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A software tool for simulating contaminant transport and remedial effectiveness in sediment environments



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ABSTRACT

Sediments have often acted as sinks for contaminants that possess strong affinity for solids near historical pollution sources. Mathematical models describing the evolution of contaminant concentrations in sediment environments provide a scientific basis for decision support and remediation design. Herein, novel software (CapSim) is introduced including processes relevant to natural attenuation and *in-situ* treatment and containment (capping). The tool has been used as a basis for remedial design at a number of sites throughout the United States. CapSim is built on the concept of an arbitrary number of layers that each exhibit traditional porous media transport processes including sorption (linear and non-linear, transient or local equilibrium), advection, diffusion, dispersion, multicomponent linked reactions and, critically, processes specific to the sediment-water interface including bioturbation of both solids and porewater, deposition, consolidation, and interaction with the overlying surface water. A summary of recent applications and selected simulations of key features are presented.

1. Introduction

Historical failures to control pollution sources have generated a legacy of contaminated sites near industrial areas throughout the world. Sediments frequently act as sinks for such contamination, particularly when the constituents exhibit affinity for solids. There are few economically viable options for management of contaminated sediments. In-situ management, which includes monitored natural recovery (MNR), in-situ treatment with sorptive or reactive materials, and in-situ containment via placement of a capping layer, represent some of the most cost-effective approaches. MNR is a remedy that uses known naturally occurring processes to contain, eliminate or reduce the bioavailability and toxicity of contaminants in sediment. Generally, MNR involves contaminant source control, evaluation of potential attenuation mechanisms and long-term monitoring to confirm the performance. In-situ treatment normally involves the incorporation of a sorbent such as biochar or activated carbon directly into the sediment layer to reduce bioavailability but other sorbents or reagents encouraging contaminant transformation have been proposed. In-situ capping refers to the placement of a subaqueous covering of clean material over contaminated sediment that provides new substrate and buries the contaminants below the biologically active zone. The cover material may include a homogeneous medium such as sands or sediments but may also include amendments to aid containment or degradation of the contaminants. Each of these remedies seeks to reduce the availability or mobility of the contaminants over the long-term and full performance can rarely be assessed with short term monitoring. A modeling tool capable of simulating the availability, mobility and transformation of the contaminant is needed to predict whether the long-term performance criteria may be achieved. Such a tool can also be used to predict shortterm performance that can be directly compared to post-remedy monitoring.

Recent studies have demonstrated the efficacy of sand caps to mitigate environmental risks associated with sediments provided the depth exceeds that of bioturbation by benthic organisms and the amount of groundwater upwelling is not substantial (Lampert, 2010; Lampert et al., 2011, 2013; Reible et al., 2006; Thomas et al., 2014). With substantial upwelling, amended caps or *in-situ* treatment with sorptive materials such as organoclay (Sharma et al., 2009; Reible et al., 2007, 2008), biochar or activated carbon (Lin et al., 2014), and apatites (Peld et al., 2004) have been employed to improve the efficacy of the remedy. Activated carbon can be effective for hydrophobic organic compounds such as PAHs and PCBs and certain metals such as mercury. Sometimes the carbon may be placed within a capping material such as sand or within a geotextile to aid retention of the relatively light material. Clay layers have been proposed to decrease pore water advection

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and the associated contaminant transport (Reible et al., 2006), although this can lead to accumulation of upwelling water and microbially produced gas (Yuan et al., 1995). Benthic communities that contain bacteria with specific reductase enzymatic functions have been proposed if the environmental conditions are feasible for community growth (Himmelheber et al., 2008; Hyun et al., 2006; Johnson et al., 2010). Zero-valent iron as a capping material has also been proposed for treating nitroaromatics, chromium, lead, DDT, and related compounds (Agrawal and Tratnyek, 1996; Sayles et al., 1997; Wang et al., 2011; Reible et al., 2014). Yan and Reible (2015) demonstrated the potential of electrode-enhanced capping using electrodes in combination with natural degradation of phenanthrene, as well as an increase in polycyclic aromatic hydrocarbon (PAH) degrading genes in the benthic community surrounding the electrodes. Wang et al. (2014) developed a bio-reactive cap membrane comprised of polysulfone, granular activated carbon, and immobilized microorganisms (PS/GAC+) to remove nitrobenzene from sediment. The results indicated that more than 70% of the nitrobenzene present in the sediment was removed using the PS/ GAC + membrane cap. Meric et al. (2014) experimented with reactive core mats (RCMs) and found that the geotextile filtering layers provided advantageous filtering for low advective fluxes to capture COCs, while the reactive core in-between the geotextile layers provides good sorption of COCs during high advective fluxes. Red soil rich in iron, aluminum, and oxygen was used by Xia et al. (2016) to control the release of nitrogen and phosphorous from sediment to the water body, and effectively increased the water standard by decreasing the chances of algal blooms. The metallic oxides enhanced the adsorption of the nutrients.

The appropriate design approach for sites where sediment contamination requires remedial action depends on successful modeling of the long-term behavior of contaminants. Site specific conditions and desired remediation goals based upon water body uses, water standards, and habitat restoration (Reible et al., 2014) govern the capping design and must be established. When employing a cap or in-situ treatment, it is vital to choose the appropriate materials to meet remediation goals and to do so in an economical manner. Remediation goals may be a concentration at the sediment-water interface, a flux through the surface layers and into the overlying water or a porewater concentration which seeks to directly control the most available and most mobile fraction of contaminants. Materials that might be employed vary greatly in contaminant fate and transport properties. Mathematical models of the fate and transport of contaminants provide critical insight into the expected long-term behavior of various alternatives that guide remedial action and design.

Contaminant transport models often treat sediment processes relatively simply with exchange coefficients to and between one or more layers of sediment, e.g. to provide a boundary condition for water column models, or assume linear behavior to allow analytical solutions that can be readily computed (Lampert, 2010; Reible et al., 2014; Lampert and Reible, 2009). However, activated carbon amendments and/or black carbon in sediments exhibit non-linear and sometimes kinetically limited sorption (Yang et al., 2012; Hong and Luthy, 2008; Murphy et al., 2006; Werner et al., 2006). To address these and other limitations and more realistically describe surficial sediment processes, the CapSim model was developed. Key features of CapSim include the ability to simulate multiple layers of materials including mixtures of inert material and sorbents, advection/diffusion/dispersion processes, bioturbation, or mixing associated with benthic macroorganisms, resulting in transport of both solid particles and pore water, groundwater upwelling and tidal (or other oscillating) flows, sediment consolidation and deposition (i.e., moving domain), transient or equilibrium linear or nonlinear sorption, exchange at the sediment-water interface, and dynamics of multiple species with linked reactions in sediments. The model can be used to simulate the contaminant transport and release from an unremediated sediment, simulate natural recovery of sediments or predict the effectiveness of in-situ treatment or capping.

Table 1

| Conventional and | unconventional | and sediment | specific pro | cesses simu | lated by |
|------------------|----------------|--------------|--------------|-------------|----------|
| CapSim software. | | | | | |

| Conventional Process | Unconventional/Sediment Processes | | |
|--|---|--|--|
| Advection Diffusion First-order decay Equilibrium sorption/desorption | Bioturbation including particle mixing Consolidation Benthic exchange with overlying water Deposition Multispecies reaction Kinetic sorption and desorption (linear/ nonlinear) | | |

2. Model features and software design

CapSim accounts for multiple layers of varying properties and allows the user to input specific properties of the material or use typical values from a database of characteristics for different materials. The thickness of layers can be varied to describe arbitrary variations in conditions in sediment or to determine the most economical solution for a given set of design criteria. The model incorporates traditional porous media transport processes including advection, diffusion, dispersion, reaction and sorption, but also includes the capability to simulate processes specific to the near-surface sediment including deposition, consolidation, bioturbation, and exchange with the overlying water as summarized in Table 1.

2.1. Governing equations and key processes

The sediment with any potential cap or in-situ treatment is conceptualized as a one-dimensional stratified system composed of multiple layers with various physical and chemical properties. The top and the bottom of the system are in contact with the overlying water body and the underlying sediment, respectively. All layers are simulated as saturated porous media with the solid particles as immobile except in the bioturbation zone near the surface, where particles can be moved by the activities of benthic organisms (Matisoff, 1995) and when sediment continuously deposits to the surface. Dissolved organic carbon (DOC). which can preferentially absorb hydrophobic organic contaminants, is treated as a third phase besides the water and the sediment solids. This phase can contribute to the total porewater burden of these contaminants. The contaminants are distributed to all three phases and transported within the layer and across the interface between layers. The mass conservation equation for the one-dimensional multi-layered multi-species porous media system is given in Equation (1).

$$\sum_{m} \left(\varepsilon_{m} \frac{\partial \phi_{m} C_{n} (1 + \rho_{\text{DOC},i} K_{\text{DOC},n})}{\partial t} + \rho_{b,m} \frac{\partial \phi_{m} q_{m,n}}{\partial t} \right)$$
$$= -\frac{\partial F_{n}}{\partial z} + \left(\sum_{m} \varepsilon_{m} \phi_{m} \right) \sum_{l} a_{l,n} rxn_{l,i}$$
(1)

The mass loading of the nth contaminant in mobile phase consists of the free-molecular concentration C_n and its DOC associated concentration, which is calculated by the DOC concentration in the ith layer $\rho_{DOC,i}$ and the porewater-DOC partitioning coefficient, $K_{DOC,n}$ (Burkhard, 2000). The generation or consumption of the nth contaminant by reactions in porewater is summarized as $\sum_i a_{l,n} rxn_{l,i}$, where $rxn_{l,i}$ is the reaction rate of the lth reaction in the ith layer and $a_{l,n}$ is the stoichiometric coefficient of the nth chemical in the lth reaction. The porewater concentrations are continuous through layers while the DOC concentration and the reaction terms are assumed to be limited in the defined layer. ε_m and $\rho_{b,m}$ are the porosity and bulk density of the mth material. The porosities and the bulk densities of solid mixtures in the system are assumed to be the linear sums of the individual solid components properties weighted by their volumetric fractions ϕ_m . If the property of the mixture is known to be different, the mixture can be

Table 2

The equilibrium/transient sorption/desorption model used in the conservation equation.

| Sorption process | Equilibrium $(q_{m,n})$ | Kinetic sorption $\left(\rho_{b,m} \frac{\partial \phi_m q_{m,n}}{\partial t}\right)$ |
|------------------|--|---|
| Linear | $K_{d.m,n}C_n \\$ | $\phi_{m} \epsilon_{m} k_{sorp,m,n} \left(C_{n} - \frac{1}{K_{d,m,n}} q_{m,n} \right)$ |
| Langmuir | $\frac{q_{max.m,n}b_{m,n}C_n}{1+b_{m,n}C_n}$ | $\phi_{m} k_{sorp,m,n} \left(C_{n}(q_{max,m,n} - q_{m,n}) - \frac{1}{b_{m,n}} q_{m,n} \right)$ |
| Freundlich | $K_{F,m,n}C_n^{N_{F,m,n}}$ | $\phi_{m} \boldsymbol{\epsilon}_{i,m} \boldsymbol{k}_{sorp,m,n} \Biggl(\boldsymbol{C}_{n} - \left(\frac{1}{K_{F,m,n}} \boldsymbol{q}_{m,n} \right)^{\frac{1}{N_{F,m,n}}} \Biggr)$ |

defined with those properties. ϕ_m is treated as a constant parameter in each layer except in the bioturbation zone near the surface, where it becomes a continuous temporal-spatial variable governed by Equation (5).

The relationship between the individual solid concentrations $q_{m,n}$ and the porewater concentration C_n is described by equilibrium isotherms (linear or nonlinear) or nonequilibrium kinetics. In sediments, the time scale of transport processes is often much longer than the time required for the local reversible sorption/desorption reactions allowing the assumption of local equilibrium. If local equilibrium is applied, the solid phase concentrations of nth contaminant in mth solid material $q_{m,n}$ can be expressed as an explicit function of pore water concentrations C_n using appropriate sorption isotherms in Table 2¹⁵. However, sorption/desorption of some organic compounds, such as HOCs could be slow, particularly on strongly sorbing phases or solids with a microporous structure such as activated carbon, and the local equilibrium assumption may not valid (Yang et al., 2012; Pignatello and Xing, 1996; Accardi-Dey and Gschwend, 2002; Lick and Rapaka, 1996). The behavior of such contaminants in sediments is often described by a onecompartment model with sorption kinetic coefficients k_{sorp,m,n} that represents the rate of the sorption/desorption process (Ghosh et al., 2001). A solid material that is a mixture of various compartments can be modeled as materials exhibiting various kinetic and equilibrium sorption properties. Competition between sorption processes can be simulated by modeling reactions between sorbed and desorbed phases. The total solid mass within a differential element is the sum of the contaminant mass in various material components.

The vertical flux F_n in Equation (2) is driven by four potential transport processes, molecular diffusion, hydrodynamic dispersion, advection, and bioturbation. The effective diffusion coefficient $D_{n,i}$ of the nth contaminant is water diffusivity corrected for tortuosity and porosity of the diffusion pathway in porous media (Millington and Quirk, 1961; Boudreau, 1997). The diffusion flux of DOC and the associated contaminants is neglected due to its high molecular weight relative to the freely dissolved fraction and the assumption of uniform DOC concentration within a layer.

Hydrodynamic dispersion and advection describe the transport of contaminants forced externally by groundwater flow. Hydrodynamic dispersion is modeled as proportional to groundwater velocity. The proportionality constant, the hydrodynamic dispersion coefficient α_{i} , is a measure of the length scale of heterogeneities in the system or determined empirically through a tracer study (Reible et al., 2014). In the absence of site-specific information, a conservative estimate for the dispersion impact would be to scale the dispersion coefficient with the cap thickness, such as 10% of the cap thickness (Clarke et al., 1993).

$$F_{n} = -D_{n,i}\frac{\partial C_{n}}{\partial z} - \alpha_{i}U\frac{\partial C_{n}(1 + \rho_{DOC,i}K_{DOC,n})}{\partial z} + UC_{n}(1 + \rho_{DOC,i}K_{DOC,n}) + F_{bio,n}$$
(2)

The advection term with Darcy velocity *U* combines the flow forced by groundwater upwelling, pore water expression due to consolidation of a sediment or cap layer, and periodic movements due to tides or periodic flood/drainage flows. The degree of potential consolidation should be evaluated based on consolidation testing. Consolidation is modeled as an increased groundwater upwelling that decreases exponentially over time as the sediment bed reaches equilibrium. The consolidation-induced flow is calculated based on a user-supplied estimate of maximum consolidation and the time required for the consolidation to achieve 90% of the maximum consolidation to estimate a consolidation rate, k_{con} . Periodic groundwater flow velocity potential associated with tidal regions is modeled as a sinusoid function versus time. V_{max} is the maximum velocity and t_c is the period for a full tidal cycle or other periodic flow (Moore, 1999; Moore et al., 2002; Taniguchi, 2002). Equation (3) represents the collective advection term used in the modeling platform.

$$U = V_{Darcy} + V_{con,0}e^{-k_{con}t} + V_{oscillation}*\sin(2\pi t/t_c)$$
(3)

Bioturbation from the activities of the benthic organisms near the surface (5–15 cm) causes mixing of both the porewater and solids. The bioturbation is commonly characterized as an expected depth and mixing intensity (Boudreau, 1997; Boudreau and Jørgensen, 2001). One common modeling approach is to assume the mixing process is random and the bioturbation flux is a Fickian diffusion process for both the free molecular and the solid-associated contaminant as shown in Equations (4) and (5). The bioturbation coefficients and the depth can be derived using soild mixing measurements (Thoms et al., 1995).

$$F_{\text{bio,n}} = -D_{\text{bio,p}} \sum_{m} \rho_{b,m} \frac{\partial \phi_m q_{m,n}}{\partial z} - D_{\text{bio,pw}} \frac{\partial C_n (1 + \rho_{\text{DOC},i} K_{\text{DOC},n})}{\partial z}$$
(4)

$$\frac{\partial \phi_{\rm m}}{\partial t} = {\rm D}_{\rm bio,p} \frac{\partial^2 \phi_{\rm m}}{\partial z^2}$$
(5)

A depth-dependent Gaussian function correction can also be used to model the biodiffusion coefficient as shown in Equation (6). The Gaussian RMS width, σ , represents the depth where the bioturbation strength drops to approximately 60% of maximum. With this model, bioturbation rates decrease with distance from the benthic interface, which may be more representative of the natural environment.

$$D_{bio,p} = D_{bio,p,0}^{*} \exp\left(-\frac{z^2}{2\sigma^2}\right); \quad D_{bio,pw} = D_{bio,pw,0}^{*} \exp\left(-\frac{z^2}{2\sigma^2}\right)$$
(6)

Deposition of solid particles from the overlying water to the top of the existing sediment or capping layers creates a top layer of temporally variable thickness. The deposition layer normally consists of clean sediment and serves as a natural capping layer, since it separates the overlying water body from the contaminated sediments and reduces the transport rate of contaminants to the overlying water body. The deposition of sediment on the top is modeled by a special layer with increasing thickness over time to simulate the accumulation of solid materials.

2.2. Initial and boundary conditions

At the interface of two layers, the porewater concentrations C_n and the fluxes $F_{n,i}$ are equal for mass continuity. The solid material fractions ϕ_m and the contaminant solid concentrations $q_{m,n,i}$ are discontinuous due to the immobility of solid particles except in the cases with bioturbation, where the benthic organism activities mix the solid materials as well as porewater.

$$C_{n}|_{z=h_{i,i+1}+} = C_{n}|_{z=h_{i,i+1}-}F_{n}|_{z=h_{i,i+1}+} = F_{n}|_{z=h_{i,i+1}-}$$
(7)

The boundary between the sediments and the overlying water body is described by classic boundary layer theory where the flux across the boundary is proportional to the difference between the surface porewater concentration and the overlying water concentration as described by Equation (8)³⁷.

$$F_n = k_{bl,n}(C_n - C_{n,w})$$
(8)



Fig. 1. Comparison of no flux, constant flux and constant concentration bottom boundary conditions with and without groundwater upwelling (advection up). The concentration profiles are shown at a specific time from an initial condition of zero concentration in the upper layer and constant concentration ($C_{b,0}$) in the bottom layer. In the no-upwelling case, the zero flux and constant flux case are identical.

Where $k_{bl,n}$ is the mass transfer coefficient that defines the transport of mass through the sediment-water interface or benthic boundary layer. (Boudreau and Jorgensen, 2001) The coefficient can be evaluated using previously developed correlations with stream characteristics (Reible et al., 2014). When the turbulence in the overlying water is intense, the mass transfer through the boundary layer is rapid, and C_n can be assumed to be fixed to the concentration in the overlying water, $C_{n,w}$. A well-mixed water body with potential water flushing can also be simulated with a separate mass balance model and is described in the supplemental information.

Two types of conditions are available in the model for the bottom boundary—fixed concentration and flux-matching as described by Equations (9) and (10), respectively. Zero flux from below is a special case of the flux matching condition. The fixed concentration condition (blue line in Fig. 1) represents an infinite pollution source with a given concentration beneath the simulation domain, while the flux matching condition (red broken line) models a constant advective flux at the bottom boundary (Danckwerts, 1953) or a zero flux (red solid line). In the zero flux case with groundwater upwelling, the diffusive flux is negative to balance the upward advective flux.

Fixed concentration:
$$C_n|_{z=H} = C_{b,n}$$

$$Flux-matching:F_n|_{z=H} = UC_{b,n}$$
(10)

The initial distribution of contaminants is assumed to be uniform or linear in each layer. A more complicated initial profile simply requires definition of additional layers. For contaminants and solids without the assumption of local equilibrium, the initial solid concentrations q_{init,m, n,i} are also required by the system. Uniform initial concentration:

$$C_{n,i}|_{t=0} = C_{init, n,i}; \ q_{m,n,i}|_{t=0} = q_{init,m, n,i}$$
(11)

Linear variation in concentration:

$$C_{n,i}|_{t=0} = \frac{z - H_i}{H_i} (C_{init, \text{ top, } n,i} - C_{init, \text{ bot, } n,i}) + C_{init, \text{ top, } n,i}$$
(12)

2.3. Numerical solution

The finite difference method (FDM) is used here to solve the governing equations and auxiliary conditions. Both an implicit method and the Crank-Nicholson method are implemented. The constitutive equations with non-linear terms such as Freundlich sorption isotherm or higher order kinetic reactions are solved at each time step by Newton's method. The deposition of sediment on the top is modeled by a special layer with growing number of grids to imitate the accumulation of solid materials. To avoid discontinuities in concentration due to the growing deposition layers, the simulated results are averaged over the time span associated with that growth. For contaminants performing kinetic sorption in solids, the boundary conditions (7) to (10) have to be treated by a finite volume boundary to allow the dynamics in the surface layer to be modeled and to ensure conservation of the solid phase at the boundary grid as described in more detail in the Supplemental Information.

2.4. Software

CapSim is written entirely using the Python Programming Language (van Rossum and others, 2007) with key third party modules including Numeric Python (NumPy) for matrix and array calculations (Walt et al., 2011), Scientific Python (SciPy) for statistical analysis (Jones et al., 2001), the Math Plotting Library (Matplotlib) for visualization (Hunter, 2007). The graphical user interface is constructed using Python's builtin extensions to the Tcl/Tk library (Lundh, 1999; Grayson, 2000). Python and each of the extension modules used in CapSim are fully open source, which facilities collaborations and extension of the tools to new applications. Python is an interpreted high-level programming language, and thus it has been widely used for the development of environmental models for scientific and engineering applications (Lampert and Wu, 2015; Swain et al., 2015; Zhang et al., 2013; Palacios et al., 2013). CapSim can be run directly from the Python interpreter or installed as a compiled executable program.

2.5. Logic structure for user interaction

The developed executable program obtains the system parameters and properties, transport and reaction coefficients and numerical simulation setups, by a series of input windows. A database including the information of common environmental emerging contaminants and remediation solid materials from the literature (Mackay, 1997; Hawker and Connell, 1988; Walters and Luthy, 1984; McDonoughet al., 2007; Azhar, 2015) is provided. The coefficients and properties in the database file can be further edited and updated by users to incorporate new information. The software can also be used to execute batch files, which facilitates a series of simulations sequentially from a user-defined text value (.txt) file. This feature is especially useful for sensitivity analysis of key design parameters for the cap. The simulation cases with input information are stored in input files and can be reloaded back to the system or shared to other users. The simulated results, including porewater concentrations, fluxes, solid concentrations, water concentrations, solid material fractions, are available in the form of the temporal or spatial plots or in comma separated values (CSV) files (See Fig. 2).

3. Example application

A test case was developed to illustrate the features of the modeling platform. Most contaminated sites possess a variety of contaminants of concern that influence a remediation design as well as model parameters that vary in different situations. The following examples illustrate the application of the model for various contaminants of concern and common conditions.

3.1. Mercury and methylmercury

Mercury (Hg) and methylmercury (MeHg) are typical redox-sensitive contaminants in the sediment environment. MeHg is the major

(9)



Fig. 2. Programming Structure of the CapSim model.

Table 3

| Summary o | f the | properties | in | the | mercury | and | phenanthrene | example. |
|-----------|-------|------------|----|-----|---------|-----|--------------|----------|
| | | | | | | | • | |

| (a) Solid material properties and sorption coefficients | | | | | | | | |
|---|---------------------|-----------------------------|-------------------|-------------------|--|--------------------|-----------------------|--|
| Material | | $\rho_m(kg/L)$ | ε _m | \mathbf{f}_{oc} | K _{d,Hg} (L/kg) | K _{d,Me} | Hg(L/kg) | |
| Sand Activated Carbon Sediment | | 1 0.4 1.25 | 0.5 0.5 0.5 | 0.001 0.01 | 2 20000 3000 | 0.2 2000 400 | | |
| (b) Layer | properties | 1 | | | | | | |
| Layer | h _i (cm) | Material | | Т | Cortuosity | | $\alpha_i(\text{cm})$ | |
| 1 2 3 | 15 2 30 | Sand Activate Sedimer | ed carbo nt | n N E | Millington and Quirk Millington and Quirk Boudreau | | | |
| | | | | | | | | |

toxic form of Hg that accumulates in fish and leads to exposure to humans through the food chain (Morel et al., 1998; Kraepiel et al., 2003; Kudo and Miyahara, 1991). The methylation of Hg to MeHg and demethylation of MeHg back to inorganic Hg is commonly modeled with a pair of coupled first order reactions with reaction coefficients specified according to the local redox conditions. The redox profile in the following case is simplified to two extreme regions, an aerobic zone near the benthic surface and an anaerobic zone underlying. The methylation is assumed to only occur in the anaerobic sediment layer and the demethylation occurs uniformly in the sediment. The demethylation rate coefficient in this example is 0.005 yr^{-1} (Hintelmann et al., 2000) and the methylation rate coefficient is estimated to be 0.4 yr^{-1} from mesocosm experiments (Bireta, 2015). In the test case, a 30 cm sediment layer with an initial Hg concentration of 3 mg/kg has been capped by a 2 cm activated carbon layer and 15 cm sand layer. The top 5 cm of the sand layer is assumed to be affected by bioturbation of a uniform strength at ($D_{bio,pw,0} = 50 \text{cm}^2/\text{yr}$ and $D_{bio,p,0} = 1 \text{cm}^2/\text{yr}$). Table 3 summarizes the key model inputs for the simulation.

The MeHg concentrations simulated by CapSim in the base case were verified with results from Comsol^{*}, a commercial numerical simulation tool, as shown in Fig. 3(a). The activated carbon-sand capping layers slowed down the upward transport of the MeHg generated in the deeper layer. The potential impact from a monthly periodic groundwater discharge ($t_c = 0.08 \text{ yr}$) or a daily tidal groundwater discharge ($t_c = 0.0014 \text{ yr}$) is shown in Fig. 3 (b). The instantaneous top flux of total Hg (solid line) varied by 2 orders as the result of the periodic change of groundwater flow. The averaged flux (dashed line) increased 5 orders of magnitude over the baseline flux with a strong groundwater discharge ($\pm 600 \text{ cm/yr}$). In the case with a strong tidal impact ($\pm 0.6 \text{ cm/day}$) (Yim and Mohsen, 1992), the averaged flux of Hg at benthic surface (dotted line) increased to $1.7 \mu \text{g/cm}^2/\text{yr}$.

3.2. Phenanthrene

Phenanthrene is a hydrophobic contaminant that sorbs onto high carbon content materials. The phenanthrene sorption in sand and sediments were normalized to the organic fraction of the sorbing phases with a logK_{oc} = 4.57, and its sorption in activated carbon was modeled with a Freundlich isotherm q= $1.03 \times 10^7 \times C^{0.44}$ (Walters and Luthy, 1984). The sediment system of the mercury example was used with the exception that layer 2 was composed of pure sand or a 0.1% by weight activated carbon-sand mixture. The phenanthrene porewater concentrations in the sediment layer and at the bottom were fixed at 100 µg/kg. The overlying water was assumed to be a well-mixed lake with a benthic transfer coefficient $k_{bl} = 0.00273$ cm/hr and a constant



Fig. 3. Model verifications of Hg and MeHg case (a) and sensitivity analysis on oscillating advection flow (b).



Fig. 4. Model verifications of phenanthrene case and sensitivity analysis on kinetic sorption, deposition and bioturbation.



Pore Water Concentration Time Profiles Benzene 5.0 cm 1.6e+04 1.4e+04 1.2e+04 Concentration (µg/L) 1.0e+04 8.0e+03 6.0e+03 4.0e+03 2.0e+03 0.0e+00 0 100 150 50 200 Time (yr) (b)

Fig. 5. Concentration profiles of benzene with depth at different times in Industri-Plex Site example.

zero water concentration. The fate and transport of phenanthrene in the sediment and the capping layer were simulated over 50 years. The baseline result in Fig. 4(a) with linear sorption was verified with an analytical solution (Shen and Reible, 2015). Fig. 4(b) shows the possible impacts from the kinetic sorption of activated carbon in the 2 cm activated carbon-sand layer or the aerobic biodegradation in the top two layers. With an increasing kinetic rate coefficient, the partitioning of phenanthrene in porewater and activated carbon moves toward equilibrium and the profile converges to the equilibrium case profile. The concentration of phenanthrene in the capping layer is reduced significantly by the aerobic biodegradation with a first-order rate

constant 0.12 day⁻¹ proposed by Yuan et al. (2001). Fig. 4(c) and (d) show the impacts from a sediment deposition layer to the benthic surface concentrations. The mass released to the overlying water body drops to effectively 0 with as little as a 0.02 cm/yr deposition rate to the top of the cap.

The impact from the bioturbation-driven distribution of sorbents to the migration of contaminants is shown in Fig. 4(e). A solid particle bioturbation ($D_{bio,p,0} = 3 \text{cm}^2/\text{yr}$) with a Gaussian RMS width σ = 7.5 cm in Equation (6) mixes the AC with both the sand from upper layer and the contaminated sediment in the lower layer and causes a substantial increase in porewater concentration at the surface.

Table 4

Summary of the properties for PCB-52 contaminant isolation.

| (a) Solid material properties and sorption coefficients | | | | | | | | |
|---|---------------------|----------------------|--------------------------------------|-------------------------|--|--|----------------------|--|
| Material | | ε _m | $\rho_m(kg/L)$ | \mathbf{f}_{oc} | logK _{oc} (L/kg) | $K_f\!\left(\!\frac{(\mu g/L)^N}{\mu g/kg}\right)$ | Ν | |
| Sand Activated Sediment | Carbon | 0.4 0.363 0.65 | 1.6 0.026 1.6 | 0.0001 0.01 0.056 | 5.37 5.37 | 0 1780000 0 | 0.86 | |
| (b) Layer properties | | | | | | | | |
| Layer | h _i (cm) |) 1 | Material | | Tortuosity | | $\alpha_i(cm)$ | |
| 1 2 3 | 30.5 25.4 20 | 5 // 5 | Sand Activated carbon Sediment | | Millington and Quirk Millington and Quirk Boudreau | | 2.76 2.76 2.76 | |

CapSim is conveniently structured to allow multiple simulations including Monte Carlo analysis with random variations of selected parameters. A Monte Carlo analysis on the bioturbation strength and depth was performed by 100 simulations with random choices of diffusion coefficient from 1 to 5 cm²/yr and the Gaussian RMS width σ from 5 cm to 10 cm. The mean water-sediment surface concentration at 50 years is slightly lower than the case with mean bioturbation coefficient and Gaussian RMS width (Fig. 4(f)).

4. Recent case studies with CapSim

The unique features of the CapSim model have been applied for assessment and remediation of a variety of contaminated sites since its development, including the Willamette River in Portland, Oregon (A.E.C.O.M., 2016), the Industri-Plex Superfund Site near Woburn, MA (Haley and Aldrich, 2014), Manistique Harbor and River Superfund Site, Michigan (Azhar, 2015), and the Lower Passaic River Superfund Site near Newark, New Jersey (CH2MHILL, 2013). A brief overview of the characteristics of these sites and the model application are highlighted here to illustrate the features of the software.

4.1. Portland harbor superfund site

CapSim was used in a remediation design for River Mile 13.1 in the lower Willamette River, near the Downtown Reach Area of Portland, OR (A.E.C.O.M., 2016). The existing sediment consisted primarily of silty sand and fine gravel, and it was found to contain unacceptably high levels of lead, polychlorinated biphenyls (PCBs), dioxins/furans, and PAHs. CapSim was used to design an isolation layer between the contaminated sediment and biological receptors. The steady-state, maximum contaminant concentration in a sand isolation/geotextile/ bioturbation layer matrix, along with the transient contaminant concentration model after cap instillation were used as design metrics. Three caps were used for parts of the site requiring different levels of remediation. The first area used a cap comprised solely of clean sand. This cap was estimated to provide isolation for 400 + years with a thickness of 1.5 m. The second used a thick unamended sand cap that was estimated to provide chemical contaminant isolation for more than 200 years. The thick unamended area purpose was to meet slope stability requirements, so its thickness varied from 1.5 feet to 9 feet. The final area was capped using a layer of clean sand amended with 10% by weight activated carbon. Based on designs in CapSim of a thickness of ~12 inches, the amended area was estimated to provide isolation for more than 500 years.

4.2. Industri-Plex Superfund site

The Industri-Plex Superfund Site is a former chemical and glue manufacturing facility near Woburn, MA (Haley and Aldrich, 2014). Elevated concentrations of benzene were found in the sediment of four hide piles in the Lower South Pond of the site between 2011 and 2014. Dredging was used to remove contaminated soil that was disposed of in an off-site facility. Dredging was determined to be the most prudent removal method because there was very little benzene migration within the sediments and groundwater due to small groundwater flux values in the area. Afterward, the sediment elevations would be restored. For the upland edge of the site, a geotextile layer, an Aquagate + PAC[™] layer, a wetland soil layer, and an erosion control blanket were to be used to replenish the sediment levels and cap the breakthrough of the remaining benzene. The Aquagate + PAC[™] layer consists of large particles to allow free water flow, along with an activated carbon coating to



Fig. 6. Concentration profiles of PCB-52 with depth at different times in Lower Passaic River Site example.

sorb any contaminant. The Lower South Pond area was capped and restored using a geotextile layer, a wetland soil layer, and an erosion control blanket.

CapSim was used to simulate contaminant migration through the cap layer for each area within the site. The model system was simulated with no bioturbation, no consolidation of the underlying sediment, no additional sediment deposition on top of the cap, and a constant concentration boundary condition of contaminant at the underlying sediment. A conservative modeling approach was used that excluded the biodegradation of benzene, although degradation is expected to occur. The parameters from the remedial design report were used to construct a CapSim model and simulate benzene migration through the system. Fig. 5 shows a plot using a depth of 30 cm of wetland soil and 7.5 cm of Aquablok + PAC, along with a concentration profile at a depth of 5 cm. The design team was able to alter the Aquablok + PAC depth in additional simulations to identify the design to meet containment performance requirements and minimize expenses.

4.3. Manistique Harbor and River Superfund site

The *in-situ* adsorptive potential of different cap layers for the Manistique Harbor and River Superfund site (Michigan) were analyzed using CapSim (Azhar, 2015). PCB contaminant migration rates were compared within sediment without any sorption amendments, *in-situ* amendments, and conventional cap designs (sand only) with the GAC and organoclay amendments. Mercury, arsenic, chromium, copper, PCBs, and PAHs (benzene, chlorobenzene, naphthalene) were all contaminants studied in combination with various sorbents to determine the most effective sorbent materials for each contaminant.

After using CapSim to simulate a cap with no sediment amendments, it was estimated that PCB 52 would take more than 100 years to deplete from the surface layer and would reach a steady-state flux at the surface of $440 \,\mu\text{g/m}^2$ /year due to diffusion and an upwelling rate of 1 cm/day and 157 $\mu\text{g/m}^2$ /year at a diffusion dominated upwelling rate of 1 cm/yr. PCB 18 takes less time than PCB 52 to deplete from the surface layer, while PCB 101 takes longer.

Three simulations of organophilic clay (OMC) were conducted, including the *in-situ* application of OMC, a 1 cm thick OMC mat, and an amended sand cap, with a thickness of 30 cm, containing OMC. In the first and third simulations 0.8 lb/ft² of OMC were added in the overlaying sediment and sand, respectively. The OMC simulations were modeled assuming a linear sorption isotherm (Reible et al., 2008).

The GAC simulations tested the efficacy of GAC as a sorbent for PCB 18, 52, and 101. The simulations were the same as the OMC simulations, but with GAC (0.4 lb/ft^2) in place of OMC. The GAC sorption was modeled using the Freundlich isotherm. CapSim results for GAC sorption of PCB 52 with 10 cm of sediment are shown below. The 1 cm mat of GAC simulation and 30 cm of sand mixed with OMC results were excluded because, regardless of upwelling rate, CapSim predicted a surface breakthrough time of more than 1000 years for each case (Azhar, 2015).

4.4. Lower Passaic River Superfund site

The Lower Passaic River is the location of a former alkali manufacturing facility that contains elevated concentrations of 2,3,7,8-TCDD (dioxins/furans), PCBs (PCB 52), PAHs (phenanthrene), mercury, and other chemicals (CH2MHILL, 2013; Hicks and Collins, 2017). A proposed remedy involves dredging of the most highly contaminated sediment transport to an off-site facility for further treatment. A cap would then be placed over the remaining sediment, along with a geotextile layer and an armor cap to decrease erosion of the cap and increase its lifetime.

CapSim was employed to predict the transport of the previously mentioned contaminants through the active cap placed on the newly dredged surface sediment. The cap used for each simulation was a mixture of 25% Aquagate + PAC and 75% sand to ensure that breakthrough of each contaminant was greater than 100 years. The geotextile layer, placed between the active layer and sand, was a nonwoven 100% plastic filter fabric, and the armor layer was determined to need a thickness of 12 inches and a D_{50} stone size of 4.5 inches. The design criteria only specified that the remediation must meet a breakthrough of at least 100 years, but the cap efficacy provides more than 250 years of contaminant isolation. Table 4 and Fig. 6 show the properties of the layers and results with PCB-52 transport.

5. Summary

Assessment and remediation of contaminated sediments requires predictive models of the evolution of future contaminant levels under a variety of different scenarios. A new open source software tool, CapSim, has been developed that incorporates classical transport processes and, importantly, unique sediment transport processes including bioturbation, deposition and consolidation. The software contains a graphical user interface to expedite the application for new users, but it can also be run in batch mode for sensitivity analysis or Monte Carlo simulations. A database of key parameter values for important compounds and empirical relationships to estimate other parameters is incorporated into the software to facilitate its application to new systems. CapSim has been applied for assessment and remediation of a variety of contaminants in different locations throughout the United States. The software provides an approach for rapid assessment of the feasibility of remediation designs for contaminated sediments.

Software availability

The CapSim source code is freely available on the World Wide Web at: https://github.com/EnvironmentalSoftware/CapSim.

An executable installer for the software is also available upon request sent to Danny Reible (danny.reible@ttu.edu).

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envsoft.2018.08.014.

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