makes sense physically because the increased mixing rate in the layer reduces the concentrations there (contaminants are transported more rapidly in the bioturbation layer). If advection dominates (high Pe_1), the concentration profile approaches unity; again this is the expected result for an advection problem at steady state. The deviation near the boundary layer is a result of the simplifying assumptions made in the formulation of the top boundary condition. For high advection a more appropriate boundary condition would be a zero gradient. However, the profiles still approach the expected result and provide a reasonable estimation of cap performance even under these conditions. Clearly, at steady state in a high upwelling velocity system a cap will have limited effectiveness.

Now consider a system with degradation (Case II). For simplicity, the Damkohler number in the chemical isolation layer is assumed to be four. The value of D_2 was again taken as $10D_1$, and again it is assumed that $Sh = 10$. The decay rate in the bioturbation layer is taken as ten times that in the chemical isolation layer, a reasonable assumption due to higher levels of nutrients, organic matter, and electron acceptors. These assumptions result in $Pe_2 = 0.05Pe_1$ and $Da_2 = 0.25Da_1 = 1$. Figure 4 shows the dimensionless concentration profiles for $0.1 < Pe_1 < 200$. When compared with the no decay situation, the concentration profiles are lower, as expected. In general, the graphs perform as anticipated mathematically. The concentrations in the bioturbation layer are significantly decreased versus the underlying sediment concentrations. Hence, if it can be proven that a contaminant will decay in a cap, capping is an extremely attractive alternative for remediation.

To evaluate the effects of mass transfer resistance on model output, consider the systems presented in Cases I and II with $Sh = 0.1$ rather than 10 (Cases III and IV). Figure 4 also shows the results for these parameters. For Case III, the concentrations in the cap are minimally reduced even when diffusion-dominated (low Pe_1). The performance

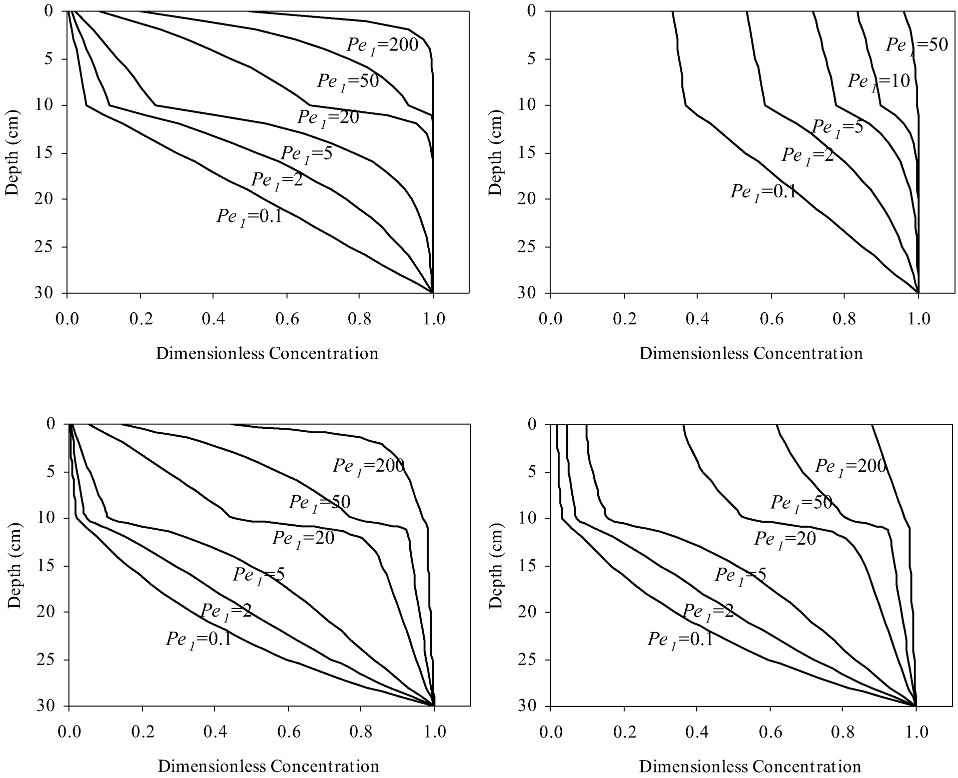


Figure 4. Steady state model behavior. Top left, Case I ($Da_1 = Da_2 = 0$, $Sh = 10$). Bottom left, Case II ($Da_1 = 4$, $Da_2 = 1$, $Sh = 10$). Top right, Case III ($Da_1 = Da_2 = 0$, $Sh = 0.1$). Bottom right, Case IV ($Da_1 = 4$, $Da_2 = 1$, $Sh = 0.1$). The dashed lines represent the interface between the chemical isolation and the bioturbation layers.

is as expected theoretically, with a linear profile in the containment layers at low Pe_1, which approaches a uniform profile for high values of Pe_1. In Case IV, the importance of decay on long term capping success is demonstrated. For a diffusion-dominated system, the bioturbation layer concentrations are drastically reduced over pre-cap levels, even with mass transfer resistance at moderately high advection ($Pe_1 = 5$). Again, as the upwelling velocity is increased, the cap performance is limited.

It is important to note that the model presents steady state concentrations, which may not be realized for many years. Capping may still be a viable option in a case where the transient migration through the containment layer is sufficiently long that natural attenuation processes not included in the models are expected to render the contaminants inconsequential. Steady state predictions beyond this time frame may not be considered important.

These results show the importance of the ground water upwelling velocity in the effectiveness of a cap. The upwelling velocity is a critical parameter in a transient analysis as well as it often controls the steady state flux. Upwelling velocities of the order of cm/day or more may be high enough to effectively negate the effectiveness of a cap even for moderately sorbing contaminants. In addition, the local equilibrium assumption may fail under the influence of extremely high upwelling. So, if capping is under consideration

Downloaded By: [reible@mail.utexas.edu] At: 00:03 24 June 2009

for management of contaminated sediments, it is important for the designer to measure or make a good estimate of the upwelling velocity before making a final decision. Due to the inherent heterogeneity in this parameter, it is also important to evaluate a range of values of upwelling velocity for predicting concentrations that will be used in design and decision making.

The traditional material used for capping sediment is clean sand. However, as demonstrated by these modeling results, a passive sand cap may not be an effective long-term approach for contaminated sediment management for high seepage/low degradation systems. For this reason, one current research focus (Reible et al., 2007; McDonough et al., 2007) is on active capping; that is, capping with materials that may enhance sequestration/degradation in situ or decrease the seepage flow rates through a sediment cap.

Conclusions

In this article, the key processes controlling chemical migration in a cap isolation layer and in the overlying biologically active layer have been highlighted. A simple means for incorporating these processes into an analytical modeling approach has been developed. The approach is subject to a number of limitations. First, several of the models for individual processes are simplistic (e.g. deposition, linear pore water partitioning, first-order decay). The underlying sediment is assumed to maintain a constant concentration. A more robust approach to assessing the concentration in the sediment would be to model fate and transport within the layer based on an initial concentration profile. However, this approach would normally require a numerical simulation in the full-advection diffusion case. Finally, the model is based on two homogeneous layers. Predicting transient concentration profiles in more complex sediment caps with more than two homogeneous layers or with nonlinear sorption would require a more robust approach. The steady state model presented here, however, would still be valid provided the values of diffusion/dispersion coefficients and decay rates were the same. For predicting transient performance of a cap under these scenarios, a numerical solution to the governing equations would be required. The exact solutions presented here represent an important check for future models of this kind.

The model presented here allows calculation of the steady state concentration profile and flux in a sediment cap. When coupled with a transient model of advection, diffusion, and reaction in the chemical isolation layer, this approach forms a relatively simple means of evaluating sediment caps. If the steady state condition is sufficient for achieving remediation objectives, there is no need for a more complicated transient approach. A spreadsheet that computes the analytical model output is available at http://www.caee.utexas.edu/reiblegroup/downloads.html for interested parties.

Downloaded By: [reible@mail.utexas.edu] At: 00:03 24 June 2009

References

Azcue, J.M., Zeman, A.J., Mudroch, A., Rosa, F., and Patterson, T. 1998. Assessment of sediment and porewater after one year of subaqueous capping of contaminated sediments. *Water Sci. Technol.* **37**, 323–329.

Baker, J.E., Capel, P.D., Eisenreich, S.J. 1985. Influence of colloids on sediment-water partition coefficients of polychlorobiphenyl congeners in natural waters. *Environ. Sci. Technol.* **20**, 1136–1143.

Bear, J. 1972. *Dynamics of Fluids in Porous Media*. Elsevier, New York.

Beckles, D., Chen, W., Hughes, J. 2007. Bioavailability of polycyclic aromatic hydrocarbons sequestered in sediment: microbial study and model prediction. *Environ. Toxicol. Chem.* **26**, 878–883.

Boudreau, B. 1986. Mathematics of tracer mixing in sediments, I. Spatially-dependent, diffusive mixing. *Am. J. Sci.* **286**, 161–198.

Boudreau, B. 1997. *Diagenetic Models and Their Implementation: Modeling Transport Reactions in Aquatic Sediments*. Springer-Verlag, New York.

Boudreau, B., and Jorgensen, B. 2001. *The Benthic Boundary Layer*. Oxford University Press, New York.

Chin, Y.P., Gschwend, P.M. 1992. Partitioning of polycyclic aromatic hydrocarbons to marine pore water organic colloids. *Environ. Sci. Technol.* **26**, 1621–1626.

Cook, P.G., Favreau, G., Dighton, J.C., Tickell, S. 2003. Determining natural groundwater influx to a tropical river using radon, chlorofluorocarbons, and ionic environmental tracers. *J. Hydrol.* **277**, 74–88.

Crank, J., and Nicolson, P. 1947. A practical method for numerical evaluation of solutions of partial differential equations of the heat conduction type. *Proc. Camb. Phil. Soc.* **43**, 50–64.

Danckwerts, P.V. 1953. Continuous flow systems. *Chem. Eng. Sci.* **2**, 1–13.

Hulburt, H.M. 1944. Chemical processes in continuous-flow systems: reaction kinetics. *Ind. Eng. Chem.* **36**, 1012–1017.

Hyun, S., Jafvert, C., Lee, L., and Rao, P. 2006. Laboratory studies to characterize the efficacy of sand capping a coal tar-contaminated sediment. *Chemosphere* **63**, 1621–1631.

Imberger, J., and Hamblin, P. 1982. Dynamics of lakes, reservoirs, and cooling ponds. *Annu. Rev. Fluid Mech.* **14**, 153–187.

Lee, D.R. 1977. A device for measuring seepage fluxes in lakes and estuaries. *Limnol. Oceanogr.* **22**, 140–147.

Lu, X., Reible, D.D., and Fleeger, J.W. 2006. Bioavailability of polycyclic aromatic hydrocarbons in field-contaminated Anacostia River (Washington, DC) sediment. *Environ. Toxicol. Chem.* **25**, 2869–2874.

Lyman, W.J, Reehl, W.F. and Rosenblatt, D.H. 1990. *Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds*. American Chemical Society, Washington, DC.

Malusis, M., and Shackelford, C. 2002. Theory for reactive solute transport through clay membrane barriers. *J. Contam. Hydrol.* **59**, 291–316.

McCafree, R.J., Myers, A.C., Davey, E., Morrison, G., Bender, M., Luedtke, N., Cullen, D., Froelich, P., and Klinkhammer, G. 1980. The relation between pore water chemistry and benthic fluxes of nutrients and manganese in Narragansett Bay, Rhode Island. *Limnol. Oceanogr.* **25**, 31–44.

McDonough, K., Murphy, P., Olsta, J., Zhu, Y., Reible, D., and Lowry, G. 2007. Development of a sorbent-amended thin layer sediment cap in the Anacostia River. *Soil Sed. Contam.* **16**, 313–322.

McGroddy, S.E., and Farrington, J.W. 1995. Sediment porewater partitioning of polycyclic aromatic hydrocarbons in three cores from Boston Harbor, Massachusetts. *Environ. Sci. Technol.* **29**, 1542–1550.

Millington, R.J., and Quirk, J.M. 1961. Permeability of porous solids. *Trans. Far. Soc.* **57**, 1200–1207.

Murphy, P., Marquette, A., Reible, D. and Lowry, G.V. 2006. Predicting the performance of activated carbon-, coke-, and soil-amended thin layer sediment caps. *J. Environ. Eng.* **132**, 787–794.

Palermo, M., Maynord, S., Miller, J. and Reible, D. 1998. *Guidance Document for In Situ Subaqueous Capping of Contaminated Sediments*, EPA 905-B96–004.

Parametrix. 1998. St. Paul Waterway Area Remedial Action and Habitat Restoration Project. Final 1998 Monitoring Report.

Rabideau, A., and Khandelwal, A. 1998. Boundary conditions for modeling transport in vertical barriers. *J. Environ. Eng.* **124**, 1135–1139.

Reible, D.D, Lampert, D.J., Constant, D., Mutch, R., and Zhu, Y. 2007. Active capping demonstration in the Anacostia River in Washington, DC. *Remed. J.* **17**, 39–53.

Rowe, P.K., and Booker, J.R. 1985. 1-D pollutant migration in soils of finite depth. *J. Geotech. Eng.* **111**, 479–499.

Rubin, H., and Rabideau, A. 2000. Approximate evaluation of contaminant transport through vertical barriers. *J. Contam. Hydrol.* **40**, 311–333.

Downloaded By: [reible@mail.utexas.edu] At: 00:03 24 June 2009

Schlautman, M.A., and Morgan, J.J. 1993. Effects of aqueous chemistry on the binding of polycyclic aromatic hydrocarbons by dissolved humic materials. *Environ. Sci. Technol.* **27**, 961–969.

Schwarzenbach, R., Gshwend, P., and Imboden, D. 2003. Chapter 9, Sorption I: Introduction and sorption processes involving organic matter and Chapter 11: Sorption III: Sorption processes involving inorganic surfaces. *Environmental Organic Chemistry*, 2nd ed., pp. 275–330 and 387–458. Wiley & Sons, Hoboken, New Jersey.

Simpson, S., Pryor, I., Mewburn, B., Batley, G., and Jolley, D. 2002. Considerations for capping metal-contaminated sediments in dynamic estuarine environments. *Environ. Sci. Technol.* **36**, 3772–3778.

Thibodeaux, L.J. 1996. Chapter 5: Chemical exchange between water and adjoining earthen material. *Environmental Chemodynamics*, pp. 255–368. John Wiley, New York.

Thoma, G., Reible, D., Valsaraj, K., and Thibodeaux, L. 1991. Efficiency of capping contaminated bed sediments in situ. 1. Laboratory-scale experiments on diffusion-adsorption in the capping layer. *Environ. Sci. Technol.* **25**, 1578–1584.

Thoms, S.R., Matisoff, G., McCall, P.L., and Wang, X. 1995. *Models for Alteration of Sediments by Benthic Organisms*, Project 92-NPS-2, Water Environment Research Foundation, Alexandria Virginia.

Van Genuchten, M. 1981. Analytical solutions for chemical transport with simultaneous adsorption, zero order production and first order decay. *J. Hydrol.* **49**, 213–233.

Wehner, J., and Wilhelm, R. 1956. Boundary conditions of flow reactor. *Chem. Eng. Sci.* **6** 89–93.

Zeman, A., and Patterson, T. 1997. Preliminary results of demonstration capping project in Hamilton Harbour. *Water Qual. Res. J. Can.* **32**, 439–452.

Downloaded By: [reible@mail.utexas.edu] At: 00:03 24 June 2009

S.S. PAPADOPULOS & ASSOCIATES, INC.
Environmental & Water-Resource Consultants

Memorandum

Date: November 23, 2010

From: Charles Andrews

To: Caryn Kiehl-Simpson

Subject: **Active Capping Transport Model – Version 2.0**

The Active Capping Transport Model is a computer program developed by David Lampert and Danny Reible at the University of Texas. The model calculates one-dimensional vertical transport of a contaminant through a sediment cap considering the processes of advection, diffusion, dispersion, reaction, bioturbation, deposition, consolidation, and retardation with local equilibrium between sediment, pore water, and dissolved organic matter. Excellent background documents that describe the processes simulated with the model are "*Guidance for In-Situ Subaqueous Capping of Contaminated Sediments: Appendix B: Model for Chemical Containment by a Cap*" (Palermo and others 1996) and a paper published in Soil and Sediment Contamination by Lampert and Reible (2009). I highly recommend that all users of Active Capping Transport Model read and familiarize themselves with these background documents.

The Active Capping Transport Model was developed as a MATLAB program and is run within the MATLAB environment. I have reviewed several versions of the Active Capping Transport Model and described the results of my reviews in memoranda dated January 6, 2009 and November 5, 2010. In my reviews, I noted several coding issues in the Active Capping Transport Model. These coding issues have all been addressed.

The Active Capping Transport Model Version 2.0 was developed to simulate contaminant transport in a six layer system; model parameters can vary from layer to layer. The governing equation in the Active Capping Transport Model is:

$$R\frac{\partial C}{\partial t} = -U\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} - n\lambda C \qquad (1)$$

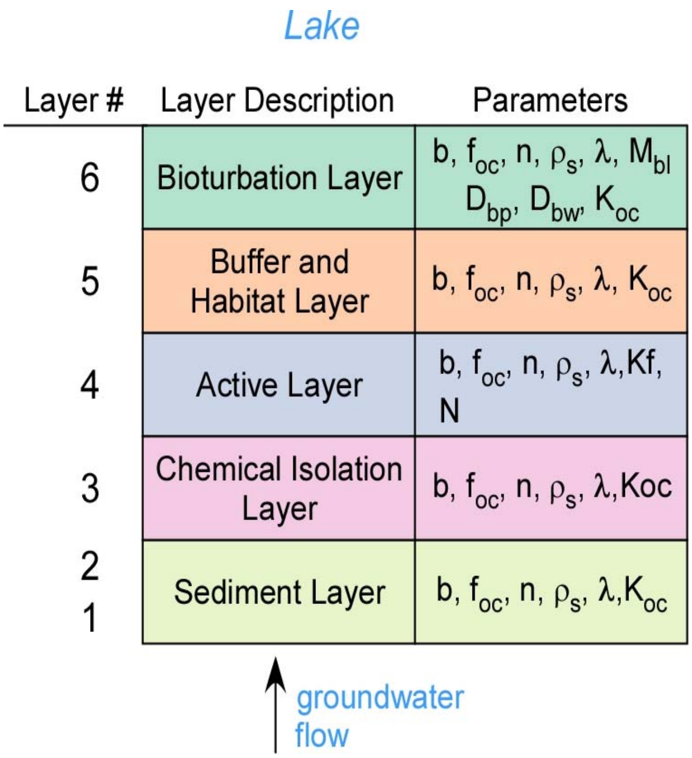
where: C = concentration;
U = Darcy velocity;
D = effective diffusion/dispersion coefficient (sum of diffusion and dispersive coefficients);
R = retardation factor for compound of interest; and
λ = first-order degradation rate.

The governing equation is solved using a two-point upstream centered finite-difference scheme in space with the Crank-Nicolson method. The model automatically creates a finite-difference grid with sufficiently fine-vertical spacing to minimize numerical dispersion; for typical problems a vertical spacing of 0.5 centimeters is specified. The time step size is increased with time from start of simulation for computational efficiency.

A schematic of the 6-layer system simulated with the Active Capping Transport Model is shown to the right. The bottom two layers represent the underlying sediment. These layers can be specified at a constant concentration, can be specified with a finite thickness with depth varying concentrations to simulate a depleting source with time, and can be specified with a constant concentration at base of sediment layer.

Overlying the sediment layer is the chemical isolation layer, which in turn is overlain by an active layer – a layer containing activated carbon.

Overlying the active layer is the buffer and habitat layer, which in turn is overlain by a bioturbation layer. In the real world, the bioturbation zone develops in the upper part of the buffer and habitat layer. In the model the bioturbation zone is treated as a separate layer with properties that differ from those in the underlying layer. At the top of the bioturbation layer, a mass transfer coefficient (M_{bl}) specifies the rate of contaminant transfer to the overlying lake water.



Layer #	Layer Description	Parameters
6	Bioturbation Layer	$b, f_{oc}, n, \rho_s, \lambda, M_{bl}$ D_{bp}, D_{bw}, K_{oc}
5	Buffer and Habitat Layer	$b, f_{oc}, n, \rho_s, \lambda, K_{oc}$
4	Active Layer	$b, f_{oc}, n, \rho_s, \lambda, Kf,$ N
3	Chemical Isolation Layer	$b, f_{oc}, n, \rho_s, \lambda, Koc$
2 1	Sediment Layer	$b, f_{oc}, n, \rho_s, \lambda, K_{oc}$

The model parameters that are specified for the layers are shown on the schematic above and are defined as follows (note that parameters must be specified in units listed below):

b = layer thickness (cm)
n = porosity
λ = first order decay rate (1/yr)
N = Freundlich coefficient
ρ_s = particle density (g/cm^3)
M_{bl} = mass transfer coef. (cm/hr)

f_{OC} = fraction organic carbon content
Kf = Freundlich coefficient (ug/kg)(L/ug)^N
D_{bw} = water biodiffusion coefficient (cm^2/yr)
D_{bp} = particle biodiffusion coefficient (cm^2/yr)
K_{OC} = organic carbon partition coefficient for specific contaminant (specified for sediment, sand and bioturbation layers separately, L/kg).

Note that the Freundlich coefficients (Kf and N), which are contaminant specific, are specified only in the active layer, and the particle biodiffusion coefficient and the water biodiffusion coefficient are only specified in the bioturbation layer.

In addition to the model parameters that are layer specific are the following parameters:

Kdoc = colloidal partition coefficient for a specific contaminant (L/kg);
Dw = diffusion coefficient for specific contaminant in water (cm^2/sec);
U = Darcy velocity (cm/yr);
Uss = steady-state Darcy velocity (cm/year),
Uc = Darcy velocity due to consolidation (cm/year),
α = dispersion length (cm); and
C_{oc} = colloidal matter concentration (mg/L).

It is important to note that the governing equation (1) has only four parameters – U, R, D and λ. One of these parameters, the first-order decay rate (λ) is specified directly. The other three parameters are derived from the parameters described above. The derivation of the parameters R, D, and U in the governing equation are described below.

The retardation factor is defined for all layers, except for the active layer, as:

$$R = \frac{n + (1-n)\rho_S K_{OC} f_{OC} + nC_{OC}K_{doc}}{1 + C_{OC}K_{doc}} \tag{2}$$

For the active layer, the retardation factor is defined as follows with sorption described by the Fruendlich isotherm:

$$R = \frac{n + (1-n)\rho_S K_f N C^{(N-1)} + nC_{OC}K_{doc}}{1 + C_{OC}K_{doc}} \tag{3}$$

The effective diffusion/dispersion coefficient (D) is defined for all layers except the sediment layer and the bioturbation layer as follows:

$$D = n^{(4/3)} D_w + \alpha\ |U| \tag{4}$$

For the sediment layer the effective diffusion/dispersion coefficient (D) is defined as:

$$D = \frac{nD_w}{1 - \ln(n^2)} + \alpha \left|U\right| \tag{5}$$

This definition uses a relationship developed by Boudreau (1996) to adjust the water diffusion coefficient for the tortuosity of a porous sediment. This relationship better defines the tortuosity relationship in natural sediments than the term used in equation 4 that is based on a relationship developed by Millington (1959). The Millington relationship works best for relatively uniform sands.

For the bioturbation layer the effective diffusion/dispersion coefficient is defined as:

$$D = n^{(4/3)} D_w + \alpha \left|U\right| + D_{bp} \rho_S (1 - n) K_{OC} f_{OC} + D_{bw} \tag{6}$$

The Darcy velocity in the Active Transport Model consists of two components: a steady-state groundwater velocity and a velocity component due to consolidation as

$$U = Uss + Uc \tag{7}$$

.The velocity component due to consolidation is defined on the basis of two parameters (*a* and *b*) as follows:

$$Uc = 30.48 * a * b * t^{(b-1)} \tag{8}$$

where *a* and *b* are coefficients, and *t* is time in years since placement of the cap.

It is important for the user of Active Capping Transport Model to note that the retardation parameter and the effective diffusion/dispersion parameter as defined by equation 1 are not equivalent to those commonly used in the groundwater literature. The retardation parameter commonly used in the groundwater literature (R') in equal to the retardation parameter defined above divided by the porosity (R = R'/n); and equivalently D = D'/n where D' is the effective diffusion/dispersion coefficient commonly used in the groundwater literature.

.

Review and Verification

I checked the accuracy of the calculated concentrations from the Active Capping Transport Model by simulating eight test cases with this computer code and with other computer codes. The other computer codes I used were MT3D (Zheng, 2006), the most-widely used groundwater transport model that has been extensively verified, and an analytical solution to equation 1 (Neville, 2005). The analytical solution was only used for test case 1 as it requires uniform properties. In using MT3D, the test cases were set up in a similar fashion to that used in the Active Capping Transport Model; a finite-difference grid with a vertical spacing of 0.5 centimeters. The TVD solution method was used in MT3D. Consolidation in MT3D was simulated by adjusting the velocity at each time step.

The input parameter values for the eight verification test cases are listed on Table 1. The various test cases were designed to test the model with various combinations of model parameters and boundary conditions. In five of the test cases, a Darcy velocity of 2 cm/year was used. When this velocity is specified, the contaminant transport is dominated by diffusive processes. The other three test cases used velocities of 10 and 20 cm/year. Only one of the test cases, test case 8, considers consolidation. The results from the test cases are presented on Figure 1 which is a series of plots of concentrations with depth as calculated with the models at various times after placement of the cap.

In test case 1, the calculated concentrations from all three models were nearly identical at all times (Figure 1). This indicates that for a media with uniform properties, that both MT3D and the Active Capping Transport Model correctly solve equation 1. This provides a level of confidence that MT3D is an appropriate code to use for verification of the Active Capping Transport Model.

The calculated concentrations from MT3D and the Active Capping Transport Model for tests cases 2 through 8 at various times since placement of the cap are also shown on Figure 1. For each of the test cases, nearly identical concentrations were calculated by MT3D and the Active Capping Transport Model. This provides confidence that the Active Capping Transport Model correctly solves the governing equation.

Conclusions

The Active Capping Transport Model is an appropriate model to use for the evaluation and design of sediment caps for Onondaga Lake. Based on the evaluations described in this memorandum, the computer model accurately solves the governing equation. The computer code for the model is concisely written and is relatively easy to understand. The model is very efficient which makes it feasible to easily conduct Monte Carlo type simulations.

References

Boudreau, B. 1996. The Diffusive Tortuosity of Fine-Grained Unlithified Sediments: *Geochimica et Cosmochimica Acta* 60, no. 16: 3139-3142.

Lambert, D. and D. Reible, 2009. An Analytical Approach for Evaluation of Capping of Contaminated Sediments. Soil and Sediment Contamination. 18:470-488.

Millington, R.J., 1959. Gas diffusion in porous media. Science, Vol. 130:100-102.

Neville, C., 2005. ADFL Analytical Solution – Version 4, User's Guide. S.S. Papadopulos & Associates, Inc. Bethesda, MD.

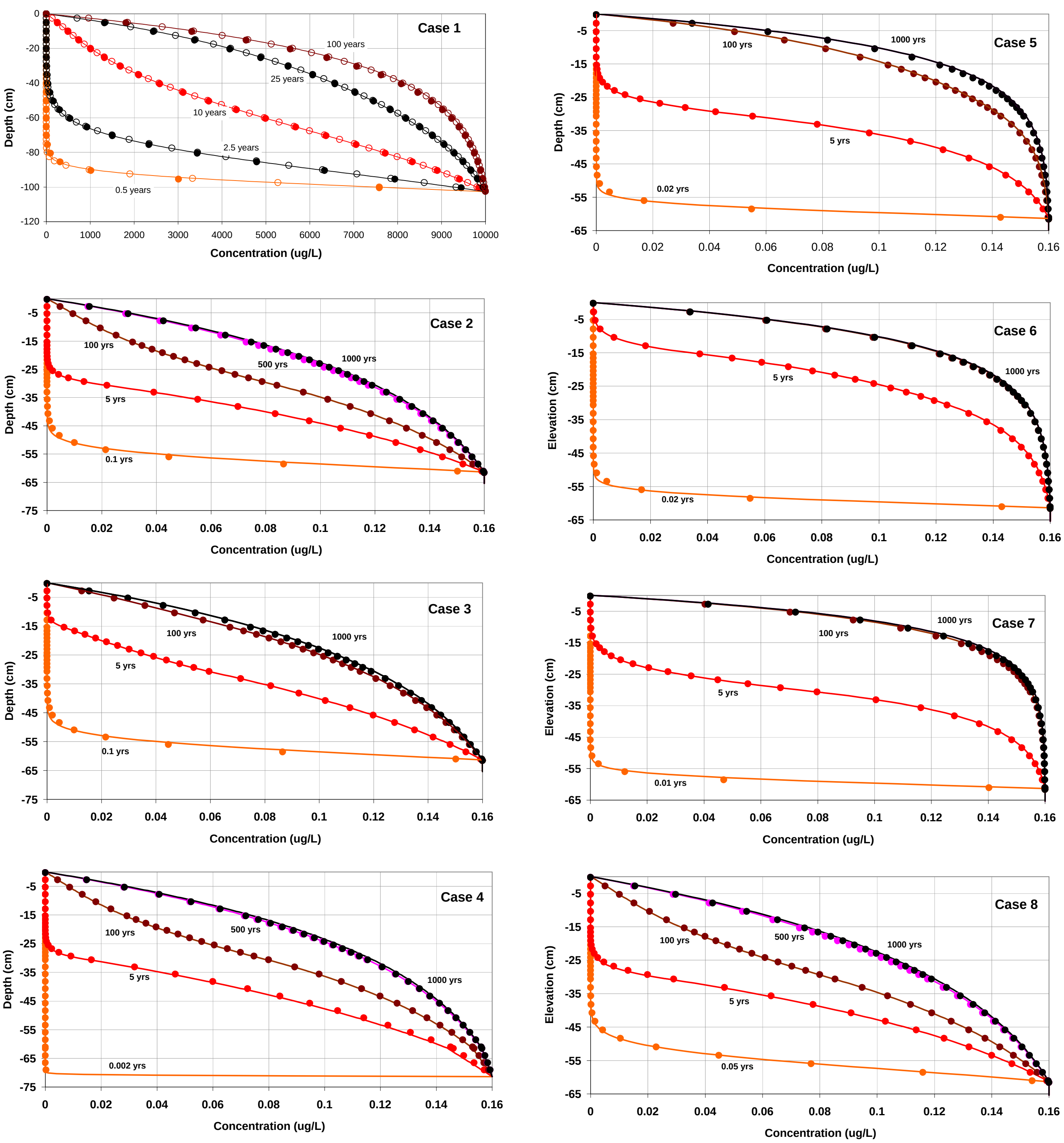
Palermo, M.R., S. Maynord, J. Miller, and D. Reible, 1996. Guidance for in-situ subaqueous capping of contaminated sediments. Environmental Protection Agency, EPA 905-B96-004, Great Lakes National Program Office, Chicago, Il. Available at http://www.epa.gov/grtlakes/sediment/iscmain/appndb.pdf.

Zheng, C. 2006. MT3DMS v5.2, A modular three-dimensional multispecies transport model for simulation of advection, dispersion and chemical reactions of contaminants in groundwater systems. Supplemental User's Guide. U.S. Army Corps of Engineers Technical Report, October 2006.

Table 1
Input Parameter Values for Test Cases

Parameter	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6	Case 7	Case 8
Contaminant Properties (Contaminant Specific)								
Contaminant	Toluene	Mercury	Mercury	Mercury	Mercury	Mercury	Mercury	Mercury
log Koc	2.35	2.35	2.35	2.35	2.35	2.35	2.35	2.35
log literature Koc - for sand layers	0	2.35	1.00	2.35	2.35	1.00	2.35	2.35
log Kdoc		0	0	0	0	0	0	0
Dw	5.2E-06	4.7E-06	4.7E-06	4.7E-06	4.7E-06	4.7E-06	4.7E-06	4.7E-06
Flow and System Properties (Site Specific)								
Darcy Velocity	2	2	2	2	10	10	20	2
depositional velocity	0	0	0	0	0	0	0	0
hydrodynamic dispersivity	0.42	6.13	6.13	6.13	6.13	6.13	6.13	6.13
boundary layer mass transfer coeff.	0.33	0.36	0.36	0.36	0.36	0.36	0.36	0.36
colloidal matter concentration	0	0	0	0	0	0	0	0
Sediment Properties (Site Specific)								
sediment porosity	0.4	0.79	0.79	0.79	0.79	0.79	0.79	0.79
sediment particle density	2.6	2.62	2.62	2.62	2.62	2.62	2.62	2.62
sediment foc	0.001	0.1	0.1	0.01	0.1	0.1	0.1	0.1
sediment initial decay rate	0	0	0	0	0	0	0	0
duration for initial decay rate	0	1000	1000	1000	1000	1000	1000	1000
sediment final decay rate	0	0	0	0	0	0	0	0
Chemical Isolation Layer Properties (Design Parameters)								
layer thickness	30	30.48	30.48	30.48	30.48	30.48	30.48	30.48
layer porosity	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
layer particle density	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
layer foc	0.001	1E-07	1E-07	1E-07	1E-07	1E-07	1E-07	1E-07
layer initial decay rate	0	2.1E-09	2.1E-09	2.1E-09	2.1E-09	2.1E-09	2.1E-09	2.1E-09
layer final decay rate	0	2.1E-09	2.1E-09	2.1E-09	2.1E-09	2.1E-09	2.1E-09	2.1E-09
Active Layer Properties (Design Parameters)								
active layer thickness (sand plus AC)	17.0	0.3846	0.3846	0.3846	0.3846	0.3846	0.3846	0.3846
active layer porosity	0.4	0.35	0.35	0.35	0.35	0.35	0.35	0.35
active layer particle density (calculated)	2.6	0.80	0.80	0.80	0.80	0.80	0.80	0.80
active layer Freudlich Kf	0.22	22.36	22.36	22.36	22.36	22.36	22.36	22.36
active layer Freundlich 1/n	1	1	1	1	1	1	1	1
active layer initial decay rate	0	2.1E-09	2.1E-09	2.1E-09	2.1E-09	2.1E-09	2.1E-09	2.1E-09
active layer final decay rate	0	2.1E-09	2.1E-09	2.1E-09	2.1E-09	2.1E-09	2.1E-09	2.1E-09
Buffer and Habitat Restoration Layer Properties (Design Parameters)								
Habitat Restoration Layer thickness	55.7	30.48	30.48	30.48	30.48	30.48	30.48	30.48
Buffer Layer thickness	0	0	0	0	0	0	0	0
layers porosity	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
layers particle density	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
layers foc (CI and non-bio HR)	0.001	0.1	0.1	0.1	0.1	0.1	0.1	0.1
layers initial decay rate	0	2.1E-09	2.1E-09	2.1E-09	2.1E-09	2.1E-09	2.1E-09	2.1E-09
layers final decay rate	0	2.1E-09	2.1E-09	2.1E-09	2.1E-09	2.1E-09	2.1E-09	2.1E-09
Bioturbation Layer Properties (Site Specific)								
bioturbation depth	5.5	15.24	15.24	15.24	15.24	15.24	15.24	15.24
bioturbation layer porosity	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
bioturbation layer particle density	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
bioturbation layer foc	0.001	0.1	0.1	0.1	0.1	0.1	0.1	0.1
bioturbation layer initial decay rate	0	2.1E-09	2.1E-09	2.1E-09	2.1E-09	2.1E-09	2.1E-09	2.1E-09
bioturbation layer final decay rate	0	2.1E-09	2.1E-09	2.1E-09	2.1E-09	2.1E-09	2.1E-09	2.1E-09
Pore Water Biodiffusion Coefficient	0	4.7E-06	4.7E-06	4.7E-06	4.7E-06	4.7E-06	4.7E-06	4.7E-06
Particle Biodiffusion Coefficient	0	0	0	0	0	0	0	0
Bioturbation Layer logKoc	0	2.35	2.35	2.35	2.35	2.35	2.35	2.35
Consolidation Data								
parameter a	0	0	0	0	0	0	0	0.211
parameter b	0	0.235	0.235	0.235	0.235	0.235	0.235	0.235
total time for consolidation (years)	0	30	30	30	30	30	30	30
Simulation Parameters								
Simulation length (years)	100	1,000	1,000	1,000	1,000	1,000	1,000	1,000
Minimum number of grid points	150	150	150	150	150	150	150	150
Minimum number of time steps	400	400	400	400	400	400	400	400
Answer 1 for yes and 0 for no								
Infinite source?	1	1	1	0	1	1	1	1
Infinite source at sediment bottom?	1	1	1	1	1	1	1	1

Note: Shaded cells indicate parameters changed relative to Test Case 2.



MT3D results plotted as solid dots, Active Capping Transport Model results plotted as solid lines and in Case 1 AFLD results plotted as open circles.

Figure 1 Comparison of Calculated Concentrations for Test Cases 1 through 8

S.S. PAPADOPULOS & ASSOCIATES, INC.
Environmental & Water-Resource Consultants

Memorandum

Date: January 6, 2009

From: Charles Andrews

To: Files

Subject: **Active Capping Transport Model – Version 2.0**

Introduction

Active Capping Transport Model is a computer program developed by David Lampert and Danny Reible at the University of Texas. The model calculates one-dimensional vertical transport of a contaminant through a sediment cap considering the processes of advection, diffusion, dispersion, reaction, bioturbation, deposition and retardation with local equilibrium between sediment, pore water, and dissolved organic matter. An excellent background document that describes the processes simulated with the model is “Guidance for In-Situ Subaqueous Capping of Contaminated Sediments: Appendix B: Model for Chemical Containment by a Cap” (Palermo and others 1996). I highly recommend that all users of Active Capping Transport Model read and familiarize themselves with this background document.

I reviewed Version 2.0 of the Active Capping Transport Model dated December 10, 2008. The model was developed as a MATLAB program and is run within the MATLAB environment. I used MATHLAB Version 7.7 to run the program. The model reads input data from an Excel spreadsheet and writes model outputs to an Excel spreadsheet. The model will not run on earlier versions of MATLAB that do not support reading and writing from Excel files.

Active Capping Transport Model Version 2.0 was developed to simulate contaminant transport in a five layer system; model parameters can vary from layer to layer. The governing equation in the Active Capping Transport Model is:

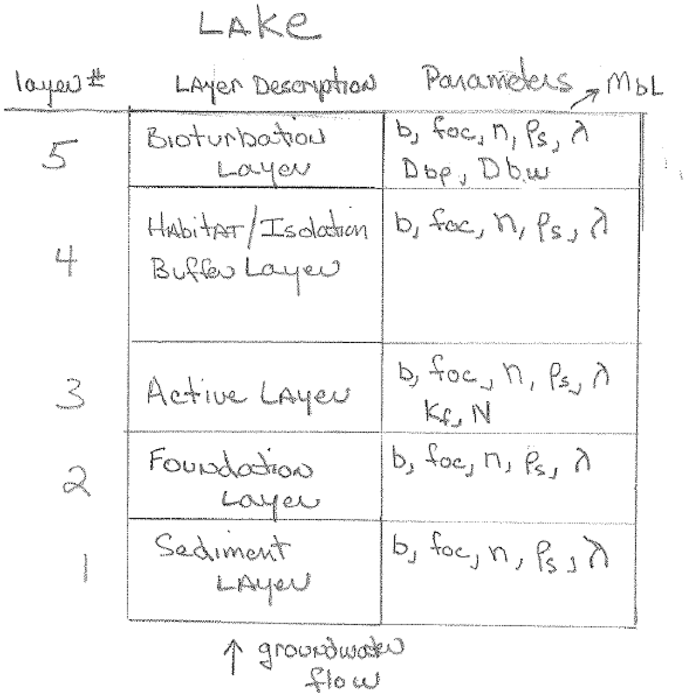
$$R\frac{\partial C}{\partial t} = -U\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} - n\lambda C \qquad (1)$$

where: C = concentration;
U = Darcy velocity;
D = effective diffusion coefficient (sum of diffusion and dispersive coefficients);
R = retardation factor for compound of interest; and
λ = first-order degradation rate.

7944 WISCONSIN AVENUE, BETHESDA, MARYLAND 20814-3620 • TEL: (301) 718-8900 • FAX: (301) 718-8909
www.sspa.com • e-mail: CAndrews@sspa.com

The governing equation is solved using a two-point upwind centered finite-difference scheme in space with the Crank-Nicolson method. The model automatically creates a finite-difference grid with sufficiently fine-vertical spacing to minimize numerical dispersion; for typical problems a vertical spacing of 0.5 centimeters is specified. The time step size is increased with time from start of simulation for computational efficiency.

A schematic of the 5-layer system simulated with the Active Capping Transport Model is shown to the right.



layer #	Layer Description	Parameters
5	Bioturbation Layer	b, foc, n, ρ_s, λ D_{bp}, D_{bw}
4	Habitat/Isolation Buffer Layer	b, foc, n, ρ_s, λ
3	Active Layer	b, foc, n, ρ_s, λ Kf, N
2	Foundation Layer	b, foc, n, ρ_s, λ
1	Sediment Layer	b, foc, n, ρ_s, λ

The bottom layer is the sediment layer. This layer can be specified at a constant concentration or it can be specified with a finite thickness with depth varying concentrations to simulate a depleting source with time.

Overlying the sediment layer is the cap foundation layer, which in turn is overlain by an active layer – a layer containing activated carbon.

Overlying the active layer is the habitat/isolation/buffer layer, which in turn is overlain by a bioturbation layer. In the real world, the bioturbation zone develops in the upper part of the habitat/isolation/buffer layer. In the model the bioturbation zone is treated as a separate layer with properties that differ from those in the underlying layer. At the top of the bioturbation layer, a mass transfer coefficient (M_{bl}) specifies the rate of contaminant transfer to the overlying lake water.

The model parameters that are specified for each layer are shown on the schematic above and are defined as follows (note that parameters must be specified in units listed below):

b = layer thickness (cm)
n = porosity
λ = first order decay rate (1/yr)
N = Freundlich coefficient

foc = fraction organic carbon content
ρ_s = particle density (g/cm^3)
Kf = Freundlich coefficient (ug/kg)(L/ug)^N
D_{bp} = particle biodiffusion coefficient (cm^2/yr)
D_{bw} = water biodiffusion coefficient (cm^2/yr)

Note that the Freundlich coefficients (Kf and N), which are contaminant specific, are specified only in the active layer, and the particle biodiffusion coefficient and the water biodiffusion coefficient are only specified in the bioturbation layer.

In addition to the model parameters that are layer specific are the following parameters:

Koc = organic carbon partition coefficient for a specific contaminant (L/kg);
Kdoc = colloidal partition coefficient for a specific contaminant (L/kg);
Dw = diffusion coefficient for specific contaminant in water (cm^2/sec);
U = Darcy velocity (cm/yr);
α = dispersion length (cm);
C_{oc} = colloidal matter concentration (mg/L); and
M_{bl} = upper layer mass transfer coefficient (cm/hr).

It is important to note that the governing equation (1) has only four parameters – U, R, D and λ. Two of these parameters, the Darcy velocity (U) and the first-order decay rate (λ) are specified directly. The other two parameters are derived from the parameters described above. The derivation of the parameters R and D in the governing equation are described below.

The retardation factor is defined for all layers, except for the active layer, as:

$$R = \frac{n + (1-n)\rho_S K_{OC} f_{OC} + nC_{OC}K_{doc}}{1 + C_{OC}K_{doc}} \tag{2}$$

For the active layer, the retardation factor is defined as follows with sorption described by the Fruendlich isotherm:

$$R = \frac{n + (1-n)\rho_S K_f NC^{(N-1)} + nC_{OC}K_{doc}}{1 + C_{OC}K_{doc}} \tag{3}$$

The effective diffusion coefficient (D) is defined for all layers except the sediment layer and the bioturbation layer as follows:

$$D = n^{(4/3)}D_w + \alpha\,|U| \tag{4}$$

For the sediment layer the effective diffusion coefficient (D) is defined as:

$$D = \frac{nD_w}{1 - \ln(n^2)} + \alpha\ |U| \tag{5}$$

This definition uses a relationship developed by Boudreau (1996) to adjust the water diffusion coefficient for the tortuosity of a porous sediment. This relationship better defines the tortuosity relationship in natural sediments than the term used in equation 4 that is based on a relationship developed by Millington (1959). The Millington relationship works best for relatively uniform sands.

For the bioturbation layer the effective diffusion coefficient is defined as:

$$D = n^{(4/3)} D_w + \alpha\ |U| + D_{bp} \rho_S (1-n) K_{OC}\, f_{OC} + D_{bw} \tag{6}$$

It is important for the user of Active Capping Transport Model to note that the retardation parameter and the effective diffusion parameter as defined by equation 1 are not equivalent to those commonly used in the groundwater literature. The retardation parameter commonly used in the groundwater literature (R') in equal to the retardation parameter defined above divided by the porosity (R = R'/n); and equivalently D = D'/n where D' is the effective diffusion coefficient commonly used in the groundwater literature.

Review and Verification

I checked the computer code for Active Capping Transport Model (parsons.m) to verify that the model input parameters specified for model layers were correctly converted into the parameters used in the governing equation. These conversions are made on lines 99-199 and 329 to 330 of the model code. In the latest version of the code that I reviewed, these conversions were correct except for the calculation of the retardation coefficient with a Freundlich isotherm (equation 3). I modified the code to correctly calculate the retardation coefficient using equation 3 (in the version of the code I reviewed, the term "n+" in the numerator on the right hand side was missing).

I checked the accuracy of the calculated concentrations from the Active Capping Transport Model by simulating four test problems with this computer code and with other computer codes. The other computer codes I used were MT3D (Zheng and Wang, 1998), the most-widely used groundwater transport model that has been extensively verified, and an analytical solution to equation 1 (Neville, 2005). In the first three test cases, a Darcy velocity of 2 cm/year was used. When this velocity is specified, the contaminant transport is dominated by diffusive processes. The fourth test case used a Darcy velocity of 10 cm/year.

The four test problems consisted of the following: 1) problem with uniform properties in the five model layers, 2) problem with uniform properties except for porosity which was varied from layer to layer, 3) problem with sorption in active layer simulated with Freundlich isotherm (in other test problems the Freundlich coefficient N was specified as 1 to simulate linear sorption), and 4) identical to test problem 3 except that Darcy velocity increased from 2 cm/year to 10 cm/year. The model parameters specified for the Active Capping Transport Model for the four test problems are listed below in the format that they appear in the Excel spreadsheet used for model input.

Input Parameter Values for Test Problems

	Test Problem 1	Test Problem 2	Test Problem 3	Test Problem 4	
Contaminant Properties (Contaminant Specific)					
log Koc	2.34947	2.34947	2.34947	2.34947	log L/kg
log Kdoc	0	0	0	0	log L/kg
Dw	5.2187E-06	5.2187E-06	5.2187E-06	4.8541E-06	cm2/s
Flow and System Properties (Site Specific)					
Darcy Velocity	2	2	2	10	cm/yr
depositional velocity	0	0	0	0	cm/yr
hydrodynamic dispersivity	0.42361	0.42361	0.42361	0.42361	cm
boundary layer mass transfer coeff.	0.328	0.328	0.328	0.328	cm/hr
colloidal matter concentration	0	0	0	0	mg/L
Sediment Properties (Site Specific)					
sediment porosity	0.4	0.4	0.4	0.4	
sediment particle density	2.6	2.6	2.6	2.6	g/cm3
sediment foc	0.001	0.001	0.001	0.001	
sediment decay rate	0	0	0	0	yr-1
Foundation Layer Properties (Design Parameters)					
foundation layer thickness	30	30	30	30	cm
foundation layer porosity	0.4	0.5	0.4	0.4	
foundation layer particle density	2.6	2	2.6	2.6	g/cm3
foundation layer foc	0.001	0.001	0.001	0.001	
foundation layer decay rate	0	0	0	0	yr-1
Active Layer Properties (Design Parameters)					
active layer thickness	**17.0**	**17.0**	**17.0**	**17.0**	cm
active layer porosity	0.4	0.8	0.35	0.35	
active layer particle density	2.6	0.8	0.8	0.8	g/cm3
active layer Freudlich Kf	0.22	0.22	5,000.00	5,000.00	ug/kg*(ug/L)$^{-n}$
active layer Freudlich n	1	1	0.44	0.44	
active layer decay rate	0	0	0	0	yr-1
Isolation, Buffer, and Habitat Restoration Layer Properties (Design Parameters)					
Habitat Restoration Layer thickness	40.48	40.48	40.48	40.48	cm
Chemical Isolation Layer thickness	15.24	15.24	15.24	15.24	cm
Buffer Layer thickness	0	0	0	0	cm
isolation layers porosity	0.4	0.3	0.4	0.4	
isolation layers particle density	2.6	2.2286	2.6	2.6	g/cm3
isolation layer foc	0.001	0.001	0.001	0.001	
isolation layer decay rate	0	0	0	0	yr-1
Bioturbation Layer Properties (Site Specific)					
bioturbation depth	5.5	5.5	5.5	5.5	cm
bioturbation layer porosity	0.4	0.4	0.4	0.4	
bioturbation layer particle density	2.6	2.6	2.6	2.6	g/cm3
bioturbation layer foc	0.001	0.001	0.001	0.001	
bioturbation layer decay rate	0	0	0	0	yr-1
Pore Water Biodiffusion Coefficient	0	0	0	0	cm2/yr
Particle Biodiffusion Coefficient	0.00	0.00	0.00	0.00	cm2/yr

The results from the test simulations are shown on the following pages. The analytical solution was only used for test problem 1 as it requires uniform properties. In using MT3D, the problem were set up in a similar fashion to that used in the Active Capping Transport Model; a finite-difference grid with a vertical spacing of 0.5 centimeters was used and the TVD solution method.

In test problem 1 the calculated concentrations from all three models were nearly identical (Figure 1). For the second test problem, the solutions from MT3D and the Active Capping Transport Model compared well (Figure 2). For the third test problem, the solutions from MT3D and the Active Capping Transport Model did not compare well (Figure 3). In the MT3D simulation, based on results for 100 years, it appears that the effective retardation coefficient in the active layer is higher than in the Active Capping Transport Model. Another simulation was made in which the Freundlich coefficient (Kf) in MT3D was reduced by 15.5% to check if the differences between the models were related to specification of retardation coefficient. The results from this MT3D simulation compared very well with the results from the Active Capping Model for test problem 3.

It was determined that the discrepancy between the MT3D solution and the Active Capping Transport Model solution was the result of differences in time-step sizes. The Active Capping Transport Model was rerun for test problem 3 with each time step reduced by a factor of 32 and the solution compared well with the MT3D solution (Figure 4). Test problem 4 was also run with a reduced time step size and the comparison between the MT3D solution and the Active Capping Transport Model solution is good.

The reduction factor of 32 was chosen arbitrarily. Initially chose a factor of 8 and this did not produce acceptable results, the factor was then increased to 32 and the results were acceptable.

Conclusions

The Active Capping Transport Model is an appropriate model to use for the evaluation and design of a sediment cap for Onondaga Lake. Based on our evaluations that computer model accurately solves the governing equation. In addition, note that the computer code for the model is concisely written and is relatively easy to understand. The model is very efficient which makes it feasible to easily conduct Monte Carlo type simulations.

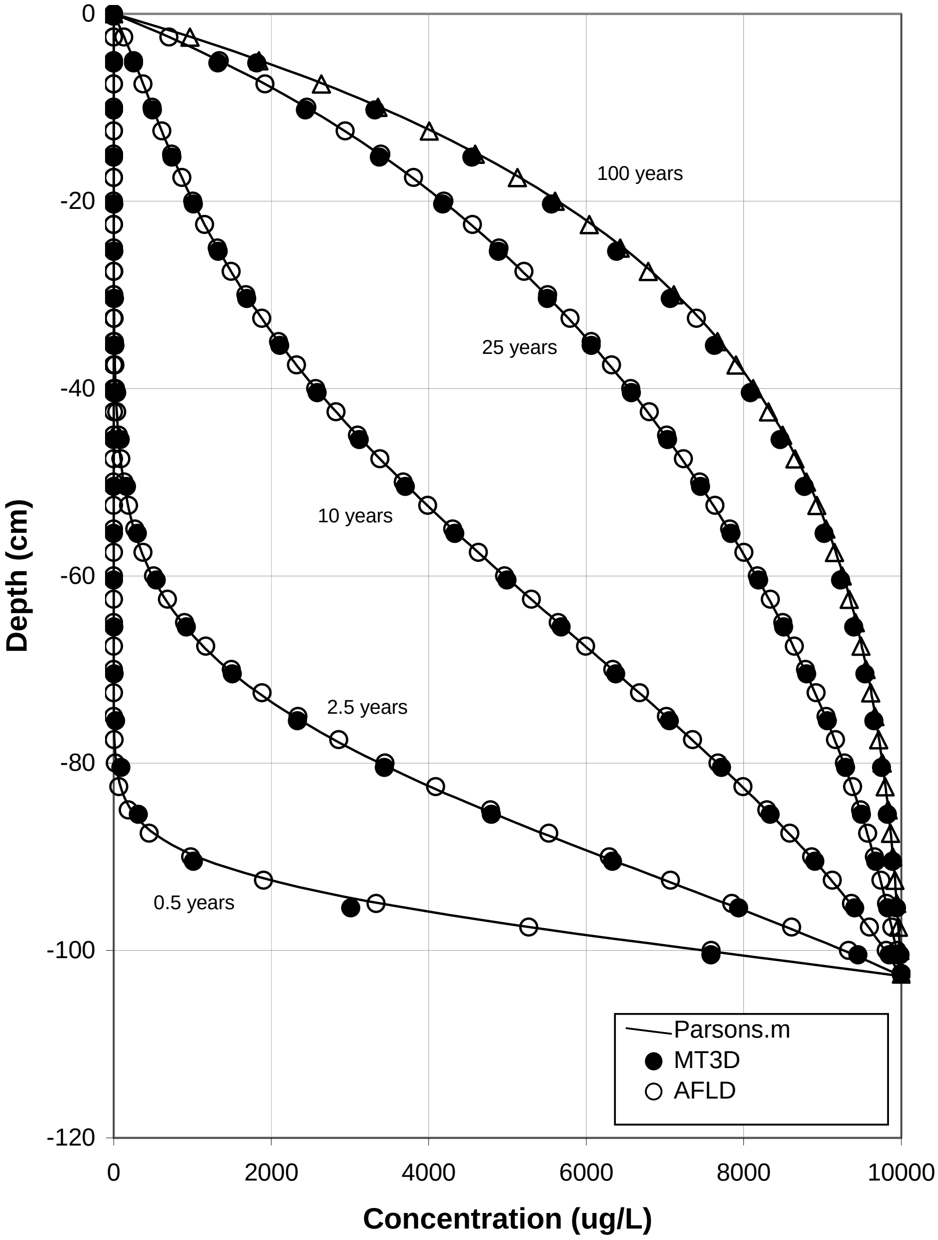


Figure 1 Test Problem 1 Uniform Properties

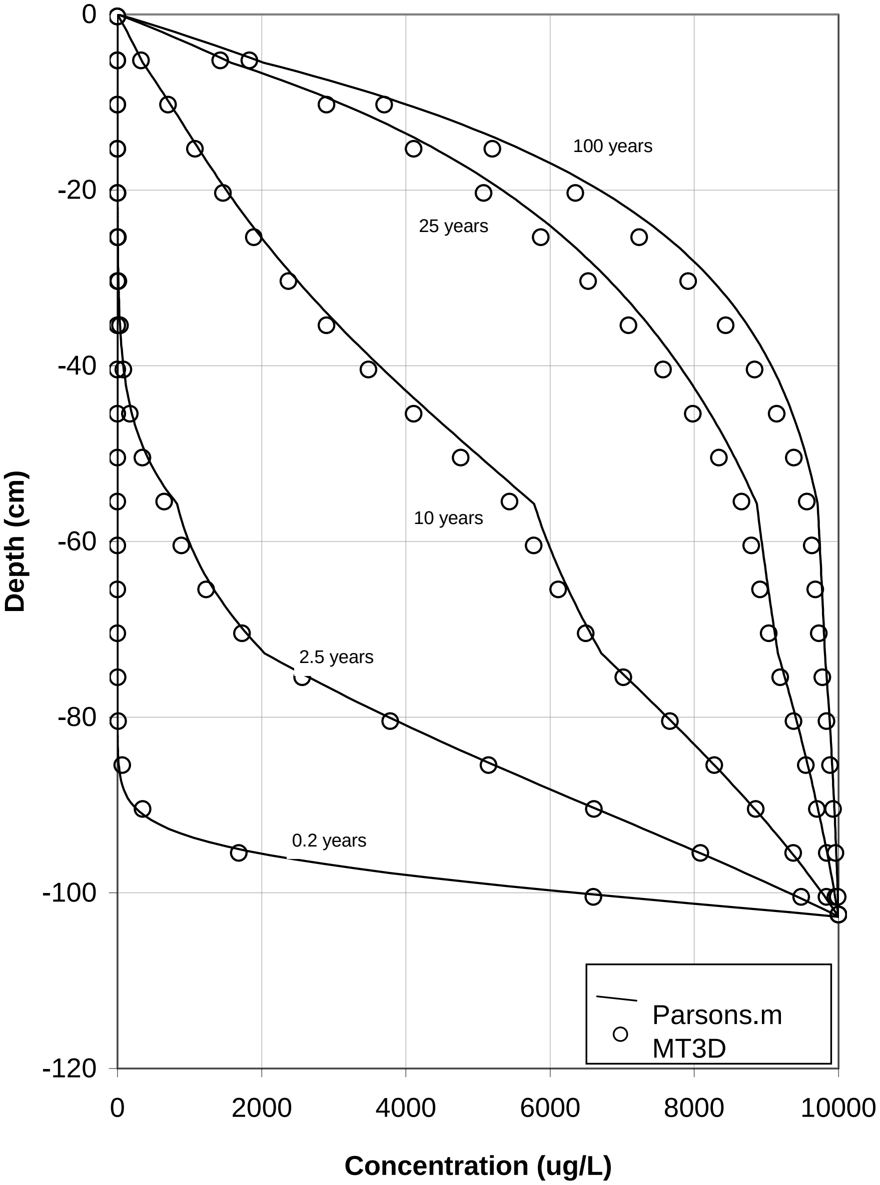


Figure 2 Test Problem 2 -- Non-Uniform Properties (porosity varies among five layers)

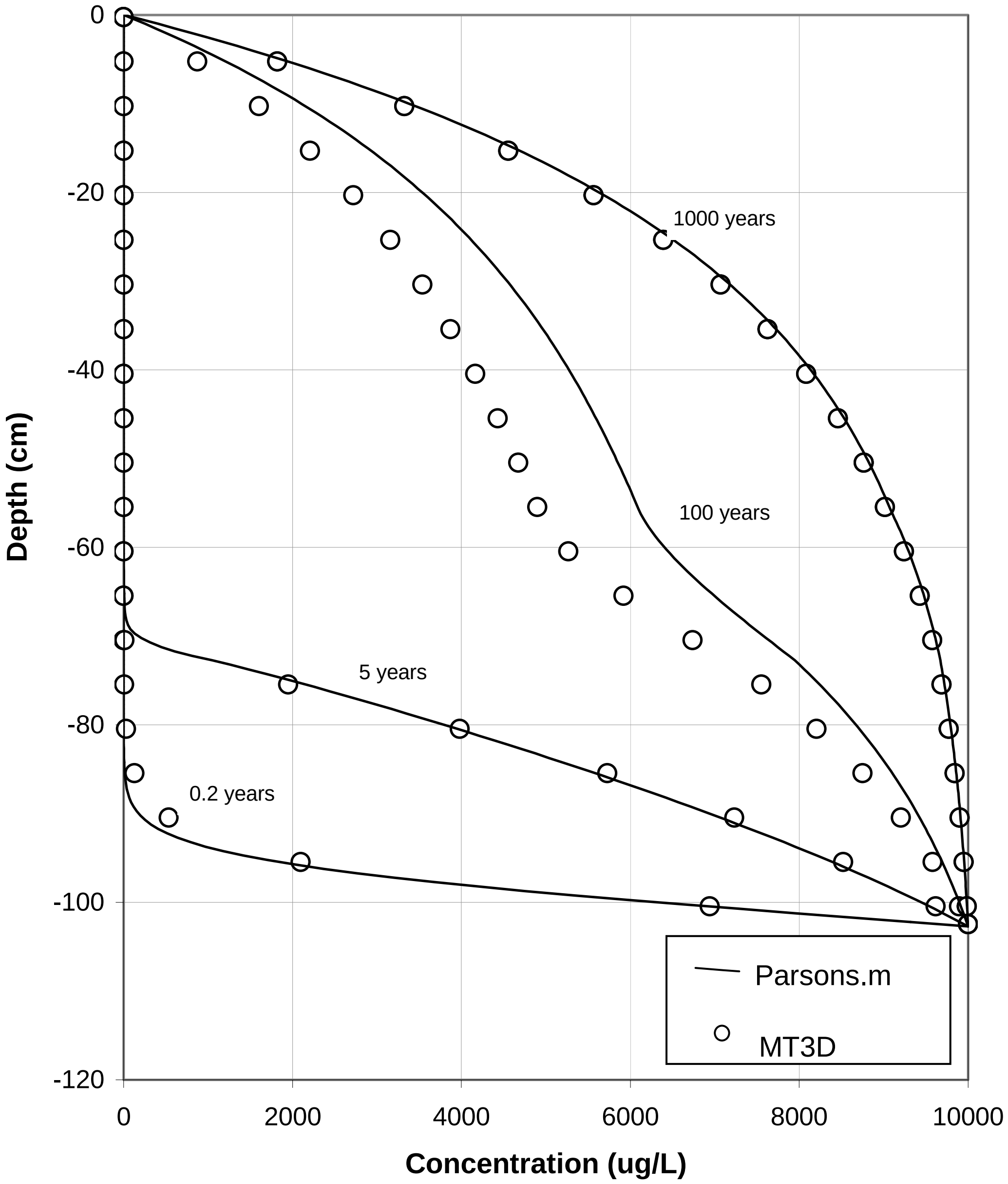


Figure 3 Test Problem 3

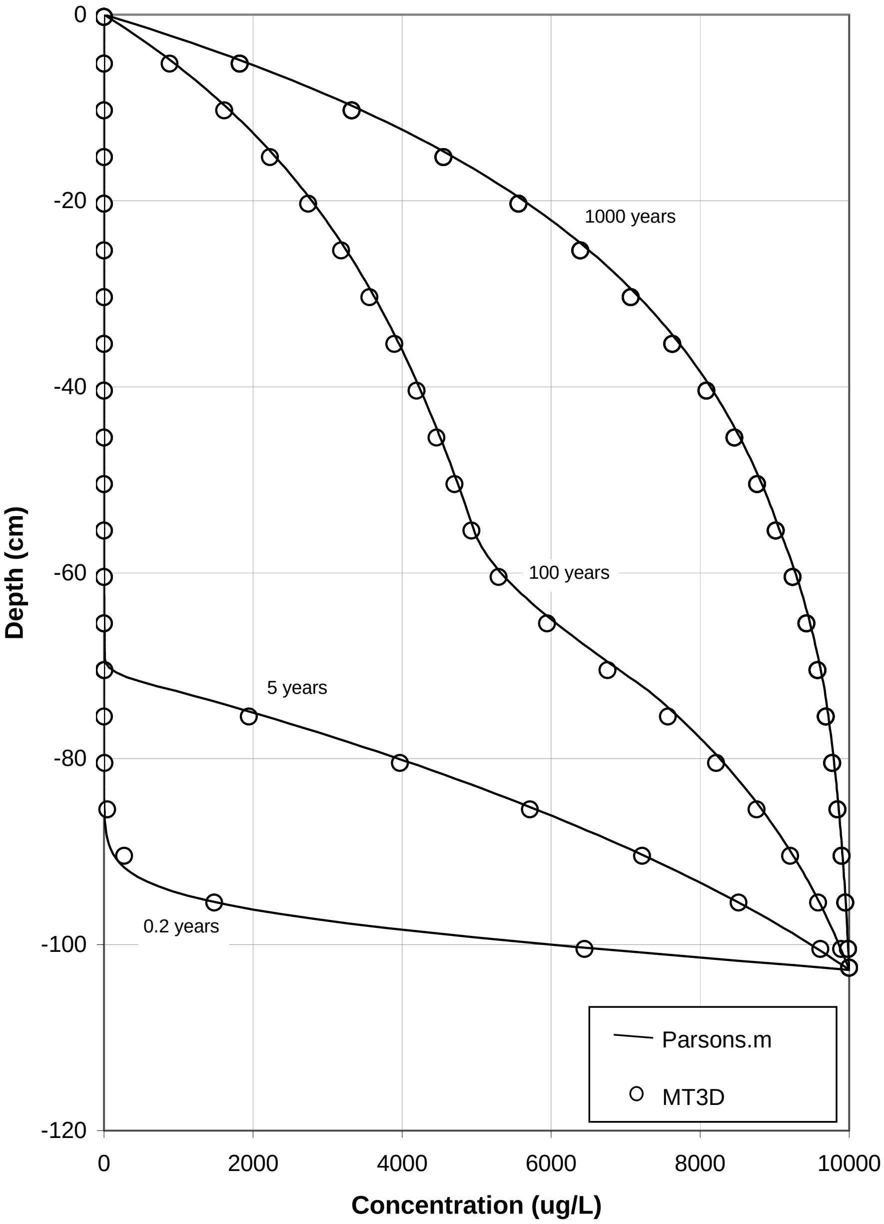


Figure 4 Test Problem 3 (decreased time step size in Parsons.m)

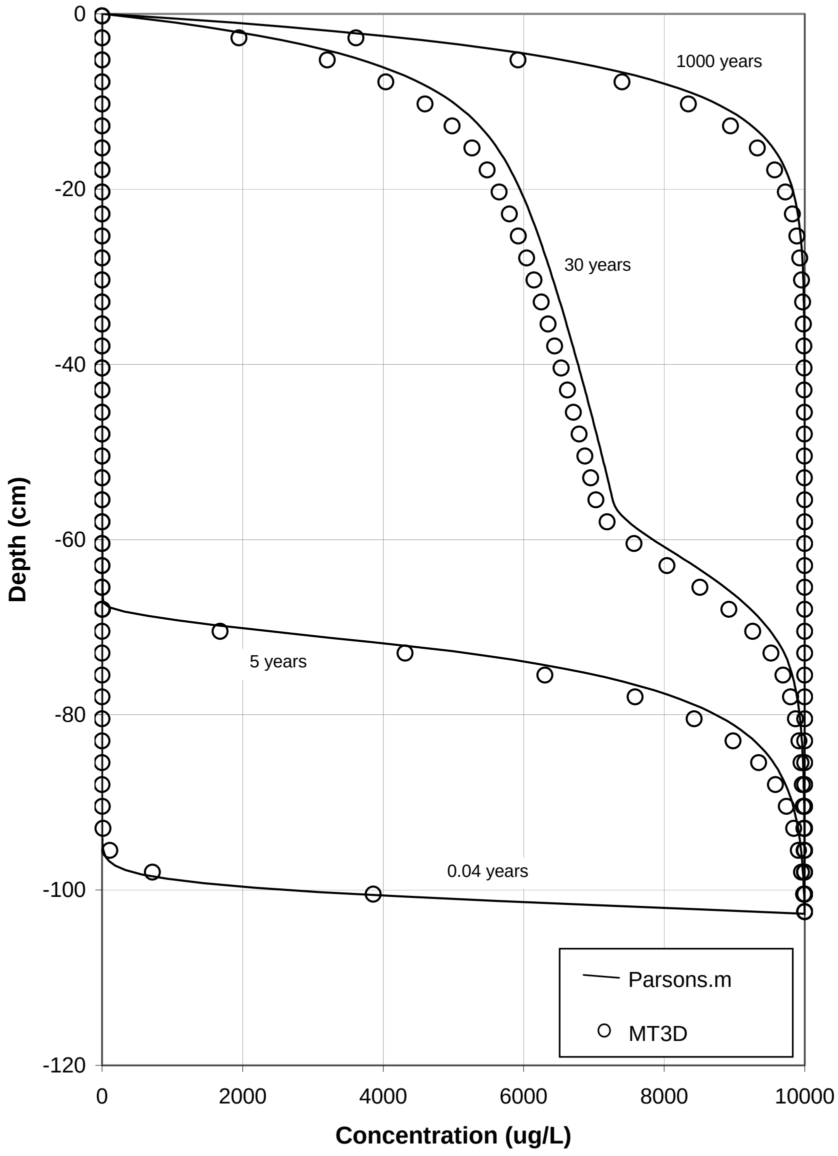


Figure 5 Test Problem 4 (decreased time step size in Parsons.m)

References

Boudreau, B. 1996. The Diffusive Tortuosity of Fine-Grained Unlithified Sediments: *Geochimica et Cosmochimica Acta* 60, no. 16: 3139-3142.

Millington, R.J., 1959. Gas diffusion in porous media. Science, Vol. 130:100-102.

Neville, C., 2005. ADFL Analytical Solution – Version 4, User's Guide. S.S. Papadopulos & Associates, Inc. Bethesda, MD.

Palermo, M.R., S. Maynord, J. Miller, and D. Reible, 1996. Guidance for in-situ subaqueous capping of contaminated sediments. Environmental Protection Agency, EPA 905-B96-004, Great Lakes National Program Office, Chicago, Il. Available at http://www.epa.gov/grtlakes/sediment/iscmain/appndb.pdf.

Zheng, C. and P. Wang, 1998. MT3DMS, A modular three-dimensional multispecies transport model for simulation of advection, dispersion and chemical reactions of contaminants in groundwater systems. Documentation and User's Guide. U.S. Army Corps of Engineers Technical Report, June 1998.