Chapter 13

MODELING MERCURY FATE AND TRANSPORT IN AQUATIC SYSTEMS

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Mercury in the aquatic environment is a neurotoxin with several known adverse effects on the natural ecosystem and the human health. Mathematical modeling is a costeffective way for assessing the risk associated with mercury to aquatic organisms and for developing management plans for the reduction of mercury exposure in such systems. However, the analysis of mercury fate and transport in the aquatic environment requires multiple disciplines of science ranging from sediment transport and hydraulics, to geochemistry and microbiology. Also, it involves the knowledge of some less understood processes such as the microbial and diagenetic processes affecting the chemical speciation of mercury and various mechanisms involved in the mass-exchange of mercury species between the benthic sediments and the overlying water. Due to these complexities, there are many challenges involved in developing an integrated mercury fate and transport model in aquatic systems. This paper identifies the various processes that are potentially important in mercury fate and transport as well as the knowns and unknowns about these processes. Also, an integrated multi-component reactive transport modeling approach is suggested to capture several of those processes. This integrated modeling framework includes the coupled advective-dispersive transport of mercury species in the water body, both in dissolved phase and as associated to mobile suspended sediments. The flux of mercury in the benthic sediments as a result of diffusive mass exchange, bio-dispersion, and hyporheic flow, and the flow generated due to consolidation of newly deposited sediments is also addressed. The model considers in addition the deposition and resuspension of sediments and their effect on the mass exchange of mercury species between the top water and the benthic sediments. As for the biogeochemical processes, the effect of redox stratification and activities of sulfate and iron-reducing bacteria on the methylation of mercury is discussed, and the modeling approach is described. Some results for the application of the model to the Colusa Basin Drain in California are presented. At the end of the paper, the shortcomings of our current knowledge in predicting the fate of mercury in water-sediment systems, the potential improvements, and additional complexities required to make the model more realistic, are discussed

Keywords: aquatic, mercury, methylation, resuspension, shear stress, iron, non-cohesive, massexchange, MCM, QWASI, diagenesis, sorption

1. Introduction

Mercury in the aquatic environment is a neurotoxin with several known adverse effects on the natural ecosystem and on human health. A large number of water bodies around the world are contaminated with mercury as a result of direct anthropogenic activities such as mining, or indirectly via dry and wet deposition of mercury. An essential component of any conceptual or mathematical model of mercury fate and transport involves the types and rates of mercury transformations. Important among the different chemical forms or "species" is its methylated form (MeHg) which is the most bioavailable. Mercury is believed to be methylated in anoxic waters and sediments [85] and then transported (upward usually) to oxic zones through advection and turbulent dispersion, and in case of benthic methylation, also through molecular diffusion in porous media. There are also speculations that the sometimes large concentrations of methylmercury in surface waters of deep lakes and oceans cannot arise solely as a result of transport from deeper layers, and so there should be some MeHg production in oxic layers [85]. In any case, the most accepted theory is that methylation of mercury is a bacterial-mediated process mainly done by sulfate reducing bacteria, [8] [9] [43] [44]. However, it was recently found that iron reducing bacteria can also mediate mercury methylation [37]. Further, [29] noted in their measurements in sediments from eight sites including lakes, and freshwater and brackish estuaries that methylation rates, %MeHg (MeHg to total Hg ratio), and absolute MeHg concentrations were not significantly correlated to the availability of sulfate as a terminal electron acceptor for SRB. In shallower waters and also waters with larger mixing, the anoxic and in particular sulfate and iron reducing conditions more often occur in benthic sediments and at certain depths where oxygen and nitrate are depleted.

[53] noted apparent higher %MeHg downstream of reservoirs in river systems suggesting that the higher organic content due to settling in these systems promoted microbially mediated processes. Monperrus et al. (2007) [84] measured methylation in the oxic waters of the euphotic zone of the Mediterranean Sea and suggested a microbially mediated pathway due to the higher methylation rates observed during periods of higher temperatures and high biological turnover. Hg reduction and de-methylation were also studied and both were mainly attributed to photochemical processes near the surface. Thus, while current conceptual models treat anoxic biotic transformation to MeHg as important, this is not certain at all and much more remains to be done in order to fix the understanding.

Mathematical modeling is one cost-effective approach to evaluate the associated risk and the utility of remediation options. There have been many efforts to develop realistic mercury cycling models for aquatic environments including lakes, wetlands, rivers and coastal waters. These efforts can be categorized into a) models that have treated the air-water-sediment system as respective batch reactors exchanging mercury species through rate-limited

processes (e.g., [26] [33] [56]) without explicit consideration of transport of mercury species as dissolved or associated with sediments; b) models that have treated mercury as a non-reactive conservative metal mainly being transported as bound to sediments [102]; and c) models that have emphasized the detailed geo-chemical cycling of mercury [47] [48] [138]. Also there are bioaccumulation models focused on the uptake of different forms of mercury by living species in the aquatic system [52]. More recently some researchers have coupled a more sophisticated representation of physical processes including the hydrodynamics, sediment transport and the biogeochemical transformation of mercury in the water body using one-dimensional [19] [20] [135] [76] [77], two-dimensional [107] and three-dimensional [94] [93] [136] approaches.

In the following review we first consider sediment transport processes and modeling, because of the fundamental role of sediments as vehicles for mercury and other metal species. Then we turn to models developed specifically for mercury in surface aquatic systems.

1.1. Sediment transport

From a historical point of view, the interest in predicting sediment transport (and the resulting changes in riverbed morphology) has been driven mainly by the need to enable undisturbed navigation of vessels in rivers and channels [44]. Several empirical and semi-empirical predictors have been developed to describe the changes in river beds due to bed-load and suspended sediment movement, and to estimate the decrease in reservoir storage capacity. In the last twenty years, the attention on sediment transport has been enhanced by the important role that sediment plays in transporting adsorbed pollutants, considering all the environmental and social implications of the transport of contaminants.

When the water velocity increases close to the bottom of a water body, the particles of the bed start to move. The conditions for this incipient motion have been quantified since the seminal experimental work of [101], and details can be found in books, book chapters, and e-books such as those of [60] [40] and [88], respectively. Further increase in velocity results in entrainment of particles into suspension. Several expressions for predicting the entrainment rate of sediment into suspension (mostly for non-cohesive sediment) have been proposed by diverse authors (see, [54] [114] [115] [117] [41] for instance). In those equations, the rate of sediment entrainment into suspension is described by the difference between the bed shear stress due to currents and waves, and the critical bed shear stress, which is a function of sediment grain size and density. In some formulations, the wall-friction (shear) velocity is used as a surrogate of the bed shear stress. The main deposition parameter, the particle settling velocity, is also determined from grain and liquid properties: sediment density, grain shape and the viscosity of liquid. The transport parameter is then calculated, which further determines the conditions and areas of resuspension,

transport and deposition of moving sediment. The processes and equations which can be used to determine onshore – offshore and longshore transport due to currents and waves in coastal areas are described in the literature (e.g., [74]).

Numerous sediment transport models have been constructed from these principles for river and estuary simulation, mostly for non-cohesive sediments (e.g., [116] [120] [86] [34] [73] [68] [93] [123] [6] [87] [30]). However, these models are valid only for uniform grain size and non-cohesive sediment, conditions rarely met in natural waters. With increasing discharge, finer non-cohesive fractions (silt and fine sands) usually enter into suspension, while other, coarser fractions require higher shear stresses to initiate their movement, first as bed-load and later as suspended particles. Such phenomena can often be observed in the coastal zone, where sediment composition is heterogeneous due to spatially and temporally varying hydrodynamic conditions [110]. Multi-fractional techniques (e.g. [97]) and models (e.g., [128]) have therefore been developed to increase the accuracy of non-cohesive sediment transport modeling. One such approach is dividing suspended sediment into washload and coarse suspended sediment, as described in [19].

Cohesive sediments, on the other hand, are more difficult to describe and particularly to simulate with a numerical model. The mechanisms and equations of cohesive sediment erosion and resuspension are well described in the literature (e.g., [126]); however, they have not been adopted for use in mathematical models of sediment transport that deal with transport of particlebound pollutants. Few models for estuarine waters include the simulation of cohesive sediments; moreover, their authors report relatively poor agreement with measurements of sediment concentration in the water column [50] [123] [70]. Even more complicated is the modeling of transport of colloidal particles and pollutants bound to colloids as the particle movement cannot be described in accordance to available formulae of sediment transport (valid for non-cohesive sediment). On the other hand, the role of colloidal particles in transporting the contaminants to/from the deeper sediment layers has been overlooked in the literature. A few models are capable of simulating colloid-facilitated transport in saturated and unsaturated porous media (e.g., [78] [32] [59] [105]), while at present no known sediment transport model for surface waters accounts for colloids.

With some exceptions, only qualitative agreement among model predictions and measurements in natural environments can be expected; often, model results are in accordance with measurements by an order of magnitude or at best a factor of three (e.g., [109] [132] [93] [94]). Using the one-dimensional coupled US-EPA models, the same level of agreement was achieved in the Idrijca and Soča Rivers [135], while spatiotemporal moments showed significantly better agreement for the Carson River [19], mostly due to a very large quantity of measured data used for the calibration of the model. The studies of sediment transport in coastal areas [55] [93] as well as studies of riverine sediment transport [21] [135] have confirmed that the transport of particulate-bound

mercury represents a major part of its overall transport in rivers, lakes and estuaries. Moreover, a single major flood event can account for more than 90% of the total annual mercury transport. Therefore, it is very important to calibrate the sediment transport models in accordance with high discharges, although it is very difficult to ensure enough measurements for calibration and validation of models in such conditions. Furthermore, it has been established that concentrations of suspended matter are different during the increasing and decreasing flow at the same discharge [46] [125] [66]. The hysteresis phenomenon has often been observed, but rarely measured and/or modeled [2]. The ratio between discharge and sediment discharge is a function of the characteristics of each stream and catchment and as such cannot be generalized. Moreover, sediment transport also depends on the availability of sediment, which is again a function of the stream itself. For the Carson River, an unlimited quantity of material was reported [19], while the situation in the Idrijca and Soča is different due to dams and the geology of the stream and the catchment [135]. In the case of rivers having dams, the transport capacity in the basin is heavily decreased and sediment is stored in the reservoir. Furthermore, during floods, large quantities of fine sediment deposited during low flows can be released from the upstream accumulations.

Mass balances of sediment and sediment-bound pollutants are often established, either solely from measured data or from combined modeling results and measurements [108] [93] [133] [94] [75] [127] [96] [63]. They are a valuable tool, which is often helpful in deciding which type of model to apply and which parameters need to be measured in the future. The simulation results, on the other hand, are often used to improve the mass balances.

1.2. Model tools for understanding mercury fate and transport

Early models have used relatively simplistic assumptions to predict the dispersion of mercury in water bodies. For example, Turner and Lindberg (1978) [111] used a simple dilution model to describe the decline of mercury concentration in a river-reservoir system downstream of a chemical plant. Clearly, since the effect of sedimentation was not taken into account, the model over-predicted the mercury concentration downstream of the release point.

Not all earlier models have adopted such a simplistic approach. Herrick et al. (1982) [52] developed a model for mercury cycling in woodland streams that considers mercury and methyl-mercury to be in five phases (sediment, water, invertebrates, detritus and fish), and the detritus phase is discretized into several bins representing various compositions and sizes of organic particles. However, this model does not have a transport component and the deposition and resuspension of particles were not accounted for. Fontaine (1984) [38] developed a fully non-equilibrium one-dimensional reactive transport model for the fate of metals in aquatic systems. Three phases of metals (i.e., dissolved, particulate and associated with organic substrates) were considered in the model.

The mass-exchange between the phases and also between the water column and sediments were all considered to be kinetically controlled. A relatively sophisticated model was used for sorption and geochemical transformation of various mercury species.

[71] developed a mass balance model based on the concept of aquivalence and fugacity called QWASI (Quantitative Water-Air-Sediment Interaction) for lake systems. They considered the effects of inflow and outflow of chemicals (dissolved or particle-bound), diffusive mass exchange from/to sediments, resuspension/deposition and burial, and dry and wet deposition, and solved the system assuming a steady-state condition overall. In each compartment (water and sediments), concentrations of sorbed and dissolved species were assumed to be in equilibrium. No transport process was considered in this model. [26] used a modified version of QWASI to simulate cycling of mercury in a hypothetical lake. Ethier et al. (2008) [33] further simplified QWASI by assuming an instant equilibrium between different species of mercury and applied the resulting model to Big Dam West, Canada.

Using a similar approach, [56] developed a lake dynamic mercury cycling model called MCM. They considered three vertical compartments of epilimnion, hypolimnion, and sediments and four biotic compartments including phytoplankton, zooplankton, a prey and a predator fish species. Mercury species include elemental, reactive and methylmercury. The distinct feature of MCM compared to even more recently developed models is its more sophisticated treatment of the rates of methylation and de-methylation. While methylation was considered to be a function of reactive mercury concentration, sulfate ion, dissolved organic content and temperature through a Monod type relationship, the latter was considered as a function of methylmercury concentration, H+ and dissolved organic carbon. Leonard et al. (1995) [67] used MCM to predict the fate of mercury in the Great Lakes. Harris et al. (1996) [49] upgraded MCM to simulate mercury cycling in a group of lakes. Knightes and Ambrose (2007) [62] applied this model to 91 lakes in Vermont and New Hampshire and found that the performance of the model is inadequate as a prediction tool. Kotnik et al. (2002) [65] applied the same reaction rate functional forms suggested by Hudson et al. (1994) [56] to simulate mercury cycling in Lake Velenje, Slovenia. The approach of considering lake systems with well mixed layers has been adopted by some other researchers recently. [61] developed a spreadsheetbased steady-state mass balance model (SERAFM) for mercury cycling and evaluation of wildlife exposure risk. Similar to other models, SERAFM categorizes mercury into three species (Hg0, HgII, MeHg) and in five phases (abiotic solids, phytoplanktonic, zooplanktonic, detrital and associated with dissolved organic matter). Also, the aquatic system was modeled with three compartments (epilimnion, hypolimnion, and sediments) in addition to an equilibrium sorption assumption. [15] applied SERAFM to a constructed wetland and a stream in Nevada, USA.

In most of the models used for circulation of mercury in lake systems including QWASI [71] and MCM [49] the system is considered as horizontally well mixed, sometimes with single-layer and sometimes with multi-layer water columns with a uniform and time invariant mass exchanges between the layers. Although this approach may be appropriate for small lakes with mainly depositing suspended particles, it is inadequate for more complicated systems including rivers, coastal areas as well as larger lakes where the circulation of water and resuspension of sediments plays an important role in mercury cycling. Assumptions of net deposition and of equilibrium between particulate and dissolved mercury phases artificially restrict re-entrainment of mercury. On the other hand, most of the surface water metal cycling models developed in the past have relied on the partitioning coefficient (K_D) concept. As opposed to organic chemicals, the value of K_D for metals is sensitive to the chemical conditions such as pH, occurrence of complexing ligands, and redox potential among others [45] [92]. Thus, the constant K_D approach may lead to erroneous results in some applications.

Faced with these shortcomings, researchers have used two distinct pathways to improve the modeling approaches for mercury. One group (mainly hydrologists) have improved the treatment of flow and sediment transport and the other group (mainly geochemists) have focused on using more accurate and complicated biogeochemical reaction networks. [121] briefly reviewed mercury models applied to rivers, lakes and coastal zones.

Among the group of researchers focusing on the hydrological processes are [103], who used the cohesive sediment and pollutant transport model TSEDH [103] coupled with the hydrodynamic circulation model RMA-2V to model mercury cycling in Clear Lake, California. They considered multiple layers of bed sediments with different critical shear stresses but did not consider the different distribution of mercury in each layer. Bale (2000) [5] suggested using an advection-dispersion transport model and as well as incorporating a more mechanistic approach to calculate rates of deposition and resuspension to simulate the fate of mercury in Clear Lake. He used a slightly modified version of the reaction-rate functional forms proposed by [49]. Another way to consider heterogeneity and transport without explicitly modeling the hydrodynamics and sediment transport is to use compartmental models where the flow and mass exchange between the compartments are given as model parameters. AScI (1992) [1] incorporated the kinetic transformation subroutine from MCM into the water quality model WASP4 and called the resulting model MERC4. [51] coupled MERC4 with both a fish bioenergetics/bio-uptake model and a lake eutrophication model to predict the transport and fate of mercury in Onondaga Lake, NY. The lake eutrophication model was used to estimate the planktonic populations and their settling rates.

In systems where the transport is more important such as rivers, hydrodynamic forces affecting plays a more important role. In [19] Carroll et al. used MERC4 along with WASP and the RIVMOD hydrodynamic model to

simulate mercury transport in the Carson River, Nevada. They modeled sorption and desorption as kinetically controlled processes. This model was also applied to the Idrijca and Soca River systems in Slovenia [135].

STATRIM, a two-dimensional model of mercury transport and fate, was developed first for coastal environments [107], where mercury in its particulate form was considered for the first time in marine environments. The model used annually averaged input data combined with depth-averaged parameters and was subsequently upgraded to a three-dimensional non-steady state model (PCFLOW3D). The PCFLOW3D model together with a new sediment transport module was further used to simulate resuspension and other sediment and mercury processes in coastal environments [132] [93] [94] and applied to the Mediterranean Sea with simplified sediment transport and some improvement in the biogeochemical transformation and atmospheric mass exchange modules [136]. This model incorporates mercury methylation/de-methylation and other Hg transformations such as reduction-oxidation. Different forcing factors were considered, the most important being extreme (flood-wave) river inflow, extreme wind-induced currents and waves.

Among the works focusing on the biogeochemical cycling are models mainly devoted to the geochemistry of mercury in the water column, including the full reaction network affecting mercury speciation in batch systems (i.e., [47] [138]). An extensive review of the biogeochemical cycling of mercury in aquatic systems can be found in [85] and, for marine environments, [35-36]. [11] developed a steady state fate and transport model called TRANSPEC by incorporating the geochemical speciation model MINTEQ+ with the aquivalence/fugacity approach introduced by [72], but including a more sophisticated geochemical reaction network. The species were assumed to be in chemical equilibrium; however, the mass transfer between various compartments (water, air, and sediments) was considered as a dynamic process. In this model, flow between various water body compartments and also resuspension/deposition were considered as steady pre-specified processes. The model was applied to predict the fate of Zn in several lakes in Canada [11-12].

Although many reversible abiotic geochemical reactions affecting the speciation of metals can be treated as equilibrium reactions, their microbemediated transformations are typically slow, irreversible in typical modeling time-scales and kinetically controlled. In case of mercury, both methylation and de-methylation are known to be bacteria-mediated. [39] modified TRANSPEC to handle kinetically controlled reactions and called the resulting model BIOTRANSPEC. They also included the effect of uptake by fish in their model. They applied the model to mercury cycling in Lahontan reservoir in Nevada, USA. The methylation and de-methylation rates were considered constant but site-specific rates.

Because sulfate reducing bacteria, and possibly iron-reducing bacteria, are the most important microorganisms in the formation of methylmercury in temperate locations, it is important that attempts to quantify rates of mercury

methylation consider redox-specific and kinetically-controlled microbiallydriven degradation reactions, within the context of equilibrium multiphase and multicomponent chemical conditions. Modeling platforms available for coupling microbe-mediated kinetics with multicomponent geochemical equilibria are available as subroutines that can be linked with other models. Tools such as PHREEQC2 [89] can be used for exploration of the relationship between mercury methylation and ambient chemical conditions as controlled by ambient microbial communities. PHREEQC2 is a computer program that can perform speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, as well as arbitrarily defined kinetics associated with microbially-mediated reactions.

The rate of release of the methylmercury produced in sediment layers is a function of the depth of the layers. Sediment diagenesis models focusing on modeling redox stratification have been developed in the past [10] [13] [14] [113] and have been used to predict the cycling of contaminants and nutrients in lakes [16] [17] [100], deep seas [69], as well as in coastal zones and estuarine sediments. These models however have not been integrated with fate and transport models representing the overlying waters. Particularly in the case of mercury cycling, it is important to integrate redox zonation in the sediments and its effect on mercury methylation with (a) the release mechanisms of the produced MeHg to the overlying water and (b) with the transport processes in the overlying water. In the present work a framework for coupling the sediment processes with the cycling of mercury in the overlying water is introduced.

2. Model Development

The objective of this section is to introduce a modeling framework applicable to a wide variety of surface water bodies including lakes, estuaries, rivers and coastal zones. The formulation is developed considering a two-dimensional representation of the water column; however, at the end of the chapter demonstration results are generated assuming a one-dimensional case. To preserve the generality of the modeling framework, an unlimited number of suspended solid phases are considered in the model. Depending on the aquatic system being studied, these phases can be assigned to mineral abiotic solids, phytoplanktonic, detrital, or various classes or size categories of suspended solids. The model is also capable of predicting the fate and transport of an unlimited number of major components and ligands influencing the speciation of mercury and the redox zonation in the sediments. The choice of these major components are also problem dependent. The computational domain of the model is considered to be the overlying water (assumed to be totally mixed in the vertical direction) and the active benthic sediment layer. The depth of the benthic sediment layer should be chosen based on the problem. Also, the twodimensional representation of the water body can be easily replaced by a threedimensional one by a generalization of the governing equations. This step may

be necessary in problems involving deep water bodies where the anoxic layer can be present in the water column or in cases where vertical mixing does not occur due to temperature stratification. As it was explained in the Introduction, the aim here is to track the vertical distribution of mercury and the rest of major components involved in the active bed sediment layer. This is necessary since, first, the rate of release of contaminants from the sediments to the overlying water as a result of both diffusive mass exchange and resuspension depends on the distribution of contaminants in the sediment layers, and, second, the rate of methylmercury production depends on the magnitude of overlap between the sulfate or iron reducing layer and the layers containing reactive mercury.

2.1. Fate and transport of mercury in the overlying water

The depth-averaged fate and transport governing equations for the species in the overlying water considering a kinetic mass transfer between the phases can be written as [76-77]:

$$\frac{\partial HC_{i}}{\partial t} + \frac{\partial UHC_{i}}{\partial x} + \frac{\partial VHC_{i}}{\partial y} = \frac{\partial}{\partial x} \left(D_{hx}H \frac{\partial C_{i}}{\partial x} \right) + \frac{\partial}{\partial y} \left(D_{hy}H \frac{\partial C_{i}}{\partial y} \right) + k_{b} \left[c_{i} \left(0 \right) - C_{i} \right]$$

$$-H\sum_{j=1}^{n} \phi_{j}k_{j} \left(K_{Dij}C_{i} - S_{ij} \right) + qC_{in} + k_{at,i} \left(C_{i,at} - C_{i} \right) - u_{j}\theta_{0}c_{i} \left(0 \right) + HR_{i} + \psi_{i}$$

$$\frac{\partial H\phi_{j}S_{ij}}{\partial t} + \frac{\partial UH\phi_{j}S_{ij}}{\partial x} + \frac{\partial VH\phi_{j}S_{ij}}{\partial y} = \frac{\partial}{\partial x} \left(D_{xj}H \frac{\partial\phi_{j}S_{ij}}{\partial x} \right) + \frac{\partial}{\partial y} \left(D_{yj}H \frac{\partial\phi_{j}S_{ij}}{\partial y} \right)$$

$$(1)$$

$$dt \quad dx \quad dy \quad dx \quad (J \quad dx) \quad dy \quad (J \quad dy) \quad (J \quad d$$

in which t[T] is time; x and y [L] are spatial coordinates; $C_i[M_o/L^3]$ is the dissolved concentration of chemical i in bulk water; U and V [L/T] are the depth averaged velocity components; D_{hx} and D_{hy} [L²/T] are the mechanical dispersion coefficients for dissolved species in the x and y directions; k_b is the sedimentwater mass exchange coefficient for the dissolved species [L/T]; $c_i(0)$ is the pore-water concentration of species *i* at the topmost layer of sediments $[M_c/L^3]$; k_i [T⁻¹] is the mass exchange coefficient between the suspended solid phase j and water; ϕ_i [M/L³] is the concentration of the suspended solid phase category *j*; K_{Dii} [L³/M] is the water-solid distribution coefficient for solid phase j and species *i*; $S_{ij}[M_c/M]$ is the sorbed phase concentration of species *i* to solid phase j; R_i and R_{sij} are the sum of rates of elimination or production of species i at phase j due to reactions for dissolved and sorbed phases, respectively; q $[L^3 T^{-1}L^{-2}]$ is the amount of inflow/outflow per surface area; $\phi_{i,in}$ [M/L³] is the concentration of solid phase j in the inflow; $S_{ij,in}$ [M_c/M] is the concentration of species *i* sorbed to solid phase class *j* in the lateral influx; $k_{at,i}[L/T]$ is the atmospheric exchange rate coefficient for species *i*; $C_{i,at}$ [M_c/L³] is the saturation

concentration for species *i* calculated using Henry's law; D_{xj} and D_{yj} [L²/T] are the dispersion coefficient for suspended particles in the *x* and *y* directions respectively; Er_j [ML⁻² T⁻¹] is the sediment resuspension rate for solid phase class *j*; w_{pj} [L/T] is the deposition rate parameter for solid phase class *j*; $s_{ij}(0)$ [M_c/M] is the sorbed concentration of chemical species *i* to solid phase *j* at the topmost layer of the bed sediments; u_j [L/T] is the pore water velocity in bed sediments due to consolidation or hyporheic flow (downward defined as positive); θ_0 is the bed sediment porosity at the sediment-water interface and Ψ_{ij} [LT⁻¹M_cL⁻³] is a source term representing for example the effect of plant uptake and decomposition.

2.2. Sediment Resuspension/Deposition

To solve Eq. (2), the transport of the suspended solid phase needs to be modeled. Many commercial and open-source software packages are available for modeling the transport of cohesive or non-cohesive sediments in various systems including rivers, estuaries or coastal areas [e.g., MIKE 21(DHI), HEC-6 (USACE), STAND [137] and GSTARS [131]. Many of these models assume quasi-equilibrium conditions to calculate the suspended and bed loads (e.g., HEC-6, GSTARS). Although this approach is appropriate for engineering purposes such as studying the morphological changes of the water body and sedimentation in reservoirs and similar applications, it is insufficient for tracking contaminants associated with sediments. The general formulation used in sediment transport models is represented by an advection-dispersion governing equation:

$$\frac{\partial H\phi_{j}}{\partial t} + \frac{\partial UH\phi_{j}}{\partial x} + \frac{\partial VH\phi_{j}}{\partial y} =$$

$$\frac{\partial}{\partial x} \left(D_{xj}H \frac{\partial \phi_{j}}{\partial x} \right) + \frac{\partial}{\partial y} \left(D_{yj}H \frac{\partial \phi_{j}}{\partial y} \right) + Er_{j} - w_{pj}\phi_{j} + q\phi_{j,in}$$
(3)

The main difference between various sediment transport models is essentially the way they calculate Er and deposition terms. [40] lists all different formulas used to calculate the sediment entrainment for non-cohesive sediments. [41] suggested a formulation for mixed size sediments. The fall velocity estimated using the Stokes equation or empirical relationships (e.g., [27]) is often used to model the deposition of non-cohesive sediment. Since the main mechanism for settling of cohesive sediments is coagulation and flocculation, their rate of deposition depends on the concentration of sediments. [80] suggested the following relationship for the rate of deposition:

$$w_p = pv_s \tag{4}$$

in which p is a factor to incorporate the effect of shear stress, calculated as:

$$p = 1 - \tau_b / \tau_{cd} \tag{5}$$

So no deposition occurs when the shear stress τ_b is above the critical shear stress τ_{cd} in Eq. (5). v_s is the fall velocity which is considered as a function of the concentration of particles, as suggested by [80]:

$$v_s = \alpha_8 C_s^{4/3} \tag{6}$$

Suggested equations for the rate of resuspension of cohesive sediments typically have the following form:

$$Er = M\left(\tau_b - \tau_c\right) \tag{7}$$

where M is the erodibility coefficient that can be a function of the degree of consolidation of sediments, their size distribution and factors affecting their stability such as biofilm formation or armoring due to the existence of mixtures of large and fine particles. Some researchers have proposed more complicated power-law or exponential relationships between the erosion rate and the bed shear stress [23].

Some models have addressed the effect of the depth of erosion into the erodibility rate [98] and only a few of them have incorporated the effect of consolidation into the model directly by defining distinct layers of bed sediments [99].

2.3. The fate of mercury in sediments (burial, resuspension, diffusive mass exchange)

Several benthic sediments contaminant fate and transport models have been developed in the past mainly to address sediment diagenesis and nutrient cycling in the sediments [10] [13] [112]. In these models the sediment layer is represented by a one-dimensional column sometimes with a dispersion coefficient and porosity changing with depth as a result of consolidation (e.g., [13]). The top boundary condition (the overlying water) is typically considered to have a fixed concentration of compounds and the burial is modeled using a transformation of coordinates. Here we propose a 3-D model for the transport of contaminants in the sediments in order to incorporate the spatial heterogeneities in resuspension and deposition. The governing equation for multi-phase transport in the sediments can be expressed as:

$$\frac{\partial(\theta c_i)}{\partial t} + \frac{\partial(\theta u_{fx}c_i)}{\partial x} + \frac{\partial(\theta u_{fy}c_i)}{\partial y} + \frac{\partial(\theta u_{fz}c_i)}{\partial z^*} = \frac{\partial}{\partial z^*} \left((D_m + D_B)\theta \frac{\partial c_i}{\partial z^*} \right)$$

$$-\sum_j f_j B_d k_j \left(K_{Dij}c_i - s_{ij} \right) + R_i + \sum_{j'} k_{j'0}f_{j'}B_d s_{ij'} - \psi_i$$
(8)

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$$\frac{\partial \left(f_{j}B_{d}s_{ij}\right)}{\partial t} + \frac{\partial \left(f_{j}B_{d}u_{s}s_{ij}\right)}{\partial z^{*}} = \frac{\partial}{\partial z^{*}} \left(D_{B}f_{j}B_{d}\frac{\partial c_{i}}{\partial z^{*}}\right) + B_{d}k_{j}\left(K_{Dij}c_{i} - s_{ij}\right) + R_{s,i} - \sum_{j'}k_{jj'}f_{j}B_{d}s_{ij} + \sum_{j'}k_{j'j}f_{j'}B_{d}s_{ij'}$$

$$\tag{9}$$

The first terms on the right hand side of both equations account for the effect of consolidation. The boundary conditions are as follows:

$$(D_m + D_B)\theta \frac{\partial c_i}{\partial z^*} = k_b (c_i - C_i) \text{ at } z^* = z_0$$
(10)

$$\frac{\partial c_i}{\partial z} = 0 \text{ at } z^* = -\infty$$
(11)

and for Eq. (9):

$$s_{ij}\Big|_{z^*=-\infty} = 0 \text{ for } J_0 < 0 \text{ erosion}$$
(12)

$$s_{ij}\big|_{z^*=z_0} = S_{ij} \text{ for } J_0 > 0 \text{ deposition}$$
(13)

In Eqs. (8) to (13) z^* [L] is the vertical coordinate based on a fixed datum which increases increasing upward; $c_i = c_i(x, z^*, t)$ [M_c/L³] is the dissolved concentration of species *i* in pore water in the bed sediments; s_{ii} [M_c/M] is the mass concentration of sorbed species i on solid phase j; u_{fx} , u_{fy} , u_{fz} [L/T] are the pore water velocity components; u_s [L/T] is the advective velocity of sediments due to sediment consolidation; B_d [M/L³] is the total bulk density of the sediment materials and f_i is the fraction of sediments consisting of phase *j* (i.e., planktonic, detrital, minerals); D_B [L²/T] is the mechanical diffusion coefficient due to the inhomogeneity of bed materials and the mixing due to the activities of benthic organisms; $D_m [L^2/T]$ is the molecular diffusion coefficient and θ is the porosity of the bed material. It is assumed that the effect of diffusion in the horizontal directions is negligible due to the large scales in the two directions. ψ_i is a sink term that can represent the rate of root uptake of species i; $k_{ii'}$ [1/T] is the rate of transformation of sediment phase j to phase j' and j=0 indicates dissolved phase. Including the x and y directions of pore water velocity allows for inclusion of hyporheic flow. In the derivation of Eqs. (8) and (9) it is assumed that none of the solid phases is mobile in the pore-water in benthic sediments, i.e., no colloid-facilitated transport in the benthic sediments is taken into consideration. This phenomenon can be incorporated into the model by adding advective transport terms to the solid phase.

Imposing a transformed coordinate system in order to attach the origin of the coordinate system to the sediment-water interface $z(t) = z_0(t) - z^*$ on Eqs. (8) and (9), where $z_0(t)$ is the elevation of sediment-water interface, yields:

$$\frac{\partial(\theta c_{i})}{\partial t} + \frac{\partial(\theta u_{jx}c_{i})}{\partial x} + \frac{\partial(\theta u_{jy}c_{i})}{\partial y} + \frac{\partial[\theta(u_{jz} + J_{0})c_{i}]}{\partial z} = \frac{\partial}{\partial z} \left((D_{m} + D_{B})\theta \frac{\partial c_{i}}{\partial z} \right) \quad (14)$$

$$-\sum_{j} f_{j}B_{d}k_{j} \left(K_{Dij}c_{i} - s_{ij} \right) + R_{i} + \sum_{j'} k_{j'0}f_{j'}B_{d}s_{ij'} - \Psi_{i}$$

$$\frac{\partial(f_{j}B_{d}s_{i})}{\partial t} + \frac{\partial[f_{j}B_{d}(u_{s} + J_{0})s_{ij}]}{\partial z} = \frac{\partial}{\partial z} \left(D_{B}B_{d} \frac{\partial f_{j}s_{ij}}{\partial z} \right) + B_{d}k_{j} \left(K_{Dij}c_{i} - s_{ij} \right)$$

$$+ R_{s,i} - \sum_{j'} k_{jj'}f_{j}B_{d}s_{ij} + \sum_{j'} k_{j'j}f_{j'}B_{d}s_{ij'}$$

$$(15)$$

The elevation of the sediment-water interface, $z_0(t)$, is variable with time due to erosion and deposition of sediments. The positive direction for u_f and u_s is changed according to the new coordinate system for the sake of simplicity. Therefore, henceforth positive value indicates downward flow.

The terms u_f and u_s depend on the rate of deposition or erosion at the surface and the consolidation of sediments. Here it is assumed that the porosity of sediments decreases with depth as indicated in [13] via:

$$\theta(z) = (\theta_0 - \theta_\infty)e^{-k_\theta z} + \theta_\infty$$
(16)

where θ_0 is the porosity of the topmost layer of sediments and θ_{∞} is the porosity of deep sediments. In this case, u_s and u_f can be calculated as follows, using a simple mass balance

$$u_{s} = J_{0} \left(\frac{\theta - \theta_{\infty}}{1 - \theta} \right) \tag{17}$$

$$u_f = -J_0 \left(\frac{\theta - \theta_{\infty}}{\theta}\right) \tag{18}$$

where u_s and u_f are functions of z through θ , and J_0 is the rate of change in the elevation of the sediment-water interface. In turn, $J_0 = \partial z_0 / \partial t$, which is calculated as:

$$J_{0} = \frac{1}{(1 - \theta_{\infty})\rho_{s}} \sum_{j} (w_{pj} \phi_{j} - Er_{j})$$
(19)

where ρ_s [M/L³] is the density of sediment particles. The governing equation controlling the mass balance for various solid phases in the benthic sediments can be written as:

$$\frac{\partial f_{j}}{\partial t} + \frac{\partial \left[f_{j} \left(u_{s} + J_{0} \right) \right]}{\partial z} = \frac{\partial}{\partial z} \left(D_{B} \frac{\partial f_{j}}{\partial z} \right) - \sum_{j'} k_{jj'} f_{j} + \sum_{j'} k_{j'j} f_{j'}$$
(20)

2.4. Modeling mercury bio-geochemistry

Most mercury-cycling models have lumped all inorganic species of mercury into a single species identified by reactive mercury (HgII) and, therefore, mercury species in the models include HgII, methylmercury (MeHg) and elemental mercury (Hg0). In addition, in many models the rate coefficients defining the transformation of these species have been considered constant or solely a function of temperature [19] [26] [38] [94] [93] [135] [136]. There have also been modeling studies concentrating on the detailed geochemical speciation of mercury, but these models have been applied only to batch systems [47]. Based on the effect of sulfate- and iron-reducing bacteria, some later models have considered the mercury methylation rate as a function of the concentration of sulfate ion [56] [49]. However, a high concentration of sulfate ion does not automatically lead to a higher methylation rate since, first, the activity of sulfate reducing bacteria can be inhibited by the presence of terminal elector acceptor with higher energy yield (e.g., oxygen, nitrate, and ironIII) and, second, sulfate reduction leads to production of S⁻² ions that can react with dissolved Hg and lead it to precipitate (e.g., [100]). So here we consider the rate of methylation to be proportional to the activity of sulfate reducing biomass. To do this, mercury species are categorized into four groups of HgII, MeHg, HgO and HgS (cinnabar). In addition, to predict the sulfate reduction rate at each layer of sediments the cycling of the major terminal electron acceptors including oxygen, nitrate, iron, and sulfate should be modeled. The reaction network suggested by [113] for sediment diagenesis is adopted with some simplifications, with primary redox reactions listed in Table 1, speciation reactions in Table 2, and secondary redox reactions in Table 3. The main difference between the reaction network used herein and previous models such as MCM is that the methylation rate is considered as a function of the sulfate reduction rate and not of the concentration of sulfate ion. Due to the small concentration of mercury compared to the major components affecting its speciation, it is not necessary to consider the effect of mercury speciation reactions on the concentration of major species such as oxygen and organic matter.

Table 1: Primary redox reaction network for major components affecting mercury cycling

Reaction	Rate Expression
$OM + O2 \xrightarrow{R1} TIC + \frac{1}{(C:N)}NH_4^+$	$R_{1} = k_{OM} [OM] \frac{[O_{2}]}{[O_{2}] + K_{O_{2}}}$
$OM + 0.8NO_3^- \xrightarrow{R^2} TIC + \frac{1}{(C:N)}NH_4^+ + 0.4N_2$	$R_{2} = k_{OM} [OM] \frac{[NO_{3}^{-}]}{[NO_{3}^{-}] + K_{NO_{3}^{-}}} \frac{K'_{O_{2}}}{[O_{2}] + K'_{O_{2}}}$
$OM + 0.5FeOOH \xrightarrow{R3} TIC + \frac{1}{(C:N)}NH_4^+ + 0.5Fe^{2+}$	$R_{3} = k_{OM} [OM] \frac{K'_{O_{2}}}{[O_{2}] + K'_{O_{2}}} \frac{K'_{NO_{3}}}{[NO_{3}] + K'_{NO_{3}}} \frac{[Fe^{3+}]}{[Fe^{3+}] + K_{Fe^{3+}}}$
$OM + 0.5SO_4^{2-} \xrightarrow{R4} TIC + \frac{1}{(C:N)}NH_4^+ + 0.5H_2S$	$R_{4} = k_{OM} [OM] \frac{K'_{O_{2}}}{[O_{2}] + K'_{O_{2}}} \frac{K'_{NO_{3}}}{[NO_{3}^{-}] + K'_{NO_{3}}}$ $\frac{K'_{Fe^{3+}}}{[Fe^{3+}] + K'_{Fe^{3+}}} \frac{[SO_{4}^{3-}]}{[SO_{4}^{2-}] + K_{SO_{4}^{3-}}}$
$OM \xrightarrow[R_3]{} 0.5TIC + 0.5CH_4 + \frac{1}{(C:N)}NH_4^+$	$R_{5} = k_{OM} [OM] \frac{K'_{O_{2}}}{[O_{2}] + K'_{O_{2}}} \frac{K'_{NO_{5}}}{[NO_{3}^{-}] + K'_{NO_{5}}}$ $\frac{K'_{Fe^{3+}}}{[Fe^{3+}] + K'_{Fe^{3+}}} \frac{K'_{SO_{4}^{2-}}}{[SO_{4}^{2-}] + K'_{SO_{4}^{2-}}}$

Table 2. Mercury speciation/memyration reactions	Table 2:	Mercury	speciation/methylation reactions
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Mercury Speciation Reactions			
$HgS \xleftarrow{k_{Hg,1},k_{Hg,2}} Hg^{2+} + S^{2-}$	Equilibrium		
$Hg^{2+} + OM \xrightarrow{R_{me}} MeHg$	$R_{me} = k_{me} \theta^{T-T_0} R_4 \left[Hg^{2+} \right]$		
$MeHg \xrightarrow{R_{dm}} Hg^{2+}$	$R_{me} = k_{dm} [MeHg]$		
$Hg^{2+} \xrightarrow{R_r} Hg^0$	$R_r = k_{red} \left[Hg^0 \right]$		
$Hg^{0} \xrightarrow{k_{o}} Hg^{2+}$	$R_o = k_o \left[Hg^{2+} \right]$		

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Secondary Redox Reactions		
$CH_4 + 2O_2 \xrightarrow{R_6} TIC$	$R_6 = k_6 [CH_4][O_2]$	
$4Fe^{2+} + O_2 \xrightarrow{R7} 4FeOOH + 8H^+$	$R_7 = k_7 \left[Fe^{2+} \right] \left[O_2 \right]$	
$2Fe^{2+} + H_2S \xrightarrow{R_8} 2FeS + 2H^+$	$R_8 = k_8 \left[F e^{2+} \right] \left[H_2 S \right]$	
$NH_4^+ + 2O_2 + TIC \xrightarrow{R9} NO_3^- + TIC$	$R_9 = k_9 \left[NH_4^+ \right] \left[O_2 \right]$	
$H_2S + 2O_2 \xrightarrow{R10} SO_4^{2-} + 2H^+$	$R_{10} = k_{10} [H_2 S] [O_2]$	
$H_2S + 2FeOOH + 4H^+ \xrightarrow{R11}$	$R_{11} = k_{11} [FeOOH] [H_2 S]$	
$S_0 + 2Fe^{2+}$		
$2O_2 + 2FeS \xrightarrow{R_{12}} Fe^{2+} + SO_4^{2-}$	$R_{12} = k_{12} [FeS][O_2]$	
$FeS + S_0 \xrightarrow{R13} FeS_2$	$R_{13} = k_{13} [FeS][S_0]$	
$7O_2 + 2FeS_2 \xrightarrow{R14} 4SO_4^{2-} + 2Fe^{2+}$	$R_{14} = k_{14} [FeS_2][O_2]$	
$4S_0 \xrightarrow{R15} 3H_2S + SO_4^{2-} + 2H^+$	$R_{15} = k_{15} [S_0]$	

Table 3: Primary redox reaction network for major components affecting mercury cycling

3. Numerical Implementation

Equations (1) and (2) are solved using the finite differences method. Centered differences were employed for the dispersion terms, weighted equally at the old and new time step. The advection terms were treated using upwinding. The time derivative was discretized at t and t+1 time steps using the Crank-Nicholson scheme. The equations controlling the fate of species in the benthic sediments (8) and (9) form a set of one-dimensional equations each linked to one grid cell of the overlying water body. Due to the possibility of sharp fronts of concentrations in the sediments, especially in the sorbed phase, a higher-order method, QUICKEST, was utilized to solve these equations with Crank-Nicholson time-weighting. The coupling between the sediments and the water body was conducted using a non-sequential explicit method.

4. Demonstration Simulation (Colusa Basin Drain)

For demonstration purposes the model described above was applied to simulate the mercury cycling in the Colusa Basin Drain in Northern California. The Colusa Basin Drain transfers surface runoff and irrigation return flow from agricultural lands in the northern central valley to the Sacramento River (Figure 1). The sorption properties of the mercury were obtained from [3]. Sediment characteristics and concentrations in the Colusa Basin Drain were measured by [81] [82] Mirbagheri et al. (1988a, 1988b). In this study, a 30 km reach of the

drain is considered (Figure 1). The water body is considered one-dimensional and therefore one-dimensional versions of Eqs. (1) and (2) are considered. Also to simulate the water flow in the system, which dictate the velocities appearing in Eqs. (1) and (2), a kinematic wave model is utilized [106] (Singh, 1997). In addition, all the hyporheic flows are neglected, and therefore Eqs. (8) and (9) actually behave as a series of one-dimensional PDEs.



Figure 1: Location map of model domain and sampling stations in the Colusa Basin Drain.

4.1. Flow and sediment transport

Flow and sediment transport were modeled using the governing equations described in the previous section for a three-year simulation period (1996-98). The rating curve parameters for the river segments between stations with specified rating curves were obtained by interpolation. The upstream boundary condition for the kinematic wave model was obtained from the observed flow hydrograph provided by the U.S. Geological Survey (USGS 2000).

Figure 2 shows predicted versus measured total suspended solids at the CBD-1 station close to the downstream end of the modeling domain. Considering the uncertainties in the inflow concentrations of suspended

sediment and the variations in the sediment lateral inflow with time due to agricultural return flows, the agreement can be considered acceptable. Further, the agreement is of the same nature than comparisons reported elsewhere (see [28]). The model simulation reflects high-frequency variations that are not captured by the lower-frequency sampling, indicating that data collection techniques might benefit by either cumulative (averaged) sampling and/or higher-frequency sampling. Figure 3 shows the net deposition rate (deposition-erosion) over the reach for the period of modeling. The reason for larger deposition rates compared to resuspension is the amount of sediments carried by the lateral inflow.



Figure 2: Measured and modeled suspended sediment concentration at CBD-1 Station.

Deposition mainly takes place at kilometers 20 to 30 in the river due to smaller velocities in that region, and to larger erosion rates in the upstream reach that provide source material for the deposition zone. Higher erosion rates during high flow conditions, followed immediately by a higher rate of deposition in lower flow velocity regions (kilometers 20-30) after each high flow event can be noticed. Figure 3 shows the accumulation of sediments due to deposition and erosion processes during the modeling period. The largest deposition rate occurs in river kilometers 20-30 due to the lower flow velocity in that region.

4.2. Multi-component reactive transport

The forward and reverse solid-water mass exchange coefficients are assumed to be large enough to mimic equilibrium sorption conditions. It should be noted that all the organic matter in this demonstration study was assumed to be easily mineralizable and therefore only one organic carbon pool was considered for the

sake of simplicity. Other recent studies have considered up to three pools of organic matter with different mineralizability degrees [10] [113]. The effect of temperature on the methylation reaction rate was ignored in this simulation.



Figure 3: Net deposition (deposition-erosion) rate $(g/m^2 day)$ versus time along the reach during the simulation period. Positive values indicate deposition whereas negative values represent erosion.

Figure 4 shows the measured vs. modeled total and methylmercury in the water column, close to the downstream end of the domain. It can be seen that the model nicely predicts the total mercury concentration considering its ability to capture the concentration of suspended sediments. There is a large correlation between the total mercury and suspended solids. The majority of the total mercury is carried by the sediments. This fraction increases during the high flow conditions due to the resuspension of sediments containing mercury. Although the model does predict the magnitude of the methylmercury concentration relatively well, it sometimes misses the trends, as is common with the current state-of-the-art (see [28]). This can be attributed to ignoring the temperature effects and also the margin of error in measuring the concentration of methylmercury production considering the fact that its production requires certain chemical conditions including an anoxic region in the sediments. These

regions, involving dead zones and the areas where vegetation can slow down the flow, have scales smaller than the grid size and therefore cannot be captured in the model. On the other hand it should be noted that the spatial resolution determines the resolution of the gradients in sediment and its fluxes. Sampling schemes are typically designed on much smaller (e.g., bucket) scales than the scale of the numerical grid.

	ruote in Doundary conditions and outer para		ilouening study
Parameter		Value	Reference
	<i>OM</i> -particle associated (mMols/g)	0.603	(a)
	OM-dissolved(mM)	0.853	(a)
ary ons	$O_2(\mathrm{mM})$	0.390	(a)
unda	NO ₃ (mM)	0.103	(a)
Bol Cor	NH4 ⁺ (mM)	0.011	(a), calc'd
	Fe ³⁺ (mMols/g)	0.003	(a)
	SO4 ²⁻ (mM)	2.1	(a)
K _D (OM) (L/kg)		707	(a), calc'd
K _D (NH ₄	+)(L/kg)	691	(b)
k_{OM} (Yr ⁻¹)		25	(b)
$k_{NH4+} (\mathrm{mM}^{-1}\mathrm{Yr}^{-1})$		20	(b)
K _{O2} (mN	()	0.02	(c)
K _{NO2} (m)	M)	0.002	(c)
K _{SO4} (ml	M)	0.02	(c)
K _{Fe} (mM	[)	0.002	(c)
Bio/mec	chanical-dispersion coeff. (cm ² /Yr)	$14500e^{-0.25z}$	(b) modified
D_{O2} (cm	² /Yr)	369	(c)
D _{NH4} (cr	n ² /Yr)	309	(c)
D _{NO3} (cm	n ² /Yr)	309	(c)
$D_{OM}(cm^2/Yr)$		298	(c)
Organic Matter (C:N) ratio		0.13	(b)
O ₂ atmo	spheric exchange coeff. (Yr ⁻¹)	8000	(d)
O ₂ satur	ation concentration (mM)	0.9	calc'd from (d)
K _D (Hg ²⁺	⁺)(L/kg)	125800	(e)
K _D (MeH	Ig)(L/kg)	125800	(e)
k _{me}		186	(f)
k _{dm}		0.365	(f)

Table 4: Boundary conditions and other parameters used in the modeling study

(a) USGS, 2000; (b) Canavan et al., 2007; (c) Berg et al., 2003; (d) Chapra, 1996; (e) Allison and Allison, 2005; (f) Calibration.

TSS Concentration Lateral Inflows (mg/L)	1370 mg/L ^(assumed)
Erosion parameter $\tau_c / \rho C_f$ (m ² /s ²)	0.25 ^(calibrated)
Deposition parameter $\tau_{bc} / \rho C_f (m^2/s^2)$	0.30 ^(calibrated)
Deposition rate coefficient $\alpha_{_8}$	1.0 ^(a)
Uniform lateral inflow rate (m ³ /day.m)	$3 \times 10^{-6} Q_{upst}$ (estimated from flow data)
Erosion rate coefficient E (gr/m ² .day)	43.2 ^(calibrated)
Spatial horizontal grid size (m)	1072
Number of horizontal grids (river reach)	30
Vertical grid size in sediments(m)	0.03
Number of vertical grid points	12
Minimum dry density of bed material (kg/L)	0.8 ^(b)
Maximum porosity θ_0	0.631 ^(b)
Minimum porosity θ_{∞}	0.3 ^(b)
Porosity decrease rate k_{θ} (1/m)	10 ^(b)

Table 5: Parameters used to model cohesive sediment Transport in the reach.

(a) Partheniades, 2007; (b) within the reasonable range from the literature



Figure 4: Measured total and methylated mercury at CBD-1 Station.

5. Future Directions

5.1. Mercury bioavailability and methylation

The development of a more comprehensive understanding of the biotic and abiotic processes that control Hg transformations are noted by a majority of authors as a key point for further research. It is thus important to study these processes and to quantify the roles of the environmental factors that govern Hg transformation. Research has shown that Hg methylation and de-methylation occur in both the water column and sediments and can occur from a variety of biotic and abiotic pathways [84] [7].

It is clear that Hg reduction, oxidation, methylation, and de-methylation are governed by complex processes still to be determined and quantified. A detailed study of the effect of environmental factors such as temperature, bioavailable organic matter, total Hg (and Hg++) concentrations, and microbial activity on Hg transformation rates will contribute to model development and to MeHg remediation strategies continued worldwide.

The primary missing links in current mathematical model formulations of reaction networks include a) de-methylation in the water column and benthic zones; b) complete mercury speciation; and c) transience in amount and type of available organic matter and its interaction with the cycle. Other phenomena of importance may include phytoplankton cycling, which can increase organic matter concentrations within the water column and thus increase methylation rates. Phytoplankton may also provide a residence for sulfate reducing bacteria or other cells of interest, and deposition of phytoplankton from the water column to the benthos provides another source of organic matter at the interface. Although data about mercury methylation by phytoplankton are scarce [24], hypothesized relationships can be explored within reaction network models by adjusting solution concentrations or by developing and testing kinetic reactions.

5.2. Sediment particle size heterogeneity, compaction, erodibility and mercury transport

The size of particles significantly controls the mass exchange of contaminants between sediments and the bulk water. Smaller particles have a larger surface area per unit mass and therefore can absorb larger amounts of metals on their surfaces. The rate of mass transfer between the particles and the water body is also a function of particle size due to the fact that intra-particle diffusion controls the mass exchange [78]. On the other hand, the deposition/resuspension and the transport of particles are largely influenced by their size. These make it important for future models to consider multiple size mixtures of sediments, instead of assuming uniformly-sized particles. This is especially important in cases where high floods capable of resuspending a large range of particle sizes play a major role in the transport of sediments and, therefore, in the transport of

the mercury bound to them. Sediment resuspension predictors capable of handling multi-disperse sediment particles have been developed in the past (e.g., [41]) but not many efforts have been made to develop coupled sediment-contaminant models based on multi-disperse sediment mixtures. One reason can be the large computation expense involved in solving the mass exchange with a range of particle sizes and the lack of experimental data on the effect of sediment particle sizes on the sediment-water mass-exchange rates.

Although much progress has been made in modeling sediment dynamics in water bodies in terms of quantifying sediment fluxes, not much research has been conducted on the processes controlling the interactions among different size categories of suspended and bed sediments. This can especially be important in the fate of solid-bound contaminants that often exhibit variation in concentration with particle size. The mixing and sorting of the different fractions of top sediments is a controlling factor in the burial rates of mercury and also in how the resuspension of sediments releases mercury back to the overlying water. Also consolidation or cementation as a result of biomass growth can influence the stability or erodibility of sediments, this is an important factor in the fate of buried mercury contaminants in water bodies. These processes have not been studied in the context of classical sediment transport models, although they play a large role in the fate, transport, and attenuation of solid-bound contaminants.

The knowledge gained in the recent years regarding transport of cohesive sediment is comparatively less massive than that of non-cohesive particles. Cohesiveness is the result of small-scale mechanisms which promote interactions of generally chemical nature among particles. Formulas for resuspension of cohesive/non-cohesive sediments in large water bodies are lacking. In fact, most formulas have been developed from laboratory experiments, and there are reasonable questions as to whether these formulas are applicable to larger scales. Recent work [23] has shown that laboratory formulas for sediment resuspension can be adapted to predict resuspension in shallow lakes.

An almost completely unexplored field is the case of non-dilute mixtures (say, larger than 2-5% in volume concentration). Under these conditions, the transport of mercury could vary significantly due to the changes in the diffusivity of sediment occurring under non-dilute conditions. Very recent work by [58] suggests that while the Schmidt number is smaller than one for dilute mixtures, it is larger than one for non-dilute cases. (We recall herein that the Schmidt number is defined as the ratio between the eddy viscosity of the carrier phase and the diffusivity of the disperse phase.) More research is needed, of experimental and numerical nature, to clarify these issues.

Another unaddressed issue is the nature of rainfall events. Initial rainfalls tend to mobilize more source sediment from watersheds than later serial rainfalls, with an extreme case being the rain-on-snow event in which only the river-bed and river bank erosion contributes to sediment transport [19]. In the

case of serial flood events in a relatively short time period, the sediment transport can be by an order of magnitude lower than during the previous flood event. Therefore, the "history" of flood events needs to be recorded and considered, which is seldom done in sediment transport modeling. A possible way of increasing the reliability of the relation between flow and sediment transport is to use artificial intelligence tools, such as the "model-tree" technique [91] [119]. These techniques and models have successfully been applied in ecological modeling (e.g., [68] [31] [4]).

5.3. Mercury fate and transport in wetlands

5.3.1. Plant uptake and release of mercury

Lacking motility, plants control their surroundings by chemical means. Besides providing the structure for wetlands, trapping and holding particles, plants deliver oxygen and exude organic matter to the sub-surface. In addition, as they carry nutrient metals upward, they bring along mercury, to an unknown degree, in the methylated form. (Alternately, mercury may be methylated inside the plant.) The example in the literature shows a dramatic seasonal rise of percent methyl vs. total Hg in late spring [124]. In either case, these forms are bound to soluble organic matter or on colloidal particles and enter the plant with water being taken up for the normal process of transpiration. In one salt marsh example, the seasonal cycle of total Hg in the plant shoot (especially at the tips) has been studied [57]. The annual flux of mercury released as detritus was estimated to be comparable to atmospheric deposition, and may be in a more bioavailable form.

5.3.2. Wetting/drying cycles and mercury transformation/mobilization

Since mercury transformation is driven by oxidation/reduction conditions, the wetting/drying cycle due to weather (or irrigation), as well as tides in coastal areas, must be included in any modeling effort. Furthermore, wet/dry cycling produces net local transport, not merely mixing. As oxygen and subsequent electron acceptors are depleted in the sub-surface, the drying cycle delivers the former. Reduced species produced in lower layers are transported to the surface during the wetting half of the cycle.

Assuming fairly small particle concentrations, fluxes of mercury in an undisturbed sediment may be relatively low. However, upon seasonal wet/dry cycles, or irrigation-related flow changes, strong chemical gradients will move through the sediment strata as the aeration/inundation condition reverses. These intermittent episodes may be a stronger driver of microbial metabolism (and therefore mercury methylation) than the longer periods of diffusion-limited, steady-state flux. Additionally, where drying may change the cohesion of sediments, and high flows transport the majority of the time-averaged particle flux, the average condition may be less important than the departures from it, given the low solubility of both organic and inorganic mercury.

5.4. *Numerical approaches*

Numerical sediment transport models usually use the Eulerian principle, with regular or irregular grids, although it is well known that biogeochemical transformation processes are easier to describe using particle-based Langrangean models. In the particle-based methods, each particle can carry a lot of information on various parameters (e.g., concentration of different Hg species, environmental variables, etc.). However, Lagrangean methods such as particletracking and SPH (smoothed particle hydrodynamics) can only be used to describe point- or small-scale pollution domains, such as oil spills [95] [118]. The SPH method (e.g., [83]) is particularly promising; it has so far been successfully applied to simulations of two- or even multi-phase flows on local scale [25], mud-flows [18], and flushing of sediment from retention basins or through bottom outlets of the dams [42]. By coupling the environmental and pollutant information to sediment particles and using the ever increasing processor-power, Lagrangean models will more effectively compete with Eulerian approaches in the simulation of particle-bound pollutants in aquatic environments.

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List of Symbols			
Symbol	Definition	Dimensions or Units	
B_d	bulk density of the sediment materials	$[M/L^3]$	
C _i	dissolved concentration of chemical species <i>i</i> in the benthic sediments	[M/L ³]	
C_i	dissolved concentration of chemical species <i>i</i> in the water column	[M/L ³]	
$C_{i,at}$	equilibrium concentration of species <i>i</i> in the atmosphere	[M/L ³]	
D_{hx}	dispersion coefficient in x direction	$[L^2/T]$	
D_{hy}	dispersion coefficient in y direction	$[L^2/T]$	
D_m	molecular diffusion coefficient	$[L^2/T]$	

ADDEHUIA = LISUUI SVIIIDUIS	Ap	pendix -	– List	of Sv	mbols
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Er_j	sediment resuspension rate for solid phase class j	$[ML^{-2}T^{-1}]$
f_j	fraction of sediments consisting of phase j	
Н	depth of water	[L]
J_0	rate of change of the elevation of the sediment- water interface with time	[L/T]
k _{at,i}	atmospheric mass exchange coefficient for chemical species <i>i</i>	[L/T]
k _b	diffusive mass exchange coefficient with bed sediments	[L/T]
<i>K</i> _{Dij}	water-solid distribution coefficient for solid phase <i>j</i> and species <i>i</i>	[L ³ /M]
k _{jj} ,	rate of transformation of solid phase j to phase j'	[1/T]
$k_{ heta}$	rate of porosity decrease with depth	[1/L]
М	erosion rate coefficient	$[MT^{-1}/F]$
Р	a factor to incorporate the effect of shear stress on settling rate	
Q	lateral inflow per unit area	[L/T]
R_i	reaction rate for dissolved species <i>i</i>	$[M/L^3T]$
R_{sij}	reaction rate for species i sorbed to solid phase j	$[M/L^3T]$
S _{ij}	concentration of chemical species i sorbed to solid phase category j in the benthic sediments	[M/M]
S_{ij}	concentration of chemical species i sorbed to solid phase category j in the water column	[M/M]
S _{ij,in}	concentration of species <i>i</i> sorbed to solid phase class <i>j</i> in the lateral influx	[M _c /M]
u_f	vertical pore water velocity at the water-sediment interface	[L/T]
<i>u</i> _s	advective velocity of sediments due to sediment consolidation	[L/T]
U	depth averaged velocity in x direction	[L/T]
Vs	particle fall velocity	[L/T]
V	depth averaged velocity in y direction	[L/T]
W_{pj}	deposition rate parameter for solid phase class j	[L/T]
<i>z</i> *	vertical coordinate based on a fixed datum which increases upward	[L]
Z_0	elevation of the sediment-water interface	[L]

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α_8	coefficient for calculating the fall velocity	
\Box_j	concentration of suspended solid phase category j	$[M/L^3]$
θ	porosity of the bed material	
$ heta_0$	porosity at the water-sediment interface	
ψ_{ij}	source term representing for example the effect of plant uptake and decomposition	$[LT^{-1}M_{c}L^{-3}]$
ρ_s	density of sediment particles	$[M/L^3]$
$ au_b$	bed shear stress	$[F/L^2]$
$ au_{cd}$	critical shear stress for sedimentation	$[F/L^2]$

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