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

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13

14

Abstract

15 An analytical model for contaminant transport in multi-layered capped
16 contaminated sediments including the degradation of organic contaminant is
17 presented. The effect of benthic boundary layer was treated as a Robin-type
18 boundary condition. The results of the proposed analytical model agree well with
19 experimental data. The biodegradation of contaminant in bioturbation layer
20 shows a significant influence on the flux at the surface of system. The maximum
21 flux for the case with $t_{1/2,bio} = 0.07$ year can be 4.5 times less than that of the case
22 without considering the effect of biodegradation. The thickness of bioturbation
23 layer has a significant effect on the performance of the capped contaminated
24 sediment. The maximum flux for the case with $l_{bio} = 15$ cm can be 17 times larger
25 than that of the case without bioturbation layer. This may be due to the fact that
26 the effective diffusion coefficient of sand cap can be 28 times lower than D_{bio} .
27 The mass transfer coefficient should be considered for the design of the capping
28 system as the contaminant concentration at the top of system for the case with k_{bl}
29 $= 2.5 \times 10^{-5}$ cm/s can be 13 times greater than that of the case with $k_{bl} = 10^{-4}$ cm/s.
30 The proposed analytical model can be used for verification of complicated
31 numerical methods, evaluation of experimental data and design of the capping
32 contaminated sediment systems with reactive cap layers.

33 **Keywords:** Analytical model; chemical diffusion; degradation; capped
34 contaminated sediment; mass transfer coefficient; bioturbation layer

35

36 **1. Introduction**

37 Sediments contaminated with organic compounds are always found in many
38 waterways, harbors and estuaries^{1,2}. The transfer of these chemicals from the
39 sediments into overlying waters will affect the marine food web and the human using
40 these waters for recreation and supply of sea food. In order to reduce risk associated
41 with contaminant in the sediments, different remediation strategies have been
42 developed. The general characteristics of the three basic sediment management
43 options are natural recovery, capping or in situ treatment, and dredging². In order to
44 isolate the contaminants from organisms in the water and surficial sediments, in-situ
45 capping is used as a cover for placement over contaminated sediment³. The cap can be
46 constructed with multiple layered clean sediments such as sand and gravel^{1,2,4,5}. The
47 application of sand and sediment caps as a remediation technology for contaminated
48 sediments was subsequently investigated. Wang et al.⁴ and Thoma et al.⁶ found that a
49 layer of clean sand sediment successfully reduced the concentrations of the HOC
50 2,4,6-trichlorophenol in the laboratory.

51 The traditional sand caps are less effective at sites where groundwater seepage or
52 mobile contaminants are present⁷. The active caps incorporating reactive or sorptive
53 constituents are designed to reduce contaminant flux⁸⁻¹⁰. For instance, the coke and
54 other “active” materials (e.g., activated carbon and kraft lignin) are used as capping to
55 enhance sorption in order to reduce the availability of the contaminant and improve
56 the effectiveness of in situ capping^{5,11-15}. The isolation times provided by the sorbent
57 layers increased with the increase of sorption strength and capacity (activated

58 carbon>> coke \approx soil>> sand)⁵. Eek et al.¹ developed the laboratory microcosm test to
59 measure the diffusion of PAHs and PCBs from sediment with different capping layers.
60 They found that caps with passive material can significantly reduce the diffusive
61 contaminant flux through the cap.

62 It has been shown that diffusive transport is often the dominant mode of
63 contaminant transport through subaqueous caps for contaminated sediments since the
64 water flow in fine-grained sediments is very slow^{4, 16, 17}. Diffusion of contaminant
65 through layered porous media is often modeled by numerical methods. For instance,
66 Rowe et al.¹⁸ have developed the finite layer methods for contaminants transport
67 through multi-layered barrier systems. Leo and Booker¹⁹ developed the boundary
68 element method for contaminant diffusion in non-homogeneous porous media.
69 Praveen Kumar and Dodagoudar²⁰ provide an accurate methodology for numerical
70 simulation of the two-dimensional contaminant transport through the saturated
71 homogeneous porous media and landfill liners using element-free Galerkin method
72 (EFGM). The finite element method based numerical model COMPASS has also been
73 used for the analysis of contaminant diffusion in the layered porous media²¹⁻²⁴. Zhang
74 et al.²⁵ investigated contaminant transport in the two-layered system consisting of
75 compacted clay liner and the aquifer using the numerical method including the
76 finite-difference method and the numerical inversion of Laplace transform. However,
77 the use of the numerical models is restricted to experienced users and for sites where
78 field data are known in great detail.

79 Analytical solutions play an important role in understanding many scientific
80 phenomena²⁶⁻²⁸, although some simplifications need to be made in the process of
81 deriving them. In particular, analytical solutions can also play a unique role in
82 validating many new numerical methods²⁹⁻³¹. For these reasons, analytical solutions
83 have been derived in recent years for many scientific and engineering problems³²⁻³⁴.
84 This means that by using analytical solutions in this particular study, a better
85 understanding of the mechanism of contaminant diffusion can be explored, the
86 movement of contaminant plumes can be predicted, and the results of numerical
87 modeling can be verified³⁵. They are also more computationally efficient and can be
88 used to address the Robin-type boundary condition that is often not available in the
89 numerical programs^{37,38}. Some works have been done on solving the diffusion or
90 advection-dispersion equation of solute transport in two- or multi-layered porous
91 media using the Laplace transform method³⁸, the integral transform method³⁹, and an
92 approach combining the Laplace transformation method and binomial theorem⁴⁰. An
93 analytical solution for contaminant diffusion through multi-layered system was
94 presented by Chen et al.⁴¹. Li and Cleall³⁷ presented analytical solutions for various
95 combinations of fixed solute concentration and zero-flux boundary conditions applied
96 at each end of a finite one-dimensional domain considering arbitrary initial solute
97 concentration distribution throughout the media. Deng et al.⁴² proposed the integral
98 transform solution for solute transport in multi-layered porous media with the implicit
99 treatment of the interface conditions and arbitrary boundary conditions. Zhao and his
100 coworkers have conducted extensive studies to derive analytical solutions for both

101 chemical dissolution front instability problems⁴³⁻⁴⁸ and physical dissolution front
102 instability problems⁴⁹ in fluid-saturated porous media. However, the effect of
103 degradation on the transport of contaminant was not considered in the literature
104 analytical models.

105 Many types of organic contaminant (e.g., aliphatic and aromatic compounds) can
106 be significantly degraded in soils⁵⁰⁻⁵³. For the sediment capping systems, Lampert and
107 Reible⁵⁴ reported that degradation of sediment contaminant in the biologically active
108 capping may be of primary importance for the control of the contaminant release from
109 the sediments. Himmelheber et al.¹⁰ demonstrated that in situ bioreactive capping can
110 be a feasible remedial approach for the contaminated sediments. Thoma et al.⁶ also
111 found that degradation of contaminant in sediment has a great influence on
112 contaminant flux discharged. For example, the maximum flux released for the case
113 with half-life of 100 years in the sediment can be 67 times lower than the case without
114 considering degradation. Therefore, it is of great importance to consider the
115 degradation process to impede contaminant release from the sediment. In addition, the
116 boundary condition at the cap-water interface is quite complex, as it essentially
117 requires the effluent boundary condition from a porous medium; therefore, the surface
118 boundary condition for the capping sediment systems is often modeled with a mass
119 transfer coefficient². Thibodeaux⁵⁵ and Boudreau and Jørgensen⁵⁶ presented empirical
120 correlations for mass transfer coefficient based on mixing conditions in the overlying
121 water. The value of mass transfer coefficient should be conservatively estimated, as
122 its value directly affects the surficial sediment concentrations⁵⁴. However, few

123 analytical models have considered the effect of mass transfer coefficient on
124 contaminant transport through the contaminated sediment and the capping layer.

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

134 **2. Mathematical model**

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

- 137 1. Contaminant diffusion is one-dimensional and follows Fick's second law.
- 138 2. The porous medium is isotropic, homogeneous and saturated.
- 139 3. Adsorption is a linear and equilibrium process.
- 140 4. Biodegradation model of organic contaminant in the medium is based on first-order
141 kinetics. Due to its mathematical simplicity, its easy implementation into transport
142 models, and the necessity of determining only a single parameter, the biodegradation
143 model most frequently used is first-order kinetics⁵⁷.

144 Based on the above assumptions, one dimensional model for organic
 145 contaminant in a finite composite media of M layers is developed (see Fig. 1). The
 146 thickness of m layer is l_m . The system consists of the contaminated sediment, the
 147 capping layers and the benthic boundary layer. The governing equations of
 148 contaminant transport in the soils can be expressed as¹⁸:

$$149 \quad R_{dm} \frac{\partial C_m}{\partial t} = D_m^* \frac{\partial^2 C_m}{\partial z^2} - \lambda_m C_m \quad (m=1, 2, 3, \dots, M) \quad (1)$$

150 where $C_m(z, t)$ is the concentration of contaminant in soil layer m ; D_m^* is the
 151 effective diffusion coefficient in the soil layer m ; R_{dm} is retardation factor of the soil
 152 layer m ; z is the coordinate with downward positive; t is time; and λ_m is the
 153 biodegradation rate¹⁸:

$$154 \quad \lambda_m = \ln 2 / t_{1/2} \quad (m=1, 2, 3, \dots, M) \quad (2)$$

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

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

$$158 \quad C_m(L_m, t) = C_{m+1}(L_{m+1}, t) \quad (m=1, 2, 3, \dots, M-1) \quad (3)$$

$$159 \quad n_m D_m^* \frac{\partial C_m(L_m, t)}{\partial z} = n_{m+1} D_{m+1}^* \frac{\partial C_{m+1}(L_{m+1}, t)}{\partial z} \quad (m=1, 2, 3, \dots, M-1) \quad (4)$$

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

161 For the top surface boundary, a Robin-type boundary condition is applied. The bottom
 162 condition is a type of Neumann boundary condition. The boundary conditions for the
 163 problem can then be expressed as follows^{6, 60}:

$$164 \quad \frac{\partial C_1(0, t)}{\partial z} = 0 \quad (5)$$

165
$$D_M^* \frac{\partial C_M(L_M, t)}{\partial z} = k_{bl} C_M(L_M, t) \quad (6)$$

166 where k_{bl} is the mass transfer coefficient in the benthic boundary layer. Eq.5 is
167 mathematically known as a second-type or Neumann boundary condition and
168 represents an impermeable base stratum. This bottom boundary may be assumed to
169 not allow any transmission of contaminant⁵⁸. Eq.6 is known as the Robin-type
170 boundary condition which is taken as a flux-matching relationship between the top of
171 the sediment cap and the benthic boundary layer⁵⁴. When k_{bl} tends to be infinite, the
172 top boundary condition tends to be a zero concentration boundary condition. However,
173 when k_{bl} tends to be 0, the top boundary condition would tend to be a zero flux
174 boundary condition. This indicated that the mass transfer coefficient has a great
175 influence on contaminant transport in the capped sediment system. It is also indicated
176 that the analytical solution of this paper can be applied to the situation of zero
177 concentration boundary condition and zero flux boundary condition (i.e., Eq. 5).

178 The following equation can be used to estimate k_{bl} ⁵⁴:

179
$$k_{bl} = D_w / \delta \quad (7)$$

180 where D_w is the molecular diffusion coefficient of the compound in water with typical
181 values ranging from 10^{-5} cm²/s to 10^{-6} cm²/s; and δ is thickness of the diffusive
182 boundary layer, in most natural conditions $\delta \ll 1$ cm. δ in the microcosm test was
183 measured to be 1.7 ± 0.2 mm by the alabaster method¹. The corresponding minimum
184 of k_{bl} is 5.9×10^{-6} cm/s. Furthermore, the mass transfer coefficient reported by the field
185 studies ranged from 2.8×10^{-5} cm/s to 4.6×10^{-4} cm/s^{61,62}. The mass transfer coefficients
186 obtained in the laboratory experiments ranges from 1.5×10^{-6} cm/s to 5.1×10^{-5} cm/s,

187 which are much lower than those obtained by the field studies due to overestimation
188 of pore water concentrations or artificially high fluxes^{63,64}. In this study, 2.5×10^{-5} ,
189 5×10^{-5} and 10^{-4} cm/s will be used in the following analysis.

190 The initial conditions are assumed to be

$$191 \quad C_m(z,0) = C_{m,int}(z) \quad (m=1, 2, 3, \dots, M) \quad (8)$$

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

193 It should be pointed out that compared with the one-dimensional
194 partial-differential equation considered in this study, much more complicated
195 two-dimensional partial-differential equations have been considered in the process of
196 deriving analytical solutions for both chemical and physical dissolution front
197 instability problems in fluid-saturated porous media⁴³⁻⁴⁹. Therefore, the factors
198 including solute dispersion, mineral dissolution ratio^{65,66}, medium permeability
199 anisotropy⁶⁷, temperature effect^{68,69}, non-linear adsorption⁷⁰, complex degradation
200 processes⁷¹, consolidation-induced advection⁷² were neglected in this study.

201 Analytical solution

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

$$204 \quad \omega = \frac{z}{l_1} \quad (9)$$

$$205 \quad C^* = \frac{C}{C_0} \quad (10)$$

$$206 \quad \tau = \frac{D_1^* t}{R_d l_1^2} \quad (11)$$

207
$$D_{am} = \frac{\lambda_m l_m^2}{D_m^*} \quad (m=1, 2, 3, \dots, M) \quad (12)$$

208
$$Sh = \frac{k_{bl} l_M}{D_M^*} \quad (13)$$

209 where ω , C^* and τ are dimensionless depth, dimensionless concentration and time
 210 factor, respectively. The Damköhler number (D_{am}) and Sherwood number (Sh)
 211 represent the ratio of reaction rate to the transport phenomena rate occurring in a
 212 system and the ratio of the total rate of mass transfer to the rate of diffusion,
 213 respectively⁵⁴.

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

216
$$a_m \frac{\partial C_m^*}{\partial \tau} = \frac{\partial^2 C_m^*}{\partial \omega^2} - \frac{D_{am} C_m^*}{c_m^2} \quad (m=1, 2, 3, \dots, M) \quad (14)$$

217 where

218
$$a_m = \frac{R_{dm} D_1^*}{R_{d1} D_m^*} \quad (m=1, 2, 3, \dots, M) \quad (15)$$

219
$$c_m = \frac{l_m}{l_1} \quad (m=1, 2, 3, \dots, M) \quad (16)$$

220 The dimensionless boundary conditions are as follows:

221
$$C_m^* = C_{m+1}^* \quad (m=1, 2, 3, \dots, M-1) \quad (17)$$

222
$$n_m D_m^* \frac{\partial C_m^*}{\partial \omega} = n_{m+1} D_{m+1}^* \frac{\partial C_{m+1}^*}{\partial \omega} \quad (m=1, 2, 3, \dots, M-1) \quad (18)$$

223
$$\left. \frac{\partial C_M^*}{\partial \omega} \right|_{\omega=0} = 0 \quad (19)$$

224
$$\left. \frac{\partial C_1^*}{\partial \omega} \right|_{\omega=\frac{L_M}{l_1}} = Sh C_1^* \Big|_{\omega=\frac{L_M}{l_1}} \quad (20)$$

225 The initial condition is changed into

$$226 \quad C_m^*(z,0) = \frac{C_{m,\text{int}}(z)}{C_0} \quad (m=1, 2, 3, \dots, M) \quad (21)$$

227 Eq. (14) can be solved by the method of the classic integral transform technique

228 (CITT)⁷³. Following the systematized procedure of the CITT, an auxiliary

229 homogeneous problem for the space variable function $\psi_m(\omega)$ in the same

230 layers of the original problem needs to be defined. An auxiliary problem can be

231 obtained by applying separation of variables to Eqs. (14)-(21):

$$232 \quad -a_m \xi_i^2 \psi_m = \frac{\partial^2 \psi_m}{\partial \omega^2} - \frac{D_{am} \psi_m}{c_m^2} = H_m \psi_m \quad (m=1, 2, 3, \dots, M) \quad (22)$$

233 The operator H_m is defined as

$$234 \quad H_m = \frac{\partial^2}{\partial \omega^2} - \frac{D_{am}}{c_m^2} \quad (m=1, 2, 3, \dots, M) \quad (23)$$

235 And the boundary conditions are as follows:

$$236 \quad \frac{\partial \psi_1}{\partial \omega} = 0 \quad (24a)$$

$$237 \quad \psi_m = \psi_{m+1} \quad (m=1, 2, 3, \dots, M-1) \quad (24b)$$

$$238 \quad n_m D_m^* \frac{d\psi_m}{d\omega} = n_{m+1} D_{m+1}^* \frac{d\psi_{m+1}}{d\omega} \quad (m=1, 2, 3, \dots, M-1) \quad (24c)$$

$$239 \quad \frac{\partial \psi_M}{\partial \omega} = Sh \psi_M \quad (24d)$$

240 The above system is an eigenvalue problem and has nontrivial solutions for a discrete

241 spectrum of the eigenvalues ξ_i ($i=1, 2, 3, \dots, \infty$). The general symbolic solution of Eq.

242 (22) can be written in terms of two linearly independent solutions $\phi_{m,i}(\omega)$ and $\theta_{m,i}(\omega)$:

$$243 \quad \psi_{m,i}(\omega) = A_{m,i} \phi_{m,i}(\omega) + B_{m,i} \theta_{m,i}(\omega) \quad (m=1, 2, 3, \dots, M) \quad (25)$$

244 where $A_{m,i}$ and $B_{m,i}$ are the parameters to be determined.

245 According to Eqs. (24a) and (25), the coefficients for the first layer can be obtained as
 246 follows:

$$247 \quad B_{1,i} = -\frac{\phi_{1,i}(0)}{\theta_{1,i}(0)} A_{1,i} \quad (m=1, 2, 3, \dots, M) \quad (26)$$

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

$$250 \quad A_{m,i} = \left(\frac{A_{m-1,i}}{k_m} \right) \frac{k_m \phi_{m-1,i}(z_{m-1}^*) \theta'_{m,i}(z_{m-1}^*) - k_{m-1} \theta_{m,i}(z_{m-1}^*) \phi'_{m-1,i}(z_{m-1}^*)}{\phi_{m,i}(z_{m-1}^*) \theta'_{m,i}(z_{m-1}^*) - \theta_{m,i}(z_{m-1}^*) \phi'_{m,i}(z_{m-1}^*)}$$

$$251 \quad + \left(\frac{B_{m-1,i}}{k_m} \right) \frac{k_m \theta_{m-1,i}(z_{m-1}^*) \theta'_{m,i}(z_{m-1}^*) - k_{m-1} \theta_{m,i}(z_{m-1}^*) \theta'_{m-1,i}(z_{m-1}^*)}{\phi_{m,i}(z_{m-1}^*) \theta'_{m,i}(z_{m-1}^*) - \theta_{m,i}(z_{m-1}^*) \phi'_{m,i}(z_{m-1}^*)}$$

$$(m=1, 2, 3, \dots, M) \quad (27)$$

$$252 \quad B_{m,i} = \left(\frac{A_{m-1,i}}{k_m} \right) \frac{k_{m-1} \phi_{m,i}(z_{m-1}^*) \phi'_{m-1,i}(z_{m-1}^*) - k_m \phi_{m-1,i}(z_{m-1}^*) \phi'_{m,i}(z_{m-1}^*)}{\phi_{m,i}(z_{m-1}^*) \theta'_{m,i}(z_{m-1}^*) - \theta_{m,i}(z_{m-1}^*) \phi'_{m,i}(z_{m-1}^*)}$$

$$253 \quad + \left(\frac{B_{m-1,i}}{k_m} \right) \frac{k_{m-1} \phi_{m-1,i}(z_{m-1}^*) \theta'_{m-1,i}(z_{m-1}^*) - k_m \theta_{m-1,i}(z_{m-1}^*) \phi'_{m-1,i}(z_{m-1}^*)}{\phi_{m,i}(z_{m-1}^*) \theta'_{m,i}(z_{m-1}^*) - \theta_{m,i}(z_{m-1}^*) \phi'_{m,i}(z_{m-1}^*)}$$

$$(m=1, 2, 3, \dots, M) \quad (28)$$

254 where $k_m = n_m D_m^*$. The value of $A_{1,i}$ is arbitrary and is set to $A_{1,i} = 1$.

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

$$256 \quad A_{M,i} \phi'_{M,i}(z_M^*) + B_{M,i} \theta'_{M,i}(z_M^*) = 0 \quad (29)$$

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

258 follows⁷³:

$$259 \quad \phi_{m,i}(\omega) = \sin(\beta_{m,i} \omega) \quad (m=1, 2, 3, \dots, M) \quad (30)$$

$$260 \quad \theta_{m,i}(\omega) = \cos(\beta_{m,i} \omega) \quad (m=1, 2, 3, \dots, M) \quad (31)$$

261 where $\beta_{m,i}$ are the layer eigenvalues, which are related to the eigenvalues ξ_i by

$$262 \quad \beta_{m,i} = \frac{(4\xi_i^2 a_m - 4D_{am} / c_m^2)^{1/2}}{2} \quad (m=1, 2, 3, \dots, M) \quad (32)$$

263 According to Eqs. (26) and (30)-(32), the coefficients for the first layer can be

264 obtained as follows:

$$265 \quad B_{1,i} = 0 \quad (33)$$

266

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

$$268 \quad A_{m,i} = [A_{m-1,i} \cos(\beta_{m-1,i} z_{m-1}^*) - B_{m-1,i} \sin(\beta_{m-1,i} z_{m-1}^*)] \frac{k_{m-1} \beta_{m-1,i}}{k_m \beta_{m,i}} \\ + \sin(\beta_{m,i} z_{m-1}^*) [A_{m-1,i} \sin(\beta_{m-1,i} z_{m-1}^*) + B_{m-1,i} \cos(\beta_{m-1,i} z_{m-1}^*)] \\ 269 \quad (m=2, 3, \dots, M) \quad (34)$$

$$270 \quad B_{m,i} = \cos(\beta_{m,i} z_{m-1}^*) [A_{m-1,i} \sin(\beta_{m-1,i} z_{m-1}^*) + B_{m-1,i} \cos(\beta_{m-1,i} z_{m-1}^*)] \\ - \sin(\beta_{m,i} z_{m-1}^*) [A_{m-1,i} \cos(\beta_{m-1,i} z_{m-1}^*) - B_{m-1,i} \sin(\beta_{m-1,i} z_{m-1}^*)] \frac{k_{m-1} \beta_{m-1,i}}{k_m \beta_{m,i}} \\ 271 \quad (m=2, 3, \dots, M) \quad (35)$$

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

$$273 \quad \psi_{m,i}(\omega) = A_{m,i} \sin(\beta_{m,i} \omega) + B_{m,i} \cos(\beta_{m,i} \omega) \quad (m=1, 2, 3, \dots, M) \quad (36)$$

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

$$275 \quad A_{M,i} \sin(\beta_{M,i} z_M^*) + B_{M,i} \cos(\beta_{M,i} z_M^*) = 0 \quad (37)$$

276 In the classification system given by Mikhailow and Ozisik⁷⁴ for self adjoint problems

277 of heat and mass diffusion, an eigenvalue problem is defined as:

$$278 \quad \frac{d}{dz} \left[\frac{d\psi_m}{dz} \right] + [\xi^2 w_m(\omega) - q_m(\omega)] \psi_m = 0 \quad (m=1, 2, 3, \dots, M) \quad (38)$$

279 where

$$280 \quad q_m(\omega) = \frac{D_m}{c_m} \quad (m=1, 2, 3, \dots, M) \quad (39)$$

$$281 \quad w_m(\omega) = a_m \quad (m=1, 2, 3, \dots, M) \quad (40)$$

282 The orthogonality property for the set of linearly independent eigenfunctions, $\psi_{m,i}(\omega)$,
 283 associated with Eq. (38) is given by:

$$284 \quad \sum_{m=1}^M \int_{z_{m-1}^*}^{z_m^*} w_m(\omega) \psi_{m,i}(\omega) \psi_{m,j}(\omega) d\omega = \delta_{ij} N_i \quad (m=1, 2, 3, \dots, M) \quad (41)$$

285 where N_i is the norm. The closed-form expression for the norm is as follows:

$$286 \quad N_i = \sum_{m=1}^M \bar{N}_{m,i} \quad (m=1, 2, 3, \dots, M) \quad (42)$$

287 where

$$288 \quad \bar{N}_{m,i} = \frac{a_m}{4\beta_{m,i}} \{ 2\beta_{m,i} (A_{m,i}^2 + B_{m,i}^2) (z_m^* - z_{m-1}^*) + 2A_{m,i} B_{m,i} [\cos(2\beta_{m,i} z_{m-1}^*) - \cos(2\beta_{m,i} z_m^*)] \\ + (A_{m,i}^2 - B_{m,i}^2) [\sin(2\beta_{m,i} z_{m-1}^*) - \sin(2\beta_{m,i} z_m^*)] \} \\ 289 \quad (m=1, 2, 3, \dots, M) \quad (43)$$

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

$$293 \quad C_m(\omega, \tau) = \sum_{i=1}^{\infty} \frac{\psi_{m,i}(\omega)}{N_i} \bar{C}_i(\tau) \quad (m=1, 2, 3, \dots, M) \quad (44)$$

294 And its corresponding inverse transform is

$$295 \quad \bar{C}_i(\tau) = \sum_{m=1}^M \int_{z_{m-1}^*}^{z_m^*} w_m(\omega) \psi_{m,i}(\omega) C(\omega, \tau) d\omega \quad (m=1, 2, 3, \dots, M) \quad (45)$$

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

$$298 \quad a_m \frac{\partial}{\partial \tau} \sum_{j=1}^{\infty} \frac{\psi_{m,i}(\omega)}{N_j} \bar{C}_j(\tau) = - \sum_{j=1}^{\infty} \frac{a_m \xi_j^2 \psi_{m,j}(\omega)}{N_j} \bar{C}_j(\tau) \quad (m=1, 2, 3, \dots, M) \quad (46)$$

299 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

$$\begin{aligned}
300 \quad & \frac{\partial}{\partial \tau} \sum_{j=1}^{\infty} \frac{\bar{C}_j(\tau)}{N_j} \sum_{m=1}^M \int_{z_{m-1}^*}^{z_m^*} a_m \psi_{m,i}(\omega) \psi_{m,j}(\omega) d\omega \\
& = - \sum_{j=1}^{\infty} \frac{\bar{C}_j(\tau)}{N_j} \xi_j^2 \sum_{m=1}^M \int_{z_{m-1}^*}^{z_m^*} a_m \psi_{m,i}(\omega) \psi_{m,j}(\omega) d\omega
\end{aligned} \quad (m=1, 2, 3, \dots, M) \quad (47)$$

301 By using the orthogonality property (Eq. 42), the following equation can be obtained:

$$302 \quad \frac{d\bar{C}_i(\tau)}{d\tau} = -\xi_i^2 \bar{C}_i(\tau) \quad (48)$$

303

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

$$304 \quad \bar{C}_i(0) = \sum_{m=1}^M \bar{f}_{m,i} \quad (m=1, 2, 3, \dots, M) \quad (49)$$

305

where

$$306 \quad \bar{f}_{m,i} = \int_{z_{m-1}^*}^{z_m^*} w_m(\omega) \psi_{m,i}(\omega) C(\omega, 0) d\omega \quad (m=1, 2, 3, \dots, M) \quad (50)$$

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

$$308 \quad \bar{C}_i(\tau) = \bar{C}_i(0) \exp(-\xi_i^2 \tau) \quad (51)$$

309

Finally, invoking the inverse formula Eq.(42) and the relationship in Eq.(51) the

310

closed-form analytical solution is obtained as follows:

$$311 \quad C_m(\omega, \tau) = \sum_{i=1}^{\infty} \frac{\psi_{m,i}(\omega)}{N_i} \bar{C}_i(0) \exp(-\xi_i^2 \tau) \quad (m=1, 2, 3, \dots, M) \quad (52)$$

312

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

313

$$J(L_M, \tau) = -n_M D_M^* \frac{\partial C_1(L_M, \tau)}{\partial \omega} \quad (53)$$

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

315

$$J(L_M, \tau) = -n_M D_M^* \sum_{i=1}^{\infty} \frac{A_{1,i} \cos(\beta_{1,i} \omega) + B_{1,i} \sin(\beta_{1,i} \omega)}{N_i} \bar{C}_i(0) \exp(-\xi_i^2 \tau) \beta_{1,i} \quad (54)$$

316

The cap effectiveness factor, which can be used as the assessment of the cap

317

performance, can be expressed as follows:

318
$$CE = \frac{J_{uc} - J_c}{J_{uc} + J_c} \quad (55)$$

319 where J_{uc} and J_c are the (hypothetical) uncapped fluxes and capped fluxes at the top of
320 the cap system , respectively.

321 **4. Results and discussions**

322 *4.1. Good experimental set-up to verify the model.*

323 Fig. 2a and 2b presents the comparison of the results of the proposed analytical
324 models with experimental data obtained from laboratory-scale simulations of capped
325 contaminated sediment⁴. In the experiments, the contaminated sediment layer in the
326 two cases was obtained from the lake bottom located at the Louisiana State University
327 campus in Baton Rouge. In the two cases, the cap materials are Balsam sand cap and
328 Tao River sand cap, respectively. The balsam sand is a proposed cap material from a
329 quarry near New Bedford and The Tao River sample was obtained from the bed of the
330 Yellow River in China. The retardation factors for the Balsam sand and Tao River
331 sand cap are 4.94 and 8.3, respectively. The effective diffusion coefficients of the
332 Balsam sand and Tao River cap are 7×10^{-10} and 8.3×10^{-10} m²/s, respectively⁶. In the
333 experiments, 1.5-cm-thick sediment was contaminated by trichloropropane (TCP) and
334 covered by a 0.7-cm-thick capping layer to impede the TCP from diffusing into the
335 surface water. The transport properties for these two layers are summarized in Table 1.
336 The initial concentration of TCP in the sediment and the capping layer is 150 mg/L
337 and 0, respectively. A zero-flux boundary condition is imposed at the bottom of the
338 sediment layer. The concentration remains zero at the top of the capping layer to

339 model the flushing effect of the surface water. The half-life of TCP is 30-60 years
 340 reported by Thoma et al. ⁶. The half-life of TCP in capping and sediment are assumed
 341 to be 100 years in this case. The solid line is the predicted flux by the proposed
 342 analytical model and the dot is the experimental data from laboratory-scale
 343 simulations (see Fig.2). It can be seen that the predicted flux is in good agreement
 344 with the experimental data for both of the capped systems. This indicates that the
 345 proposed analytical solutions are rational and can yield correct results.

346 *4.2 Dimensionless analysis of contaminant diffusion in capped contaminated*
 347 *sediments*

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

352 Fig. 3 shows the dimensionless concentration profiles for different Damköhler
 353 numbers at time factor $\tau = \frac{D_1^* t}{R_{d1} l_1^2} = 0.01$. $D_{a4} = \frac{\lambda_4 l_4^2}{D_4^*}$ is Damkohler number in the
 354 bioturbation layer. The experimental data from Gilevska et al.⁷⁵ showed that
 355 biodegradation rate of contaminant in bioturbation layer ranges from 0.4 year⁻¹ to 84
 356 year⁻¹. Damkohler number in the bioturbation layer (D_{a4}) here is assumed to be 1, 5,
 357 10 and 30, respectively. The relative concentration in the capping layer is significantly
 358 reduced with the increase of D_{a4} . For example, the relative concentration at the
 359 surface of sand layer for the case with $D_{a4}=1$ can be 2.8 times greater than that of the
 360 case with $D_{a4}=30$. The above analysis indicated that considering the effect of

361 contaminant biodegradation in bioturbation layer can improve the efficiency of the
362 capping systems.

363 Fig. 4 shows the effect of $a_2 = \frac{R_{d2}D_1^*}{R_{d1}D_2^*}$ and $Da_4 = \frac{\lambda_4 l_4^2}{D_4^*}$ on cap effectiveness
364 factor. Five cases including case 1 ($a_2=2.26, Da_4=1$), case 2 ($a_2=2.26, Da_4=5$), case 3
365 ($a_2=2.26, Da_4=10$), case 4 ($a_2=11.3, Da_4=1$) and case 5 ($a_2=22.6, Da_4=1$) were
366 selected to analyze the effects of different combinations a_2 and Da_4 on cap
367 effectiveness factor. The parameter a_2 has a less significant effect on the cap
368 effectiveness factor than that of Da_4 . For instance, the time required for CE to reach
369 0.5 for case 1 can be 1.8 and 50 times less than that of case 2 and case 5, respectively.
370 This is due to the fact that the sorbent layer is relatively thin and the diffusion barrier
371 effect is also weak. It can be seen that the cap effectiveness factor significantly
372 increases with the increment of Da_4 . For example, the time factor required for CE to
373 reach 0.5 for case 1, case 2 and case 3 is 0.02, 1.05 and 2.12, respectively. When $\tau=1$,
374 the effectiveness factor for the case 2 and case 3 is 0.5 and 0.8, respectively. It
375 indicates that biodegradation of contaminant in bioturbation layer can effectively
376 decrease flux released from capped contaminated sediment.

377 Fig.5a and 5b show the effect of sorbent layer on relative concentration over
378 time at surface of sand layer for different a_2 and c_2 . The effective remediation time
379 was designed to be the time for the concentration at the top of the sand layer to reach
380 10% of initial contaminant concentration². It can be seen that both of the
381 dimensionless retardation factor a_2 and dimensionless thickness c_2 have a great
382 influence on contaminant transport in the capping system. The effective remediation

383 time for the case with $a_2=100$ can be 22.7 times larger than that with $a_2=10$ (Fig.5a).
384 The time required to reach the maximum relative concentration for the case with
385 $a_2=20$ can be 11.2 times larger than the case with $a_2=1$. Furthermore, the maximum
386 relative concentration for the case with $a_2=20$ can be around 1.9 times less than the
387 case with $a_2=1$. As for c_2 , the effective remediation time and the time required to
388 reach the maximum relative concentration for the case with $c_2=0.01$ can be around 10
389 times larger than $c_2=0.05$, respectively (Fig.5b). If the capping system is designed to
390 be effective for a 200-year period which equals to $\tau=0.02$, the reasonable value of a_2
391 should be larger than 50 under $c_2=0.03$ for the in-situ capping system (Fig.5a).
392 Similarly, the reasonable value of c_2 should be larger than 0.05 under $a_2=20$ (Fig.5b).
393 The above analysis indicates that the proposed dimensionless analytical model can be
394 used to design a final capping system. The results also indicate that capping will be an
395 attractive alternative for remediation when the adsorption factor and the thickness of
396 sorbent layer are well designed⁷.

397 *4.3 Effect of sorbent layer and bioturbation layer on flux at surface of system*

398 Fig. 6 shows the effect of sorbent layer on the flux at surface of the system
399 ($z=L_M$). Five cases including case 1 (without sorbent layer), case 2 ($l_{sorbent}=5\text{mm}$, and
400 $R_{d2}=260$), case 3 ($l_{sorbent}=10\text{mm}$ and $R_{d2}=130$), case 4 ($l_{sorbent}=10\text{mm}$, $R_{d2}=260$) and
401 case 5 ($l_{sorbent}=20\text{mm}$, $R_{d2}=130$) are selected to analyze the effects of retardation factor
402 and thickness of sorbent layer on surface flux. For each case, there is a period of time
403 before any contaminant has transported through the cap system (isolation time),
404 followed by a period of increasing flux through the cap and into the bioactive zone

405 until a maximum is reached, and then a decrease in flux over time until the underlying
406 sediment layer is depleted⁵. The isolation time is defined as the time when the flux of
407 contaminant at the top of the cap system reaches 10% of the maximum flux simulated
408 in that case. The isolation time for case 1, case 2, case 3, case 4 and case 5 is 3.1 years,
409 5.2 years, 6.4 years, 9 years and 17 years, respectively. The maximum flux for case 1
410 can be 1.8 times larger than that of case 4. However, the time required to reach the
411 maximum flux for case 1 can be 7.5 times less than that of the case 4. The above
412 results show that increasing the adsorption properties and thickness of sorbent layer
413 would result in an effective improvement of the cap system. The isolation time for
414 case 5 can be 2.7 and 1.9 times longer than that of case 3 and case 4, respectively.
415 Furthermore, the maximum flux for case 2 can also be 1.1 times larger than that of
416 case 3. The above analysis indicates that increasing the thickness of sorbent layer
417 might be more effective than that of the improvement of adsorption factor in sorbent
418 layer.

419 Fig. 7a and 7b show the effect of bioturbation layer on the flux at the surface of
420 system under different half-lives of contaminant and thicknesses of bioturbation layer.
421 Bioturbation is the normal life cycle activity of benthic organisms that lead to mixing
422 of sediment and porewater in the near surface layer of sediments. These activities
423 have a great influence on the fate and behavior of contaminants. They are often the
424 dominant mixing process in stable sediment environments⁷⁶. Thoms et al.⁷⁷
425 summarizes the literature reported values of the depth of bioturbation at more than
426 200 sites via a variety of different organisms. It is indicated that the bioturbation depth

427 for freshwater and estuarine systems are approximately 3.1cm and 14.8cm,
428 respectively. The biodiffusion coefficients are around 1×10^{-5} cm²/s and 5×10^{-4} cm²/s
429 for freshwater and estuarine systems, respectively⁷. In order to assure that the
430 designed cap can meet the requirement of the quantitative goals, it is important to
431 analyze how the height of bioturbation layer and biodegradation of contaminant can
432 affect the performance of a cap. The range of biodegradation rate in bioturbation layer
433 is assumed to be from 0.4 year⁻¹ to 84 year⁻¹. The corresponding half-life in the
434 bioturbation layer $t_{1/2,bio}$ ranges from 0.008 to 1.73 years⁷⁵. The flux at surface of
435 system is significantly reduced with a decrease of half-life of contaminant. For
436 example, the maximum flux for the case with $t_{1/2,bio} = 0.07$ year can be 4.5 times less
437 than that of the case without considering the effect of biodegradation (Fig.7a).
438 However, the biodegradation of contaminant shows a less important influence on the
439 isolation time. For instance, the isolation time for the case with $t_{1/2,bio} = 0.07$ year and
440 case with $t_{1/2,bio} = 0.7$ year is 12.7 years and 11.2 years, respectively. The thickness of
441 bioturbation layer also has a great influence on flux at surface of system. For example,
442 the maximum flux for the case with $l_{bio} = 15$ cm can be 1.5 times greater than that of the
443 case with $l_{bio} = 5$ cm. Increasing the thickness of bioturbation layer would result in a
444 decrease of the maximum contaminant flux dispersing into water. This is due to the
445 fact that the effective contaminant transport pathway increases with the increment of
446 bioturbation layer. In addition, degradation of contaminant can play a more significant
447 role when bioturbation layer has a larger thickness. However, the maximum flux for
448 the case with $l_{bio} = 15$ cm can be 17 times larger than that of the case without

449 bioturbation layer. This may be due to the fact that the effective diffusion coefficient
450 of sand cap is 28 times lower than D_{bio} . The result from the model was in accordance
451 with the experimental studies⁷⁸. Granberg et.al.⁷⁹ also showed that bioturbation can
452 stimulate an augmented release flux of PCBs.

453 Fig.8a and Fig.8b show the flux at the surface of system under different
454 combinations of properties of sorbent layer and bioturbation layer. The case with
455 $t_{1/2,bio} = 0.7$ year and $R_{dsorbent} = 260$ is selected as a reference case to investigate the
456 relative importance of biodegradation rate in bioturbation layer and retardation factor
457 in sorbent layer (Fig.8a). It can be seen that the maximum flux for the reference case
458 can be 3.6 and 1.9 times larger than the cases with $t_{1/2,bio} = 0.07$ year, $R_{dsorbent} = 260$ and
459 $t_{1/2,bio} = 0.7$ year, $R_{dsorbent} = 2600$, respectively. The isolation time for the case with $t_{1/2,bio}$
460 $= 0.7$ year and $R_{dsorbent} = 2600$ can be 4.3 times larger than the case with $t_{1/2,bio} = 0.7$ year
461 and $R_{dsorbent} = 260$. The above results indicate that increasing half-life of contaminant in
462 bioturbation layer can significantly reduce the contaminant flux at the surface of
463 system. However, the increase of half-life of contaminant in bioturbation layer has a
464 negligible effect on isolation time. On the contrary, increasing retardation factor in
465 sorbent layer can effectively extend the isolation time although retardation factor has
466 a less influence on surface flux. The case with $l_{bio} = 10$ cm and $l_{sorbent} = 1$ mm is selected
467 as a reference case to investigate the relatively importance of thickness of bioturbation
468 layer and sorbent layer (Fig.8b). The maximum flux for the reference case can be 1.7
469 and 1.3 times larger than the case with $l_{bio} = 20$ cm, $l_{sorbent} = 1$ mm and $l_{bio} = 10$ cm,
470 $l_{sorbent} = 2$ mm, respectively. The isolation time for the case with $l_{bio} = 10$ cm, $l_{sorbent} = 2$ mm

471 is 25 years. The isolation time for the reference case and the case with $l_{bio}=20\text{cm}$,
472 $l_{sorbent}=1\text{mm}$ are 13 years and 15 years, respectively. The above results indicate that
473 surface flux is sensitive to biodegradation rate and thickness of bioturbation layer
474 although the properties of bioturbation layer have a weak effect on the isolation time.
475 However, the properties of sorbent layer include retardation factor and thickness have
476 a significant influence on both surface flux and isolation time. The above analysis also
477 indicates that increasing the adsorption properties and thickness of sorbent layer
478 would result in an effective improvement of the cap system.

479 *4.4 Effect of mass transfer coefficient*

480 Fig. 9a and 9b show the effect of the mass transfer coefficient on contaminant
481 concentration and flux at the surface of system. The mass transfer coefficient is in
482 inverse proportion to the thickness of the effective diffusive boundary layer (DBL).
483 This DBL is the thin layer of water adjacent to the sediment surface through which
484 molecular diffusion is the dominant transport mechanism for dissolved material⁸⁰. k_{bl}
485 $=2.5\times 10^{-5}$ cm/s, 5×10^{-5} cm/s and 10^{-4} cm/s are used in the following analysis
486 (according to Eq.7). The effect of mass transfer coefficient on the contaminant
487 concentration over time at the surface of system was shown in Fig. 9a. At the top of
488 the bioturbation layer, the maximum contaminant concentration for the case with k_{bl}
489 $=2.5\times 10^{-5}$ cm/s can reach 0.26 mg/L, which is 13 times larger than that of the case
490 with $k_{bl}=10^{-4}$ cm/s. The surface contaminant concentration decreases with the increase
491 of the mass transfer coefficient since the thickness of the DBL also decreases with the
492 increase of the mass transfer coefficient. It indicates that considering the effect of k_{bl}

493 ($<10^{-4}$ cm/s) may reduce the performance of the cap. Fig. 9b shows the effect of the
494 mass transfer coefficient on contaminant flux over time at the surface of the
495 bioturbation layer. The contaminant flux at the top of bioturbation layer increases with
496 the increase of k_{bl} . For example, the maximum contaminant flux for the case with k_{bl}
497 $=10^{-4}$ cm/s can be 1.3 and 1.1 times greater than that of the case with $k_{bl}=2.5\times 10^{-5}$
498 cm/s and 5×10^{-5} cm/s, respectively. The result from the model agrees with the
499 experimental studies which showed that larger mass transfer coefficient results in a
500 greater flux⁸¹. This is due to the fact that the increment in the concentration gradient
501 induced by the increase of mass transfer coefficient augments the contaminant flux at
502 the surface of system.

503 **5. Summary and conclusions**

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

512 (1) The properties of bioturbation layer have a significant effect on the performance
513 of the capped contaminated sediment system. The maximum flux for the case with
514 $t_{1/2,bio}=0.07$ year can be 4.5 times less than that of the case without considering the

515 effect of biodegradation. The effectiveness factor for the case with $D_{a4}=10$ can be
516 1.6 times than that with $D_{a4}=5$. This indicated that the effect of contaminant
517 biodegradation in bioturbation layer should be considered for the design of the
518 capping system.

519 (2) Increasing the thickness of sorbent layer might be more effective on improving
520 isolation time than that of the increment of adsorption factor in sorbent layer. The
521 isolation time for the case with $l_{sorbent}=10\text{mm}$, $R_{dsorbent}=130$ can be 1.4 and 2.7
522 times less than that of case $l_{sorbent}=10\text{mm}$ and $R_{dsorbent}=260$ and $l_{sorbent}=20\text{mm}$,
523 $R_{d2}=130$, respectively. Increasing the biodegradation rates of contaminant in
524 bioturbation layer is more effective on the decrease of surface flux than that of the
525 increment of adsorption factor in sorbent layer. The surface maximum flux for the
526 case with $t_{1/2,bio}=0.7$ year, $R_{dsorbent}=260$ can be 3.4 and 1.9 times larger than the
527 cases with $t_{1/2,bio}=0.07$ year, $R_{dsorbent}=260$ and $t_{1/2,bio}=0.7$ year, $R_{dsorbent}=2600$,
528 respectively.

529 (3) The mass transfer coefficient should be considered for the design of the capping
530 system. At the top of the bioturbation layer, the maximum contaminant
531 concentration at the surface of system for the case with $k_{bl}=2.5\times 10^{-5}$ cm/s can be
532 13 times larger than that of the case with $k_{bl}=10^{-4}$ cm/s.

533 (4) It should be noted that this study has certain limitations. For example, some
534 important factors, such as solute dispersion⁶¹, mineral dissolution ratio⁶², medium
535 permeability anisotropy⁶³, temperature effect^{64,65}, non-linear adsorption⁶⁶,
536 complex degradation processes⁶⁷, advection and consolidation-induced

537 advection⁶⁸ were neglected in this study. To further improve the analytical
538 solutions derived from this study, these factors need to be considered in the future
539 study.

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546 **Notations**

547 $C_m(z, t)$ Concentration of contaminant
548 D_m^* Effective diffusion coefficient
549 D_{am} Damköhler number
550 $F_m(x)$ Concentration distribution of the contaminant in soils
551 $J_m(z, t)$ Mass flux
552 k_{bl} Mass transfer coefficient in the benthic boundary layer
553 l_m Thickness of the soil layer m
554 R_{dm} Retardation factor
555 Sh Sherwood number
556 t Time
557 $t_{1/2}$ Half-life of contaminant in soil
558 $U_c(t)$ Average degree of diffusion

559	z	Space coordinate
560	λ_i	Biodegradation rate
561	ω	Dimensionless depth
562	τ	Time factor
563	ψ_m	Eigenfunction
564	ξ_i	Eigenvalues
565	β_m	The layer eigenvalues
566		

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800

801

List of Tables

802

803 **Tab.1.** Transport properties for capping layer and contaminated sediment for
804 comparison with experimental data

805 **Tab.2.** Parameters used in a layered sediment cap system simulations

806

807

Tab.1. Transport properties for capping layer and contaminated sediment for

808

comparison with experimental data

	Balsam sand cap	Tao river cap
Cap properties		
D_w (m ² /s)	7×10^{-10}	8.3×10^{-10}
n_1	0.38	0.5
R_{d1}	4.95	8.7
L_1 (m)	0.7	0.7
$t_{1/2, \text{capping}}$ (year)	100	100
Sediment properties		
n_2	0.45	0.45
R_{d2}	50.5	55
L_2 (m)	1.5	1.5
$t_{1/2, \text{sediment}}$ (year)	100	100
Initial TCP concentration	150	150
(mg/L)		

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812 **Tab. 2.** Parameters used in a layered sediment cap system simulations

Parameters	$L_f(\text{m})$	$D^*(\text{m}^2/\text{s})$	R_d	$t_{1/2}(\text{year})$
Bioturbation layer	0.1 ^a	$2.8 \times 10^{-9 \text{c}}$	10 ^c	1 ^d
Cap layer	0.05 ^a	$1.0 \times 10^{-10 \text{b}}$	8.7 ^c	70
Sorbent layer	0.01 ^a	$1.0 \times 10^{-10 \text{b}}$	260 ^c	70
Contaminated sediment	0.5 ^a	$1.02 \times 10^{-10 \text{b}}$	115 ^c	70 ^b

813 a: Murphy et al.⁵; b: Bortone et al.¹⁵; c: Go et al.⁷; d: Gilevska et al.⁷¹

814

815

List of figures

816 **Fig.1.** Schematic diagram of generalized domain for chemical diffusion in a layered
817 capped contaminated sediment

818 **Fig.2.** Comparisons of the results from the proposed analytical model with observed
819 TCP flux for experimental capped systems: (a) Balsam sand cap; and (b) Tao
820 River cap

821 **Fig.3.** Contaminant concentration profiles for different Damkohler number (Da_4) in
822 bioturbation layer

823 **Fig.4.** Effect of different combinations of a_2 and Da_4 on effectiveness factor

824 **Fig.5.** Effect of sorbent layer on dimensionless concentration at surface of sorbent
825 layer ($w=c_1+c_2$). (a) a_2 ; and (b) c_2

826 **Fig.6.** Effect of sorbent layer on surface contaminant flux for different combinations
827 of retardation factor and thickness of sorbent layer

828 **Fig.7.** Effect of bioturbation layers on flux at surface of system. (a) half-life of
829 contaminant; and (b) the thickness of bioturbation layer.

830 **Fig.8.** Flux at surface of system. (a) different combinations of half-life and retardation
831 factor; and (b) different combinations of sorbent layer thickness and
832 bioturbation layer thickness

833 **Fig.9.** Effect of mass transfer coefficient (a) concentration over time at surface of
834 system; and (b) flux over time at surface of system