An analytical model for chemical diffusion in layered contaminated sediment systems with bioreactive caps

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Abstract

An analytical model for contaminant transport in multi-layered capped contaminated sediments including the degradation of organic contaminant is presented. The effect of benthic boundary layer was treated as a Robin-type boundary condition. The results of the proposed analytical model agree well with experimental data. The biodegradation of contaminant in bioturbation layer shows a significant influence on the flux at the surface of system. The maximum flux for the case with $t_{1/2,\text{bio}}=0.07$ year can be 4.5 times less than that of the case without considering the effect of biodegradation. The thickness of bioturbation layer has a significant effect on the performance of the capped contaminated sediment. The maximum flux for the case with $l_{\text{bio}}=15\text{cm}$ can be 17 times larger than that of the case without bioturbation layer. This may be due to the fact that the effective diffusion coefficient of sand cap can be 28 times lower than $D_{\text{bio}}$. The mass transfer coefficient should be considered for the design of the capping system as the contaminant concentration at the top of system for the case with $k_{bl}=2.5\times10^{-5}$ cm/s can be 13 times greater than that of the case with $k_{bl}=10^{-4}$ cm/s. The proposed analytical model can be used for verification of complicated numerical methods, evaluation of experimental data and design of the capping contaminated sediment systems with reactive cap layers.

Keywords: Analytical model; chemical diffusion; degradation; capped contaminated sediment; mass transfer coefficient; bioturbation layer
1. Introduction

Sediments contaminated with organic compounds are always found in many waterways, harbors and estuaries. The transfer of these chemicals from the sediments into overlying waters will affect the marine food web and the human using these waters for recreation and supply of sea food. In order to reduce risk associated with contaminant in the sediments, different remediation strategies have been developed. The general characteristics of the three basic sediment management options are natural recovery, capping or in situ treatment, and dredging. In order to isolate the contaminants from organisms in the water and surficial sediments, in-situ capping is used as a cover for placement over contaminated sediment. The cap can be constructed with multiple layered clean sediments such as sand and gravel. The application of sand and sediment caps as a remediation technology for contaminated sediments was subsequently investigated. Wang et al. and Thoma et al. found that a layer of clean sand sediment successfully reduced the concentrations of the HOC. The traditional sand caps are less effective at sites where groundwater seepage or mobile contaminants are present. The active caps incorporating reactive or sorptive constituents are designed to reduce contaminant flux. For instance, the coke and other “active” materials (e.g., activated carbon and kraft lignin) are used as capping to enhance sorption in order to reduce the availability of the contaminant and improve the effectiveness of in situ capping. The isolation times provided by the sorbent layers increased with the increase of sorption strength and capacity (activated
Eek et al. developed the laboratory microcosm test to measure the diffusion of PAHs and PCBs from sediment with different capping layers. They found that caps with passive material can significantly reduce the diffusive contaminant flux through the cap.

It has been shown that diffusive transport is often the dominant mode of contaminant transport through subaqueous caps for contaminated sediments since the water flow in fine-grained sediments is very slow. Diffusion of contaminant through layered porous media is often modeled by numerical methods. For instance, Rowe et al. have developed the finite layer methods for contaminants transport though multi-layered barrier systems. Leo and Booker developed the boundary element method for contaminant diffusion in non-homogeneous porous media. Praveen Kumar and Dodagoudar provide an accurate methodology for numerical simulation of the two-dimensional contaminant transport through the saturated homogeneous porous media and landfill liners using element-free Galerkin method (EFGM). The finite element method based numerical model COMPASS has also been used for the analysis of contaminant diffusion in the layered porous media. Zhang et al. investigated contaminant transport in the two-layered system consisting of compacted clay liner and the aquifer using the numerical method including the finite-difference method and the numerical inversion of Laplace transform. However, the use of the numerical models is restricted to experienced users and for sites where field data are known in great detail.
Analytical solutions play an important role in understanding many scientific phenomena\textsuperscript{26-28}, although some simplifications need to be made in the process of deriving them. In particular, analytical solutions can also play a unique role in validating many new numerical methods\textsuperscript{29-31}. For these reasons, analytical solutions have been derived in recent years for many scientific and engineering problems\textsuperscript{32-34}. This means that by using analytical solutions in this particular study, a better understanding of the mechanism of contaminant diffusion can be explored, the movement of contaminant plumes can be predicted, and the results of numerical modeling can be verified\textsuperscript{35}. They are also more computationally efficient and can be used to address the Robin-type boundary condition that is often not available in the numerical programs\textsuperscript{37,38}. Some works have been done on solving the diffusion or advection-dispersion equation of solute transport in two- or multi-layered porous media using the Laplace transform method\textsuperscript{38}, the integral transform method\textsuperscript{39}, and an approach combining the Laplace transformation method and binomial theorem\textsuperscript{40}. An analytical solution for contaminant diffusion through multi-layered system was presented by Chen et al.\textsuperscript{41}. Li and Cleall\textsuperscript{37} presented analytical solutions for various combinations of fixed solute concentration and zero-flux boundary conditions applied at each end of a finite one-dimensional domain considering arbitrary initial solute concentration distribution throughout the media. Deng et al.\textsuperscript{42} proposed the integral transform solution for solute transport in multi-layered porous media with the implicit treatment of the interface conditions and arbitrary boundary conditions. Zhao and his coworkers have conducted extensive studies to derive analytical solutions for both
chemical dissolution front instability problems and physical dissolution front instability problems in fluid-saturated porous media. However, the effect of degradation on the transport of contaminant was not considered in the literature analytical models.

Many types of organic contaminant (e.g., aliphatic and aromatic compounds) can be significantly degraded in soils. For the sediment capping systems, Lampert and Reible reported that degradation of sediment contaminant in the biologically active capping may be of primary importance for the control of the contaminant release from the sediments. Himmelheber et al. demonstrated that in situ bioreactive capping can be a feasible remedial approach for the contaminated sediments. Thoma et al. also found that degradation of contaminant in sediment has a great influence on contaminant flux discharged. For example, the maximum flux released for the case with half-life of 100 years in the sediment can be 67 times lower than the case without considering degradation. Therefore, it is of great importance to consider the degradation process to impede contaminant release from the sediment. In addition, the boundary condition at the cap-water interface is quite complex, as it essentially requires the effluent boundary condition from a porous medium; therefore, the surface boundary condition for the capping sediment systems is often modeled with a mass transfer coefficient. Thibodeaux and Boudreau and Jørgensen presented empirical correlations for mass transfer coefficient based on mixing conditions in the overlying water. The value of mass transfer coefficient should be conservatively estimated, as its value directly affects the surficial sediment concentrations. However, few
analytical models have considered the effect of mass transfer coefficient on contaminant transport through the contaminated sediment and the capping layer.

The objective of this paper is to develop an analytical model for contaminant transport in multi-layered capped sediment system considering the effect of contaminant degradation, diffusion, and adsorption. The effects of bioturbation layer on contaminant transport in capped contaminated sediment system will be analyzed by using the mass transfer coefficient at the cap-water interface. The analytical solutions are compared with an observed contaminant flux. Based on the analytical solutions, the effect of degradation of organic contaminant and mass transfer coefficient on contaminant transport in capped contaminated sediment system will be analyzed.

2. Mathematical model

The analytical model for contaminant diffusion in the multi-layered capped contaminated sediment system was developed based on the following assumptions:

1. Contaminant diffusion is one-dimensional and follows Fick’s second law.
2. The porous medium is isotropic, homogeneous and saturated.
3. Adsorption is a linear and equilibrium process.
4. Biodegradation model of organic contaminant in the medium is based on first-order kinetics. Due to its mathematical simplicity, its easy implementation into transport models, and the necessity of determining only a single parameter, the biodegradation model most frequently used is first-order kinetics.\(^5\)
Based on the above assumptions, one dimensional model for organic contaminant in a finite composite media of $M$ layers is developed (see Fig. 1). The thickness of $m$ layer is $l_m$. The system consists of the contaminated sediment, the capping layers and the benthic boundary layer. The governing equations of contaminant transport in the soils can be expressed as\(^1\):

\[
\frac{R_{dm}}{m} \frac{\partial C_m}{\partial t} = D_m \frac{\partial^2 C_m}{\partial z^2} - \lambda_mC_m \quad (m=1, 2, 3, \ldots, M)
\]  

(1)

where $C_m(z,t)$ is the concentration of contaminant in soil layer $m$; $D_m^*$ is the effective diffusion coefficient in the soil layer $m$; $R_{dm}$ is retardation factor of the soil layer $m$; $z$ is the coordinate with downward positive; $t$ is time; and $\lambda_m$ is the biodegradation rate\(^1\):

\[
\lambda_m = \ln 2 / t_{1/2} \quad (m=1, 2, 3, \ldots, M)
\]

(2)

where $t_{1/2}$ is the half-life of contaminant in the soil layer $m$.

At the interface between soil layer $m$ and $m+1$, the concentration and flux of the contaminants are continuous\(^{37,41,58,59}\):

\[
C_m(L_m,t) = C_{m+1}(L_{m+1},t) \quad (m=1, 2, 3, \ldots, M-1)
\]

(3)

\[
n_mD_m^* \frac{\partial C_m(L_m,t)}{\partial z} = n_{m+1}D_{m+1}^* \frac{\partial C_{m+1}(L_{m+1},t)}{\partial z} \quad (m=1, 2, 3, \ldots, M-1)
\]

(4)

where $n_m$ is the porosity of soil layer $m$; $L_m$ is the distance of layer $m$, $L_m = l_1 + l_2 + \ldots + l_m$.

For the top surface boundary, a Robin-type boundary condition is applied. The bottom condition is a type of Neumann boundary condition. The boundary conditions for the problem can then be expressed as follows\(^6,60\):

\[
\frac{\partial C_1(0,t)}{\partial z} = 0
\]

(5)
where \( k_{bl} \) is the mass transfer coefficient in the benthic boundary layer. Eq.5 is mathematically known as a second-type or Neumann boundary condition and represents an impermeable base stratum. This bottom boundary may be assumed to not allow any transmission of contaminant\(^{58}\). Eq.6 is known as the Robin-type boundary condition which is taken as a flux-matching relationship between the top of the sediment cap and the benthic boundary layer\(^{54}\). When \( k_{bl} \) tends to be infinite, the top boundary condition tends to be a zero concentration boundary condition. However, when \( k_{bl} \) tends to be 0, the top boundary condition would tend to be a zero flux boundary condition. This indicated that the mass transfer coefficient has a great influence on contaminant transport in the capped sediment system. It is also indicated that the analytical solution of this paper can be applied to the situation of zero concentration boundary condition and zero flux boundary condition (i.e., Eq. 5).

The following equation can be used to estimate \( k_{bl} \)^\(^{54}\):

\[
k_{bl} = \frac{D_w}{\delta}
\]

where \( D_w \) is the molecular diffusion coefficient of the compound in water with typical values ranging from \( 10^{-5} \) cm\(^2\)/s to \( 10^{-6} \) cm\(^2\)/s; and \( \delta \) is thickness of the diffusive boundary layer, in most natural conditions \( \delta \ll 1 \) cm. \( \delta \) in the microcosm test was measured to be \( 1.7 \pm 0.2 \) mm by the alabaster method\(^1\). The corresponding minimum of \( k_{bl} \) is \( 5.9 \times 10^{-6} \) cm/s. Furthermore, the mass transfer coefficient reported by the field studies ranged from \( 2.8 \times 10^{-5} \) cm/s to \( 4.6 \times 10^{-4} \) cm/s\(^{61,62}\). The mass transfer coefficients obtained in the laboratory experiments ranges from \( 1.5 \times 10^{-6} \) cm/s to \( 5.1 \times 10^{-5} \) cm/s,
which are much lower than those obtained by the field studies due to overestimation of pore water concentrations or artificially high fluxes\textsuperscript{63,64}. In this study, $2.5 \times 10^{-5}$, $5 \times 10^{-5}$ and $10^{-4}$ cm/s will be used in the following analysis.

The initial conditions are assumed to be

$$C_m(z,0) = C_{m,int}(z) \quad (m=1, 2, 3, \ldots, M) \quad (8)$$

where $C_{m,int}$ is the initial concentration in soil layer $m$.

It should be pointed out that compared with the one-dimensional partial-differential equation considered in this study, much more complicated two-dimensional partial-differential equations have been considered in the process of deriving analytical solutions for both chemical and physical dissolution front instability problems in fluid-saturated porous media\textsuperscript{43-49}. Therefore, the factors including solute dispersion, mineral dissolution ratio\textsuperscript{65,66}, medium permeability anisotropy\textsuperscript{67}, temperature effect\textsuperscript{68,69}, non-linear adsorption\textsuperscript{70}, complex degradation processes\textsuperscript{71}, consolidation-induced advection\textsuperscript{72} were neglected in this study.

**Analytical solution**

The following dimensionless parameters are defined to derive the analytical solution of the proposed mathematical model:

$$\omega = \frac{z}{l_j} \quad (9)$$

$$C^* = \frac{C}{C_0} \quad (10)$$

$$\tau = \frac{D^*_i t}{R_{ij} l_i^2} \quad (11)$$
\[ D_{am} = \frac{\lambda_m l_m^2}{D_m} \quad (m=1, 2, 3, \ldots, M) \]  
\[ Sh = \frac{k_c l_m}{D_m} \]  

where \( \omega \), \( C^* \) and \( \tau \) are dimensionless depth, dimensionless concentration and time factor, respectively. The Damköhler number \( (D_{am}) \) and Sherwood number \( (Sh) \) represent the ratio of reaction rate to the transport phenomena rate occurring in a system and the ratio of the total rate of mass transfer to the rate of diffusion, respectively.  

The governing equation (1) can be rewritten in terms of the dimensionless parameters introduced above:

\[ a_m \frac{\partial C_m^*}{\partial \tau} = \frac{\partial^2 C_m^*}{\partial \omega^2} - \frac{D_{am} C_m^*}{c_m^2} \quad (m=1, 2, 3, \ldots, M) \]  

where

\[ a_m = \frac{R_{dm} D_m^*}{R_{dj} D_m} \quad (m=1, 2, 3, \ldots, M) \]  
\[ c_m = \frac{l_m}{l_1} \quad (m=1, 2, 3, \ldots, M) \]  

The dimensionless boundary conditions are as follows:

\[ C_m^* = C_{m+1}^* \quad (m=1, 2, 3, \ldots, M-1) \]  
\[ n_m D_m \frac{\partial C_m^*}{\partial \omega} = n_{m+1} D_{m+1} \frac{\partial C_{m+1}^*}{\partial \omega} \quad (m=1, 2, 3, \ldots, M-1) \]  
\[ \frac{\partial C_M^*}{\partial \omega} \bigg|_{\omega=0} = 0 \]  
\[ \frac{\partial C_1^*}{\partial \omega} \bigg|_{\omega=\frac{l_m}{l}} = Sh C_1^* \bigg|_{\omega=\frac{l_m}{l}} \]
The initial condition is changed into
\[ C_m^*(z,0) = \frac{C_{m,\text{in}}(z)}{C_0} \quad (m=1, 2, 3, \ldots, M) \quad (21) \]

Eq. (14) can be solved by the method of the classic integral transform technique (CITT). Following the systematized procedure of the CITT, an auxiliary homogeneous problem for the space variable function \( \psi_m(\omega) \) in the same layers of the original problem needs to be defined. An auxiliary problem can be obtained by applying separation of variables to Eqs. (14)-(21):

\[ -a_m \frac{\partial^2 \psi_m}{\partial \omega^2} \frac{D_{am} \psi_m}{c_m^2} = H_m \psi_m \quad (m=1, 2, 3, \ldots, M) \quad (22) \]

The operator \( H_m \) is defined as
\[ H_m = \frac{\partial^2}{\partial \omega^2} - \frac{D_{am}}{c_m^2} \quad (m=1, 2, 3, \ldots, M) \quad (23) \]

And the boundary conditions are as follows:

\[ \frac{\partial \psi_m}{\partial \omega} = 0 \quad (24a) \]
\[ \psi_m = \psi_{m+1} \quad (m=1, 2, 3, \ldots, M-1) \quad (24b) \]
\[ n_m D_m^* \frac{d \psi_m}{d \omega} = n_{m+1} D_{m+1}^* \frac{d \psi_{m+1}}{d \omega} \quad (m=1, 2, 3, \ldots, M-1) \quad (24c) \]
\[ \frac{\partial \psi_m}{\partial \omega} = Sh \psi_M \quad (24d) \]

The above system is an eigenvalue problem and has nontrivial solutions for a discrete spectrum of the eigenvalues \( \zeta_i (i=1, 2, 3, \ldots, \infty) \). The general symbolic solution of Eq. (22) can be written in terms of two linearly independent solutions \( \phi_{m,i}(\omega) \) and \( \theta_{m,i}(\omega) \):

\[ \psi_m(\omega) = A_{m,i} \phi_{m,i}(\omega) + B_{m,i} \theta_{m,i}(\omega) \quad (m=1, 2, 3, \ldots, M) \quad (25) \]

where \( A_{m,i} \) and \( B_{m,i} \) are the parameters to be determined.
According to Eqs. (24a) and (25), the coefficients for the first layer can be obtained as follows:

\[ B_{1,j} = -\frac{\phi_{1,j}(0)}{\theta_{1,j}(0)} A_{1,j} \quad (m=1, 2, 3, \ldots, M) \]  

Substituting Eq.(25) into Eqs.(24) results in the following expressions for the coefficients \( A_{m,i} \) and \( B_{m,i} \):

\[
A_{m,i} = \left( A_{m-1,i} \right) \frac{k_m \phi_{m-1,i}(z_{m-1}) \theta_{m,i}(z_{m-1}) - k_m \phi_{m,i}(z_{m-1}) \theta_{m-1,i}(z_{m-1})}{\phi_{m,i}(z_{m-1}) \theta_{m,i}(z_{m-1}) - \theta_{m,i}(z_{m-1}) \phi_{m,i}(z_{m-1})} \\
+ \left( B_{m-1,i} \right) \frac{k_m \theta_{m-1,i}(z_{m-1}) \phi_{m,i}(z_{m-1}) - k_m \theta_{m,i}(z_{m-1}) \phi_{m-1,i}(z_{m-1})}{\phi_{m,i}(z_{m-1}) \theta_{m,i}(z_{m-1}) - \theta_{m,i}(z_{m-1}) \phi_{m,i}(z_{m-1})} \\
(m=1, 2, 3, \ldots, M) \]  

\[
B_{m,i} = \left( A_{m-1,i} \right) \frac{k_m \phi_{m,i}(z_{m-1}) \theta_{m-1,i}(z_{m-1}) - k_m \phi_{m-1,i}(z_{m-1}) \theta_{m,i}(z_{m-1})}{\phi_{m,i}(z_{m-1}) \theta_{m,i}(z_{m-1}) - \theta_{m,i}(z_{m-1}) \phi_{m,i}(z_{m-1})} \\
+ \left( B_{m-1,i} \right) \frac{k_m \theta_{m,i}(z_{m-1}) \phi_{m-1,i}(z_{m-1}) - k_m \theta_{m-1,i}(z_{m-1}) \phi_{m,i}(z_{m-1})}{\phi_{m,i}(z_{m-1}) \theta_{m,i}(z_{m-1}) - \theta_{m,i}(z_{m-1}) \phi_{m,i}(z_{m-1})} \\
(m=1, 2, 3, \ldots, M) \]  

where \( k_m = n_m D^*_m \). The value of \( A_{1,i} \) is arbitrary and is set to \( A_{1,i} = 1 \).

Eqs. (24d) and (25) are used to find a symbolic general transcendental equation.

\[ A_M, \phi_{M,i}(z_{M}) + B_M, \theta_{M,i}(z_{M}) = 0 \]  

The general solution of the eigenvalue problem (Eq. 22) can be expressed as follows:

\[
\phi_{m,i}(\omega) = \sin(\beta_{m,i} \omega) \quad (m=1, 2, 3, \ldots, M) \]  

\[
\theta_{m,i}(\omega) = \cos(\beta_{m,i} \omega) \quad (m=1, 2, 3, \ldots, M) \]  

where \( \beta_{m,i} \) are the layer eigenvalues, which are related to the eigenvalues \( \xi_i \) by

\[
\beta_{m,i} = \frac{\left( 4 \xi_i^2 a_m - 4 D_{am} / c_m^2 \right)^{1/2}}{2} \quad (m=1, 2, 3, \ldots, M) \]
According to Eqs. (26) and (30)-(32), the coefficients for the first layer can be obtained as follows:

\[ B_{1,i} = 0 \quad (33) \]

For the others layers, the following recursive formulas are obtained:

\[ A_{m,i} = [A_{m-1,i} \cos(\beta_{m-1,i} z_{m-1}) - B_{m-1,i} \sin(\beta_{m-1,i} z_{m-1})] \frac{k_{m-1} \beta_{m-1,i}}{k_{m} \beta_{m,i}} + \sin(\beta_{m,i} z_{m-1}) [A_{m-1,i} \sin(\beta_{m-1,i} z_{m-1}) + B_{m-1,i} \cos(\beta_{m-1,i} z_{m-1})] \quad (m=2, 3, \ldots, M) \quad (34) \]

\[ B_{m,i} = \cos(\beta_{m,i} z_{m-1}) [A_{m-1,i} \sin(\beta_{m-1,i} z_{m-1}) + B_{m-1,i} \cos(\beta_{m-1,i} z_{m-1})] - \sin(\beta_{m,i} z_{m-1}) [A_{m-1,i} \cos(\beta_{m-1,i} z_{m-1}) - B_{m-1,i} \sin(\beta_{m-1,i} z_{m-1})] \frac{k_{m-1} \beta_{m-1,i}}{k_{m} \beta_{m,i}} \quad (m=2, 3, \ldots, M) \quad (35) \]

The eigenfunctions \( \psi_{m,i}(\omega) \) can be expressed as follows:

\[ \psi_{m,i}(\omega) = A_{m,i} \sin(\beta_{m,i} \omega) + B_{m,i} \cos(\beta_{m,i} \omega) \quad (m=1, 2, 3, \ldots, M) \quad (36) \]

Finally, using Eqs.(29)-(32) the following transcendental equation can be obtained:

\[ A_{M,i} \sin(\beta_{M,i} z_{M}) + B_{M,i} \cos(\beta_{M,i} z_{M}) = 0 \quad (37) \]

In the classification system given by Mikhailow and Ozisik for self adjoint problems of heat and mass diffusion, an eigenvalue problem is defined as:

\[ \frac{d}{dz} \left[ \frac{d \psi_{m}}{dz} \right] + \left[ z_{m}^{2} w_{m}(\omega) - q_{m}(\omega) \right] \psi_{m} = 0 \quad (m=1, 2, 3, \ldots, M) \quad (38) \]

where

\[ q_{m}(\omega) = \frac{D_{m}}{c_{m} \omega} \quad (m=1, 2, 3, \ldots, M) \quad (39) \]

\[ w_{m}(\omega) = a_{m} \quad (m=1, 2, 3, \ldots, M) \quad (40) \]
The orthogonality property for the set of linearly independent eigenfunctions, \( \psi_{m,i}(\omega) \), associated with Eq. (38) is given by:

\[
\sum_{m=1}^{M} \int_{z_{m-1}}^{z_m} w_m(\omega)\psi_{m,j}(\omega)\psi_{m,i}(\omega)\,d\omega = \delta_{ij}N_i \quad (m=1, 2, 3, \ldots, M) \tag{41}
\]

where \( N_i \) is the norm. The closed-form expression for the norm is as follows:

\[
N_j = \sum_{m=1}^{M} \overline{N}_{m,j} \quad (m=1, 2, 3, \ldots, M) \tag{42}
\]

where

\[
\overline{N}_{m,i} = \frac{a_m}{4\beta_{m,i}} \{ 2\beta_{m,i} (A_{m,i}^2 + B_{m,i}) (z_m^*-z_{m-1}^*) + 2A_{m,i} B_{m,i} [\cos(2\beta_{m,i} z_m^*) - \cos(2\beta_{m,i} z_{m-1}^*)] \\
+ (A_{m,i}^2 - B_{m,i}^2) [\sin(2\beta_{m,i} z_m^*) - \sin(2\beta_{m,i} z_{m-1}^*)] \} \quad (m=1, 2, 3, \ldots, M) \tag{43}
\]

Representing the unknown function \( C_m(\omega, \tau) \) as a series expansion in terms of the eigenfunctions \( \psi_{m,i}(\omega) \) and using the orthogonality property (Eq. 42) results in the following integral transform pair:

\[
C_m(\omega, \tau) = \sum_{i=1}^{\infty} \frac{\psi_{m,i}(\omega)}{N_i} \overline{C}_i(\tau) \quad (m=1, 2, 3, \ldots, M) \tag{44}
\]

And its corresponding inverse transform is

\[
\overline{C}_i(\tau) = \sum_{m=1}^{M} \int_{z_{m-1}}^{z_m} w_m(\omega)\psi_{m,i}(\omega)C(\omega, \tau)\,d\omega \quad (m=1, 2, 3, \ldots, M) \tag{45}
\]

Applying the inverse formula (Eq. 34) to Eq. (14) and recalling the eigenvalue problem (Eq. 22) results in

\[
a_m \frac{\partial}{\partial \tau} \sum_{i=1}^{\infty} \frac{\psi_{m,i}(\omega)}{N_j} \overline{C}_i(\tau) = -\sum_{j=1}^{\infty} \frac{a_m \xi_j^2 \psi_{m,j}(\omega)}{N_j} \overline{C}_j(\tau) \quad (m=1, 2, 3, \ldots, M) \tag{46}
\]

Applying \( \sum_{m=1}^{M} \int_{z_{m-1}}^{z_m} \psi_{m,i}(\omega)\,d\omega \) to both sides of Eq. (46) results in
By using the orthogonality property (Eq. 42), the following equation can be obtained:

$$\frac{d\overline{C}_i(\tau)}{d\tau} = -\xi_i^2 \overline{C}_i(\tau) \quad (48)$$

The initial condition (Eq. 22) can also be transformed to yield

$$\overline{C}_i(0) = \sum_{m=1}^{M} f_{m,i} \quad (m=1, 2, 3, \ldots, M) \quad (49)$$

where

$$f_{m,i} = \int_{z_{z=1}}^{z_{z_M}} w_m(\omega)\psi_{m,i}(\omega)C(\omega,0)d\omega \quad (m=1, 2, 3, \ldots, M) \quad (50)$$

Solving Eq.(48) with initial condition Eq.(49) gives the transformed field:

$$\overline{C}_i(\tau) = \overline{C}_i(0)\exp(-\xi_i^2\tau) \quad (51)$$

Finally, invoking the inverse formula Eq.(42) and the relationship in Eq.(51) the closed-form analytical solution is obtained as follows:

$$C_m(\omega, \tau) = \sum_{i=1}^{\infty} \frac{\psi_{m,i}(\omega)}{N_i} \overline{C}_i(0)\exp(-\xi_i^2\tau) \quad (m=1, 2, 3, \ldots, M) \quad (52)$$

The flux of at the surface of the cap can be obtained as

$$J(L_M, \tau) = -n_mD_M \cdot \frac{\partial C_i(L_M, \tau)}{\partial \omega} \quad (53)$$

Substituting Eq. (52) into Eq. (53) results in

$$J(L_M, \tau) = -n_mD_M \sum_{i=1}^{\infty} \frac{A_i \cos(\beta_i\omega) + B_i \sin(\beta_i\omega)}{N_i} \overline{C}_i(0)\exp(-\xi_i^2\tau)\beta_i \quad (54)$$

The cap effectiveness factor, which can be used as the assessment of the cap performance, can be expressed as follows:
where $J_{uc}$ and $J_c$ are the (hypothetical) uncapped fluxes and capped fluxes at the top of the cap system, respectively.

4. Results and discussions

4.1. Good experimental set-up to verify the model.

Fig. 2a and 2b presents the comparison of the results of the proposed analytical models with experimental data obtained from laboratory-scale simulations of capped contaminated sediment. In the experiments, the contaminated sediment layer in the two cases was obtained from the lake bottom located at the Louisiana State University campus in Baton Rouge. In the two cases, the cap materials are Balsam sand cap and Tao River sand cap, respectively. The balsam sand is a proposed cap material from a quarry near New Bedford and The Tao River sample was obtained from the bed of the Yellow River in China. The retardation factors for the Balsam sand and Tao River sand cap are 4.94 and 8.3, respectively. The effective diffusion coefficients of the Balsam sand and Tao River cap are $7 \times 10^{-10}$ and $8.3 \times 10^{-10}$ m$^2$/s, respectively. In the experiments, 1.5-cm-thick sediment was contaminated by trichloropropane (TCP) and covered by a 0.7-cm-thick capping layer to impede the TCP from diffusing into the surface water. The transport properties for these two layers are summarized in Table 1. The initial concentration of TCP in the sediment and the capping layer is 150 mg/L and 0, respectively. A zero-flux boundary condition is imposed at the bottom of the sediment layer. The concentration remains zero at the top of the capping layer to
model the flushing effect of the surface water. The half-life of TCP is 30-60 years
reported by Thoma et al.\textsuperscript{6}. The half-life of TCP in capping and sediment are assumed
to be 100 years in this case. The solid line is the predicted flux by the proposed
analytical model and the dot is the experimental data from laboratory-scale
simulations (see Fig.2). It can be seen that the predicted flux is in good agreement
with the experimental data for both of the capped systems. This indicates that the
proposed analytical solutions are rational and can yield correct results.

4.2 Dimensionless analysis of contaminant diffusion in capped contaminated
sediments

The soil and transport properties considered for these four layers are summarized
in Table 2. A zero-flux boundary condition is assumed at the bottom of the sediment
layer, and the Robin-type boundary condition and zero concentration boundary
condition are assumed at the top of the capping layer.

Fig. 3 shows the dimensionless concentration profiles for different Damköhler
numbers at time factor \( \tau = \frac{D_{a4}^* t}{R_d l_1^2} = 0.01 \). \( D_{a4}^* = \frac{\lambda_d l_1^2}{D_4^*} \) is Damköhler number in the
bioturbation layer. The experimental data from Gilevska et al.\textsuperscript{75} showed that
biodegradation rate of contaminant in bioturbation layer ranges from 0.4 year\textsuperscript{-1} to 84
year\textsuperscript{-1}. Damköhler number in the bioturbation layer (\( D_{a4} \)) here is assumed to be 1, 5,
10 and 30, respectively. The relative concentration in the capping layer is significantly
reduced with the increase of \( D_{a4} \). For example, the relative concentration at the
surface of sand layer for the case with \( D_{a4}=1 \) can be 2.8 times greater than that of the
case with \( D_{a4}=30 \). The above analysis indicated that considering the effect of
contaminant biodegradation in bioturbation layer can improve the efficiency of the
capping systems.

Fig. 4 shows the effect of $a_2 = \frac{R_{d2}D_2}{R_{d1}D_1}$ and $D_{a4} = \frac{\lambda_1D_2^2}{D_4^2}$ on cap effectiveness
factor. Five cases including case 1 ($a_2 = 2.26$, $Da_4 = 1$), case 2 ($a_2 = 2.26$, $Da_4 = 5$), case 3
($a_2 = 2.26$, $Da_4 = 10$), case 4 ($a_2 = 11.3$, $Da_4 = 1$) and case 5 ($a_2 = 22.6$, $Da_4 = 1$) were
selected to analyze the effects of different combinations $a_2$ and $Da_4$ on cap
effectiveness factor. The parameter $a_2$ has a less significant effect on the cap
effectiveness factor than that of $Da_4$. For instance, the time required for $CE$ to reach
0.5 for case 1 can be 1.8 and 50 times less than that of case 2 and case 5, respectively.
This is due to the fact that the sorbent layer is relatively thin and the diffusion barrier
effect is also weak. It can be seen that the cap effectiveness factor significantly
increases with the increment of $Da_4$. For example, the time factor required for $CE$ to
reach 0.5 for case 1, case 2 and case 3 is 0.02, 1.05 and 2.12, respectively. When $\tau = 1$,
the effectiveness factor for the case 2 and case 3 is 0.5 and 0.8, respectively. It
indicates that biodegradation of contaminant in bioturbation layer can effectively
decrease flux released from capped contaminated sediment.

Fig. 5a and 5b show the effect of sorbent layer on relative concentration over
time at surface of sand layer for different $a_2$ and $c_2$. The effective remediation time
was designed to be the time for the concentration at the top of the sand layer to reach
10% of initial contaminant concentration$^2$. It can be seen that both of the
dimensionless retardation factor $a_2$ and dimensionless thickness $c_2$ have a great
influence on contaminant transport in the capping system. The effective remediation
time for the case with $a_2=100$ can be 22.7 times larger than that with $a_2=10$ (Fig. 5a).

The time required to reach the maximum relative concentration for the case with $a_2=20$ can be 11.2 times larger than the case with $a_2=1$. Furthermore, the maximum relative concentration for the case with $a_2=20$ can be around 1.9 times less than the case with $a_2=1$. As for $c_2$, the effective remediation time and the time required to reach the maximum relative concentration for the case with $c_2=0.01$ can be around 10 times larger than $c_2=0.05$, respectively (Fig. 5b). If the capping system is designed to be effective for a 200-year period which equals to $\tau=0.02$, the reasonable value of $a_2$ should be larger than 50 under $c_2=0.03$ for the in-situ capping system (Fig. 5a). Similarly, the reasonable value of $c_2$ should be larger than 0.05 under $a_2=20$ (Fig. 5b).

The above analysis indicates that the proposed dimensionless analytical model can be used to design a final capping system. The results also indicate that capping will be an attractive alternative for remediation when the adsorption factor and the thickness of sorbent layer are well designed.

4.3 Effect of sorbent layer and bioturbation layer on flux at surface of system

Fig. 6 shows the effect of sorbent layer on the flux at surface of the system ($z=L_M$). Five cases including case 1 (without sorbent layer), case 2 ($l_{sorbent}=5\text{mm}$, and $R_{dz}=260$), case 3 ($l_{sorbent}=10\text{mm}$ and $R_{dz}=130$), case 4 ($l_{sorbent}=10\text{mm}$, $R_{dz}=260$) and case 5 ($l_{sorbent}=20\text{mm}$, $R_{dz}=130$) are selected to analyze the effects of retardation factor and thickness of sorbent layer on surface flux. For each case, there is a period of time before any contaminant has transported through the cap system (isolation time), followed by a period of increasing flux through the cap and into the bioactive zone.
until a maximum is reached, and then a decrease in flux over time until the underlying sediment layer is depleted\(^5\). The isolation time is defined as the time when the flux of contaminant at the top of the cap system reaches 10\% of the maximum flux simulated in that case. The isolation time for case 1, case 2, case 3, case 4 and case 5 is 3.1 years, 5.2 years, 6.4 years, 9 years and 17 years, respectively. The maximum flux for case 1 can be 1.8 times larger than that of case 4. However, the time required to reach the maximum flux for case 1 can be 7.5 times less than that of the case 4. The above results show that increasing the adsorption properties and thickness of sorbent layer would result in an effective improvement of the cap system. The isolation time for case 5 can be 2.7 and 1.9 times longer than that of case 3 and case 4, respectively. Furthermore, the maximum flux for case 2 can also be 1.1 times larger than that of case 3. The above analysis indicates that increasing the thickness of sorbent layer might be more effective than that of the improvement of adsorption factor in sorbent layer.

Fig. 7a and 7b show the effect of bioturbation layer on the flux at the surface of system under different half-lives of contaminant and thicknesses of bioturbation layer. Bioturbation is the normal life cycle activity of benthic organisms that lead to mixing of sediment and porewater in the near surface layer of sediments. These activities have a great influence on the fate and behavior of contaminants. They are often the dominant mixing process in stable sediment environments\(^76\). Thoms et al.\(^77\) summarizes the literature reported values of the depth of bioturbation at more than 200 sites via a variety of different organisms. It is indicated that the bioturbation depth
for freshwater and estuarine systems are approximately 3.1cm and 14.8cm, respectively. The biodiffusion coefficients are around $1 \times 10^{-5}$ cm$^2$/s and $5 \times 10^{-4}$ cm$^2$/s for freshwater and estuarine systems, respectively. In order to assure that the designed cap can meet the requirement of the quantitative goals, it is important to analyze how the height of bioturbation layer and biodegradation of contaminant can affect the performance of a cap. The range of biodegradation rate in bioturbation layer is assumed to be from 0.4 year$^{-1}$ to 84 year$^{-1}$. The corresponding half-life in the bioturbation layer $t_{1/2,\text{bio}}$ ranges from 0.008 to 1.73 years. The flux at surface of system is significantly reduced with a decrease of half-life of contaminant. For example, the maximum flux for the case with $t_{1/2,\text{bio}} = 0.07$ year can be 4.5 times less than that of the case without considering the effect of biodegradation (Fig.7a). However, the biodegradation of contaminant shows a less important influence on the isolation time. For instance, the isolation time for the case with $t_{1/2,\text{bio}} = 0.07$ year and case with $t_{1/2,\text{bio}} = 0.7$ year is 12.7 years and 11.2 years, respectively. The thickness of bioturbation layer also has a great influence on flux at surface of system. For example, the maximum flux for the case with $l_{\text{bio}} = 15$cm can be 1.5 times greater than that of the case with $l_{\text{bio}} = 5$cm. Increasing the thickness of bioturbation layer would result in a decrease of the maximum contaminant flux dispersing into water. This is due to the fact that the effective contaminant transport pathway increases with the increment of bioturbation layer. In addition, degradation of contaminant can play a more significant role when bioturbation layer has a larger thickness. However, the maximum flux for the case with $l_{\text{bio}} = 15$cm can be 17 times larger than that of the case without
bioturbation layer. This may be due to the fact that the effective diffusion coefficient
of sand cap is 28 times lower than $D_{bio}$. The result from the model was in accordance
with the experimental studies\textsuperscript{78}. Granberg et al.\textsuperscript{79} also showed that bioturbation can
stimulate an augmented release flux of PCBs.

Fig. 8a and Fig. 8b show the flux at the surface of system under different
combinations of properties of sorbent layer and bioturbation layer. The case with
$t_{1/2,bio}=0.7$ year and $R_{sorbent}=260$ is selected as a reference case to investigate the
relative importance of biodegradation rate in bioturbation layer and retardation factor
in sorbent layer (Fig. 8a). It can be seen that the maximum flux for the reference case
can be 3.6 and 1.9 times larger than the cases with $t_{1/2,bio}=0.07$ year, $R_{sorbent}=260$ and
$t_{1/2,bio}=0.7$ year, $R_{sorbent}=2600$, respectively. The isolation time for the case with $t_{1/2,bio}$
=0.7 year and $R_{sorbent}=2600$ can be 4.3 times larger than the case with $t_{1/2,bio}=0.7$ year
and $R_{sorbent}=260$. The above results indicate that increasing half-life of contaminant in
bioturbation layer can significantly reduce the contaminant flux at the surface of
system. However, the increase of half-life of contaminant in bioturbation layer has a
negligible effect on isolation time. On the contrary, increasing retardation factor in
sorbent layer can effectively extend the isolation time although retardation factor has
a less influence on surface flux. The case with $l_{bio}=10cm$ and $l_{sorbent}=1mm$ is selected
as a reference case to investigate the relatively importance of thickness of bioturbation
layer and sorbent layer (Fig. 8b). The maximum flux for the reference case can be 1.7
and 1.3 times larger than the case with $l_{bio}=20cm$, $l_{sorbent}=1mm$ and $l_{bio}=10cm$,
$l_{sorbent}=2mm$, respectively. The isolation time for the case with $l_{bio}=10cm$, $l_{sorbent}=2mm$
is 25 years. The isolation time for the reference case and the case with $l_{\text{bio}}=20\text{cm},$

$l_{\text{sorbent}}=1\text{mm}$ are 13 years and 15 years, respectively. The above results indicate that

surface flux is sensitive to biodegradation rate and thickness of bioturbation layer

although the properties of bioturbation layer have a weak effect on the isolation time.

However, the properties of sorbent layer include retardation factor and thickness have

a significant influence on both surface flux and isolation time. The above analysis also

indicates that increasing the adsorption properties and thickness of sorbent layer

would result in an effective improvement of the cap system.

4.4 Effect of mass transfer coefficient

Fig. 9a and 9b show the effect of the mass transfer coefficient on contaminant

concentration and flux at the surface of system. The mass transfer coefficient is in

inverse proportion to the thickness of the effective diffusive boundary layer (DBL).

This DBL is the thin layer of water adjacent to the sediment surface through which

molecular diffusion is the dominant transport mechanism for dissolved material$^{80}$. $k_{\text{bl}}$

$=2.5\times10^{-5}$ cm/s, $5\times10^{-5}$ cm/s and $10^{-4}$ cm/s are used in the following analysis

(according to Eq.7). The effect of mass transfer coefficient on the contaminant

concentration over time at the surface of system was shown in Fig. 9a. At the top of

the bioturbation layer, the maximum contaminant concentration for the case with $k_{\text{bl}}$

$=2.5\times10^{-5}$ cm/s can reach 0.26 mg/L, which is 13 times larger than that of the case

with $k_{\text{bl}}=10^{-4}$ cm/s. The surface contaminant concentration decreases with the increase

of the mass transfer coefficient since the thickness of the DBL also decreases with the

increase of the mass transfer coefficient. It indicates that considering the effect of $k_{\text{bl}}$
(<10^{-4} \text{ cm/s}) may reduce the performance of the cap. Fig. 9b shows the effect of the mass transfer coefficient on contaminant flux over time at the surface of the bioturbation layer. The contaminant flux at the top of bioturbation layer increases with the increase of $k_{bl}$. For example, the maximum contaminant flux for the case with $k_{bl} = 10^{-4} \text{ cm/s}$ can be 1.3 and 1.1 times greater than that of the case with $k_{bl} = 2.5 \times 10^{-5} \text{ cm/s}$ and $5 \times 10^{-5} \text{ cm/s}$, respectively. The result from the model agrees with the experimental studies which showed that larger mass transfer coefficient results in a greater flux\textsuperscript{81}. This is due to the fact that the increment in the concentration gradient induced by the increase of mass transfer coefficient augments the contaminant flux at the surface of system.

5. Summary and conclusions

An analytical model for contaminant transport in multi-layered capped contaminated sediment considering the degradation of organic contaminant was presented. The results obtained by the proposed analytical model agree well with those obtained from the laboratory tests. Based on the analytical model, the effects of half-life of contaminant in bioturbation, thickness of bioturbation layer, retardation factor of sorbent layer, thickness of sorbent layer and mass transfer coefficient on contaminant transport in capped contaminated sediment system were analyzed. The conclusions are as follows:

(1) The properties of bioturbation layer have a significant effect on the performance of the capped contaminated sediment system. The maximum flux for the case with $t_{1/2,\text{bio}} = 0.07 \text{ year}$ can be 4.5 times less than that of the case without considering the
effect of biodegradation. The effectiveness factor for the case with $D_{ad}=10$ can be 1.6 times than that with $D_{ad}=5$. This indicated that the effect of contaminant biodegradation in bioturbation layer should be considered for the design of the capping system.

(2) Increasing the thickness of sorbent layer might be more effective on improving isolation time than that of the increment of adsorption factor in sorbent layer. The isolation time for the case with $l_{sorbent}=10\text{mm}$, $R_{dsorbent}=130$ can be 1.4 and 2.7 times less than that of case $l_{sorbent}=10\text{mm}$ and $R_{dsorbent}=260$ and $l_{sorbent}=20\text{mm}$, $R_{d2}=130$, respectively. Increasing the biodegradation rates of contaminant in bioturbation layer is more effective on the decrease of surface flux than that of the increment of adsorption factor in sorbent layer. The surface maximum flux for the case with $t_{1/2,\text{bio}}=0.7 \text{ year}$, $R_{dsorbent}=260$ can be 3.4 and 1.9 times larger than the cases with $t_{1/2,\text{bio}}=0.07 \text{ year}$, $R_{dsorbent}=260$ and $t_{1/2,\text{bio}}=0.7 \text{ year}$, $R_{dsorbent}=2600$, respectively.

(3) The mass transfer coefficient should be considered for the design of the capping system. At the top of the bioturbation layer, the maximum contaminant concentration at the surface of system for the case with $k_{bl}=2.5\times10^{-5} \text{ cm/s}$ can be 13 times larger than that of the case with $k_{bl}=10^{-4} \text{ cm/s}$.

(4) It should be noted that this study has certain limitations. For example, some important factors, such as solute dispersion$^{61}$, mineral dissolution ratio$^{62}$, medium permeability anisotropy$^{63}$, temperature effect$^{64,65}$, non-linear adsorption$^{66}$, complex degradation processes$^{67}$, advection and consolidation-induced
advection were neglected in this study. To further improve the analytical solutions derived from this study, these factors need to be considered in the future study.

Acknowledgements

The financial supports from National Natural Science Foundation of China (Grants No. 41672288), the National Key R & D program of China (Grant No. 2018YFC1802303), 111 project (grant No. B18047), Fundamental Research Funds for the Central Universities (Grant No. 2017QNA4028), and Education Science Plan Project of Zhejiang Province (2017SCG220) are gratefully acknowledged.

Notations

\( C_m(z,t) \)  Concentration of contaminant
\( D_m^* \)  Effective diffusion coefficient
\( D_{am} \)  Damköhler number
\( F_m(x) \)  Concentration distribution of the contaminant in soils
\( J_m(z,t) \)  Mass flux
\( k_{bl} \)  Mass transfer coefficient in the benthic boundary layer
\( l_m \)  Thickness of the soil layer \( m \)
\( R_{dm} \)  Retardation factor
\( Sh \)  Sherwood number
\( t \)  Time
\( t_{1/2} \)  Half-life of contaminant in soil
\( U_c(t) \)  Average degree of diffusion
$z$ Space coordinate

$\lambda_i$ Biodegradation rate

$\omega$ Dimensionless depth

$\tau$ Time factor

$\psi_m$ Eigenfunction

$\xi_i$ Eigenvalues

$\beta_m$ The layer eigenvalues
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**Tab.1.** Transport properties for capping layer and contaminated sediment for comparison with experimental data

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<th>Balsam sand cap</th>
<th>Tao river cap</th>
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</thead>
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<td><strong>Cap properties</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D_w$ (m$^2$/s)</td>
<td>$7 \times 10^{-10}$</td>
<td>$8.3 \times 10^{-10}$</td>
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<tr>
<td>$n_1$</td>
<td>0.38</td>
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<tr>
<td>$R_{d1}$</td>
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<td>$L_1$ (m)</td>
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<td>100</td>
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<tr>
<td><strong>Sediment properties</strong></td>
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<tr>
<td>$n_2$</td>
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<td>0.45</td>
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<tr>
<td>$R_{d2}$</td>
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<tr>
<td>$L_2$ (m)</td>
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<td>1.5</td>
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<tr>
<td>$t_{1/2,sediment}$ (year)</td>
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<td>100</td>
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<tr>
<td><strong>Initial TCP concentration</strong> (mg/L)</td>
<td>150</td>
<td>150</td>
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### Tab. 2. Parameters used in a layered sediment cap system simulations

<table>
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<tr>
<th>Parameters</th>
<th>$L$ (m)</th>
<th>$D^*$ (m$^2$/s)</th>
<th>$R_d$</th>
<th>$t_{1/2}$ (year)</th>
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</thead>
<tbody>
<tr>
<td>Bioturbation layer</td>
<td>0.1$^a$</td>
<td>$2.8 \times 10^{-9} , ^c$</td>
<td>10$^c$</td>
<td>1$^d$</td>
</tr>
<tr>
<td>Cap layer</td>
<td>0.05$^a$</td>
<td>$1.0 \times 10^{-10} , ^b$</td>
<td>8.7$^c$</td>
<td>70</td>
</tr>
<tr>
<td>Sorbent layer</td>
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<td>$1.0 \times 10^{-10} , ^b$</td>
<td>260$^c$</td>
<td>70</td>
</tr>
<tr>
<td>Contaminated sediment</td>
<td>0.5$^a$</td>
<td>$1.02 \times 10^{-10} , ^b$</td>
<td>115$^c$</td>
<td>70$^b$</td>
</tr>
</tbody>
</table>

a: Murphy et al.$^5$; b: Bortone et al.$^{15}$; c: Go et al.$^7$; d: Gilevska et al.$^{71}$
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