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## **HOUSATONIC RIVER**

### **MODEL VALIDATION**

#### **FINAL COMMENTS**

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#### **Introduction**

In the long term, the main source of contaminants in the Housatonic River is the bottom sediments (both those in the river and in the floodplain). In this long term, environmental conditions will change with time and will be different than they are at present, especially because of and after remediation. For purposes of predicting water quality, it is therefore essential to accurately determine not only the flux of contaminants between the bottom sediments and the overlying water but also the parameters on which this flux depends. Otherwise, long-term predictions of water quality will not be accurate or believable. Because of this, my comments will emphasize processes which govern the sediment-water flux of contaminants, i.e., sediment erosion, sediment deposition, the sediment-water flux due to “diffusion”, and equilibrium partitioning.

In my last review (Model Calibration, May 13, 2005), I commented extensively on the proposed calibration of both sediment erosion and deposition by means of the measured suspended solids concentration,  $C$ . A simple example was given whereby it was easy to see that a numerical model can “predict” the observed values for  $C$  with an almost arbitrary value of erosion rate as long as the deposition rate was changed accordingly, i.e., such that the two were equal and gave the observed  $C$ . I stated “For a predictive model, the values of erosion rate and deposition rate can not both be determined from calibration of the model by use of the suspended solids concentration alone.” I later stated that “models with many unconstrained parameters and especially models which include processes that are not described correctly as far as their functional behavior is concerned can lead to non-unique solutions; these can lead to the incorrect predictions of long-term behavior.”

EPA responded by more-or-less agreeing with the above statements but then stating “This concern does not recognize that there is a constraint imposed by PCB transport that results from resuspension and deposition processes.” Although this argument has some validity, it is not sufficient or correct as I will argue below. This problem of non-unique

solutions is important, is more general than that indicated above, and is related to the necessity for accurately determining the basic processes that govern the sediment-water flux of PCBs and other hydrophobic organic chemicals (HOCs). Because of this, I will return to this problem of non-unique solutions after discussing the flux processes mentioned above. Accurate descriptions of the basic processes also depend on an adequate resolution of the bathymetry/topography of the Housatonic. Because of this, comments and suggestions on the problem of numerical gridding in the model will be made. Some discussion on unexplained results of the present model will then be given. A summary and specific suggestions for improvements to the model will conclude my comments.

### Sediment Erosion

In the previous review on Model Calibration (May 13, 2005), I commented extensively on sediment erosion. Although those comments are still valid, I won't repeat all of them here. However, I would like to repeat the following from those comments.

“In a paper by Lick et al. (2005), approximate equations for sediment erosion rates are examined. It is shown that, for fine-grained, cohesive sediments, a valid formula is

$$E = 10^{-4} \left( \frac{\tau}{\tau_c} \right)^n \quad (3)$$

where E is the erosion rate,  $\tau$  is the shear stress, and  $\tau_c$  is a critical shear stress defined as the shear stress at which an erosion rate of  $10^{-4}$  cm/s occurs;  $\tau_c$  depends on the particular sediment being tested and generally is a measured quantity. This equation is valid for fine-grained, cohesive sediments but **not** for coarse-grained, non-cohesive sediments.

“For coarse-grained, non-cohesive sediments, the appropriate formula is

$$E = A(\tau - \tau_c)^n \quad (4)$$

where A,  $\tau_c$ , and n are functions of particle diameter but not a function of density. This equation is shown to be valid for coarse-grained, non-cohesive sediments but **not** for fine-grained, cohesive sediments.

“To approximate erosion rates for all size sediments with a single, uniformly valid equation, the appropriate equation is

$$E = 10^{-4} \left( \frac{\tau - \tau_{cn}}{\tau_c - \tau_{cn}} \right)^n \quad (5)$$

where  $\tau_{cn}(d)$  is the critical shear stress for non-cohesive particles and is given by

$$\tau_{cn} = 0.414 \times 10^3 d \quad (6)$$

where  $d$  is the particle diameter. Eq. (5) is uniformly valid for both cohesive and non-cohesive sediments. It reduces to Eq. (3) as  $d \rightarrow 0$  and to Eq. (4) for large  $d$ .

“In all the work we’ve done with Sedflume on the determination of erosion rates as a function of shear stress (the number of cores is on the order of 100),  $n$  in Eq. (5) is typically about 2 or more (see Lick et al., 2005 and Chapter 3 of Notes). Because of this, I suspect that the parameters  $n = 1.59$  and  $n = 0.95$  used in the Housatonic modeling (p. 4 of Attachment B.5) are incorrect.”

One reason for the low values of  $n$  determined for the Housatonic is that the above equations are only applicable to sediments which have the same bulk properties. In order to use these equations properly, sediments with similar bulk properties must be grouped together. Properties of sediments in a single sediment core generally vary with depth due to consolidation but also because of layering due to deposition after big events. Because of consolidation with depth, sequential Sedflume measurements on one core will bias the value of  $n$  since cores at depth will be more consolidated, more difficult to erode, and will be measured later in the measurement cycle. I suggested an interpolation procedure that we had used before and which gave us reasonable results. EPA did not seem to have good results with this procedure. Attached is a description of a modified procedure which I have applied to several randomly selected cores on each of the Kalamazoo, Housatonic, and Passaic Rivers. This procedure is more fundamental and correct. In all cases, it produces an  $n$  that is equal to two or greater in Eq. (5) above, just as has been demonstrated by all Sedflume laboratory measurements that we have made. With this procedure, the coefficient modifying  $(\tau - \tau_{cn})^n$  and  $n$  are functions of depth for each representative area core and are obtained from the Sedflume data. The fact that  $n$  is two or greater is important in determining erosion rates at high shear stresses, i.e., during big events, and can lead to shear stresses higher by an order of magnitude than the  $n$ 's chosen by EPA for the Housatonic.

In that previous report, I also stated the following. “Bed armoring is an important process and causes large changes in bed shear stresses and hence large changes in erosion/deposition. This occurs, for example, when a layer of coarse sediments (as little as a few particle diameters thick) is deposited on a layer of finer, non-cohesive sediments. As the EPA model is presently configured, any deposited sediments are immediately mixed with the 6-inch surficial layer. Because of this, effective coarsening takes place very slowly (a small amount of added sediment has little effect on the average properties of the 6-inch layer). In reality, this mixing only occurs in a layer a few particle diameters thick, and this thin layer must be present in the model for realistic coarsening to occur (see SEDZLJ).”

EPA stated that the surficial layer was assumed to be 7 cm thick, not 6 inches as I stated. Since bed coarsening occurs in a layer only a few particle diameters thick, the assumption of a 7 cm mixed layer is also incorrect. **The above comments are still valid.**

## **Sediment Deposition**

I suggested the use of a dynamic flocculation theory that was recently developed and was relatively simple. EPA seems to have had problems implementing the theory. I presume from what they said that this was due to numerical stability problems. That's too bad because it would have given reviewers more confidence in the modeling of deposition rates.

## **The Sediment-Water Flux of HOCs Due to “Diffusion”**

The non-erosion/deposition flux of contaminants from the sediments to the overlying water is primarily due to molecular diffusion, bioturbation, and ground-water flow. Each of these processes behaves in a different way and hence needs to be modeled in a different way. EPA has chosen to describe all of these processes by means of a “diffusion” model based on the concept of bioturbation and the assumption of a well-mixed layer. This is the conventional, but not necessarily accurate, approach. It is not accurate simply because the mass transfer approximation (which is not a diffusion approximation) actually used by EPA does not describe or adequately approximate the HOC fluxes of molecular diffusion, bioturbation, or ground-water flow, not even in functional form. The correct functional form (especially its dependence on time) is important because, otherwise, even calibration doesn't work for long term predictions.

EPA did an extensive review of the literature on bioturbation and listed 139 documents of which 43 were retained for detailed review. This listing is somewhat misleading. Of the 43 most relevant documents, almost all are general observations, surveys of the literature, or even surveys of surveys; only about six report quantitative data or laboratory measurements of mixing due to benthic organisms. For example, the figure shown at the last meeting entitled “Bioturbation and Bioavailable Sediment Depths” is from Clarke et al. (2001) and is their interpretation of what organisms do. There is no data (given by Clarke et al. or anywhere else) to support this figure. Clarke et al. is an excellent manuscript, but it is another survey. There is no new data there. None of the documents listed by EPA report on the sediment-water flux or sediment mixing of hydrophobic organic chemicals (HOCs) due to benthic organisms. Since then, EPA has listed additional reports concerned with the flux of HOCs due to benthic organisms. However, these HOCs had relatively low partition coefficients. The only quantitative data that I know of on the effects of benthic organisms on the flux of HOCs with large partition coefficients and their resulting vertical distribution in the sediments is that by Luo et al. (2006) which is attached. Some of my comments are based on this article.

In EPA's modeling, assumptions are (1) a constant (independent of space and time) sediment-water mass transfer coefficient,  $k$ , with a value of 1.5 cm/day and (2) a surficial, well-mixed layer whose thickness is constant in time but varies spatially from 4 cm upstream to 7 cm downstream. Measured biomass varies by about a factor of 20 from upstream to downstream.

Benthic mixing is described by EPA in terms of a mixing rate (a diffusion process), also termed a subduction velocity (a convection process), a quantity which I believe is used in the model as a mass transfer coefficient between the sub-surface sediment layers. For the biologically mixed layer, the subduction velocity (values from EPA's table) varies from about  $1 \times 10^{-9}$  m/s ( $1 \times 10^{-2}$  cm/day) upstream to  $2 \times 10^{-9}$  m/s ( $2 \times 10^{-2}$  cm/day) downstream. This factor of two between upstream and downstream seems surprising since the biomass increases by a factor of 20 in the downstream direction. Even more surprising is that the mass transfer coefficient,  $k$ , is assumed constant everywhere at 1.5 cm/day. Why doesn't  $k$  increase downstream as the biomass increases by a factor of 20?

A surficial well-mixed layer whose thickness is constant in time is assumed in the analysis. An approximate and minimum time for formation of this layer can be calculated from  $t = h/v_b$ , where  $h$  is the thickness of the layer and  $v_b$  is the subduction velocity. For the upstream area,  $h = 4$  cm,  $v_b = 1 \times 10^{-9}$  m/s =  $1 \times 10^{-2}$  cm/day, and therefore  $t = 400$  days. For the downstream area,  $h = 7$  cm,  $v_b = 2 \times 10^{-9}$  m/s =  $2 \times 10^{-2}$  cm/day and therefore  $t = 350$  days. In other words, these so-called well-mixed layers are not formed instantaneously and take a minimum of 350 to 400 days to form.

This becomes a little confusing upon examination of the figure presented at the meeting entitled "Contribution to  $Db$  from different groups of benthos". Upstream,  $Db$  (for all benthos) is approximately  $2 \times 10^{-3}$  cm/day while downstream, oligochaetes (the main vertical burrowers and subductionists) contribute a  $Db$  of approximately  $2.5 \times 10^{-2}$  cm/day. The upstream number is an order of magnitude less than the number in the table cited above as  $v_b$ , is probably correct, but gives a time for formation of the well-mixed layer of almost 2000 days (6 years).

Despite the confusion, the numbers for  $Db$  are probably correct (to within less than an order of magnitude). This demonstrates (as does Luo et al. more accurately and convincingly) that so-called well-mixed layers for HOCs, if they exist, take a long time (years) to form. Is there any evidence that a well-mixed layer even exists in the Housatonic? I don't believe so.

The mass transfer coefficient,  $k$ , for the transport of HOCs by molecular diffusion alone is approximately 1.2 cm/day and decreases slowly with time at a rate which decreases as  $K_p$  increases (Deane et al. 1999, Lick et al. 2006, attached). If there is only a small number of organisms, EPA's value of  $k = 1.5$  cm/day compares well with this number. However, with benthic organisms present, Luo et al. give a mass transfer coefficient for HOCs that varies up to 10 cm/day (for benthic organism densities of  $10^4/m^2$ ) and somewhat higher for very dense concentrations of organisms; these values for  $k$  are much higher than those that EPA assumes.

No consideration is given to ground-water flow, which can be significant, is a convection and not a diffusion process, and does not involve a well-mixed layer of any sort.

## Equilibrium Partitioning

After sediment particles are resuspended, they will be transported downstream by the current and eventually settle out of the water column. During this time, the contaminant sorbed to the particle will desorb at some finite rate. The time for a particle to settle out of the water column depends on the settling speed and water depth, while the distance traveled by the particle before depositing depends on the settling time and current speed. For a reasonable range of settling speeds,  $w$ , for fine-grained particles/flocs ( $2 \times 10^{-3}$  to  $1 \times 10^{-1}$  cm/s) and water depths,  $h$ , typical of the Housatonic (1 to 3 m), the settling times ( $t = h/w$ ) are in the range (see table) from  $10^3$  s (15 min) to  $1.5 \times 10^5$  s (1.5 days). For medium and coarse grained particles, the settling times are less.

Settling Times (Seconds) for Fine-Grained Particles in the Housatonic

h(cm)	w(cm/s)	
	$2 \times 10^{-3}$	$1 \times 10^{-1}$
$1 \times 10^2$	$0.5 \times 10^5$ (0.5 days)	$1 \times 10^3$ (15 min)
$3 \times 10^2$	$1.5 \times 10^5$ (1.5 days)	$3 \times 10^3$ (45 min)

Some experimental results for the adsorption and desorption of HOCs are shown in the appended figures. These sorption times depend on the sediment concentration, particle and floc sizes, conditions of the experiment, and the value of the partition coefficient. The first three figures are for hexachlorobenzene ( $K_p = 10^4$  L/kg), while the fourth figure is for the adsorption of HOCs with  $K_p$ 's from  $10^3$  to  $6.6 \times 10^4$  L/kg. The last figure is for the desorption of a PCB with one chlorine (MCB,  $K_p = 10^3$  L/kg), hexachlorobenzene (HCB,  $K_p = 10^4$  L/kg), and a PCB with six chlorines (HPCB,  $K_p = 6.6 \times 10^4$  L/kg, a  $K_p$  which is smaller than, but comparable to, the average  $K_p$  of about  $10^5$  L/kg for PCBs in the Housatonic). In 10 days, only about 25% of the HPCB has desorbed; in 50 days, only about 55% has desorbed. As the partition coefficient increases, the amount of desorption in these time intervals will be even less. For PCBs with  $K_p = 10^5$  L/kg, the desorption times would be approximately 1.5 times greater than those for HPCB shown here.

Since desorption times are much greater than settling times, it follows that contaminants on resuspended particles will not desorb completely, or even close to completely, in the water column before the particles settle out of the water column. The chemical sorbed to the suspended particles will therefore not reach chemical equilibrium with the chemical dissolved in the water column. It follows that the assumption of equilibrium partitioning is not valid, nor even a good approximation, for the sediments in suspension or in the surficial layers of the bottom sediments.

Incidentally, finite rates of adsorption/desorption (1) will assist in explaining the high observed values of PCBs in the surficial sediments of Woods Pond, (2) the high variability in observed PCB concentrations in the sediments, and (3) probably will force a higher  $n$  in erosion formulas (consistent with all other data) since non-equilibrium sorption will not be consistent with EPA's imposed constraint due to equilibrium partitioning.

The conclusion is that finite rates of PCB adsorption and desorption have a major effect on the sediment-water flux due to resuspension/deposition and must therefore be considered in the modeling.

### **Calibration and Non-Unique Solutions**

As discussed above, the processes which govern the sediment-water flux of HOCs (sediment erosion, sediment deposition, the sediment-water flux due to "diffusion", and equilibrium partitioning) are described incorrectly and inaccurately. Each of these processes can modify the flux by factors of two to ten. Nevertheless, EPA documents indicate that there is good agreement between the calculated and measured suspended solids concentrations as well as contaminant concentrations. At the same time, sensitivity and uncertainty analyses also seem to say that the model is doing a good job. **How can this be? Are accurate models of sediment and contaminant transport and fate really unnecessary?**

The answers to these questions are in the non-uniqueness of calibrated solutions and the nature of sensitivity and uncertainty analyses. More specifically, it seems that a modeler can assume a wide range of parameters to describe a particular process and still "calibrate" the model so as to determine a mathematical solution which agrees with observations over some time interval. As discussed above, examples of parameters which significantly affect flux processes are (1) different values of the power  $n$  in erosion formulas (this gives greatly different erosion rates at high shear stresses depending on the value of  $n$ ), (2) different parameterizations for settling speeds, (3) different process models and parameters for the sediment-water flux due to "diffusion", and (4) equilibrium partitioning (equivalent to high reaction rates), frozen reaction rates, or anything in between. Calibration of a model does not guarantee that the processes in the model are described properly. At the risk of being repetitive, a water quality modeler can always get good agreement between calculated and observed quantities for a limited time interval and limited conditions, whether the fundamental processes are described properly or not. Another modeler, with quite different descriptions of processes and/or different parameters in his/her model, can get equally good agreement between the calculated and observed quantities. However, future predictions by the different models and modelers will be quite different. This has been demonstrated repeatedly (e.g., see comments on Fox River modeling (Tracy and Keane 2000) in my comments of May 2005). In other words, **calibration is necessary but not sufficient.**

As applied to the Housatonic, sensitivity and uncertainty analyses are asking the wrong questions. They do not question whether the basic processes are formulated correctly. As an example, equilibrium partitioning is assumed. Sensitivity and uncertainty analyses never question this assumption, never demonstrate that it is an inaccurate assumption, nor do they propose a suitable reaction rate.

Since equilibrium partitioning is not valid, a new parameter (the sorption rate) is introduced into the problem. Among other things, this invalidates EPA's statement (when speaking of non-unique solutions) that "there is a constraint imposed by PCB transport that results from resuspension and deposition processes." This constraint, if it exists, is incorrect because non-equilibrium sorption would impose an entirely different constraint than that imposed by equilibrium partitioning.

### **Numerical Gridding**

With the present grid, the width of the river is generally approximated as one cell. In the Housatonic, as in most rivers, there are large differences in erosion between the deeper and the shallower parts of the river. Predicting the dissimilar amounts of erosion/deposition across a cross-section of the river is crucial in predicting the long-term exposure of PCBs by erosion and/or natural recovery by deposition. Averaging across the cross-section does not describe the erosion/deposition process accurately. A minimum of three cells across the river (two shallow, near-shore cells and one deeper, center cell) should be used.

In the floodplain, our knowledge of the basic processes of erosion/deposition and the non-erosional/depositional flux is poor. Because of this, a very coarse grid can be used to approximate the processes in this area.

A better description of the bathymetry of the river will increase the computational time. Drastically decreasing the number of grid cells in the floodplain will significantly decrease the computational time. The computational time can also be decreased by (a) separating the hydrodynamics, sediment transport, and contaminant transport calculations and (b) for small and moderate flows, approximate and calculate the hydrodynamics and transport as a sequence of steady-state solutions and only treat big events in detail.

### **Unexplained Results of the Present Model**

During previous peer review meetings, John List as well as others including myself (but John was most vocal) have emphasized (a) the large unexplained variance in the PCB concentrations in the surficial (six inch) layer of the sediments and (b) the unexplained high concentrations of PCBs in the surficial layers of the sediments in Woods Pond.

EPA had no explanations for these latter two problems, but also stated that an understanding of these problems was not necessary. An understanding of these problems may not be necessary, depending on your point of view, but the problems themselves are quite interesting, deserve some discussion, and are related to the inaccurate modeling of



the basic sediment and contaminant flux processes mentioned above. Some discussion of these problems is given here.

In my comments above, I emphasized that PCB sorption times are slow relative to particle settling times and that, because of this, equilibrium partitioning (as assumed in the model) was not a good assumption. Consider the effects of this on PCB transport to Woods Pond. The upstream region of the Housatonic is erosional (on the average), and PCB concentrations near the sediment surface are relatively high (because they were deposited at an earlier time before remediation). As these sediments are eroded, PCBs tend to desorb from the suspended sediments but do not reach anywhere near chemical equilibrium before the sediments are deposited, i.e., the PCB concentrations of depositing sediments are much higher than if they had equilibrated in the overlying water. This erosion/deposition may occur several times before the sediments and their sorbed PCBs reach Woods Pond, or it may only occur once, depending on the flow rate and turbulence. Either way, the sediments deposited in Woods Pond will have higher PCB concentrations than if equilibrium partitioning was assumed, as is observed in field measurements but is not predicted by the present model.

As far as the high PCB variance throughout the river is concerned, consider the following. Sediment erosion/deposition depends on the hydrodynamics, e.g., high rates of erosion where the flows are fastest and low rates of erosion (or deposition) where the flows are slow. Because of this, large variations in erosion rates occur across the river (shallow, near-shore areas versus deeper channels in the middle) as well as along the river. This is well illustrated in previous calculations of sediment transport in rivers (Saginaw River (Cardenas et al. 1995), Fox River (Jones et al. 2000)) when a reasonably fine grid was used, i.e., 5 to 11 grid points across the river. Because of the coarse numerical grid, this is not described by the present model. i.e., everything in the model is averaged or smoothed. In some areas (e.g., upstream and/or in the center of the channel where flows are high), mostly erosion occurs and PCB concentrations reflect deposition at an earlier time and are relatively high. These sediments will be transported downstream and will deposit in a non-uniform manner depending on the hydrodynamics. These sediments will retain their high PCB concentrations. In other areas (e.g., sediments from above the upstream boundary, near-shore depositional areas which have received clean sediments from further upstream, or areas where deposition is slow such that surficial sediments can equilibrate with the cleaner overlying water), the PCB concentrations of surficial sediments may be quite low. Slow transport and multiple resuspension/deposition events can also cause low PCB concentrations of surficial sediments.

Because of episodic events, the dependence of erosion/deposition of sediments on highly variable hydrodynamics, the highly variable sources of PCBs (e.g., clean from far upstream, contaminated from deep in the sediments, differences between near-shore, shallow areas and the deeper channel in the center), and of course slow PCB desorption rates (which causes sediments to retain their PCB sorbed concentrations, either high or low), it seems quite plausible that PCB concentrations will be highly variable in space and time in the Housatonic. The present model smooths this all out.

**Does this matter?** If the only purpose of the model is to duplicate known results, then accurate models of sediment and contaminant transport and fate don't matter. However, if the model is to be used for predictive purposes, then accurate process models do matter. In the predictive mode, future conditions (such as sediment properties, contaminant concentrations in the sediments, concentrations and types of benthic organisms, sediment-water fluxes, flow rates, etc.) will be modified (for example by dredging, capping, or extreme environmental conditions), will change with time, and will be different from those for which the model was calibrated. The basic processes in the present and future are the same. However, their relative effects and significances depend on the modified conditions and will change with time. If the models describing the basic processes have incorrect functional behavior and/or inaccurate parameters, then the model will not predict the long-term behavior properly. Because of this, for the long-term prediction of sediment and contaminant fluxes, it is essential that the functional behavior and parameters of the most significant processes in the model be described correctly

### **Summary and Suggestions**

In the present model, erosion rates are too low ( $n$  is too small). During big events, erosion rates may be as large as, or greater than, 10 times that predicted at present. The major effect of this will be on the maximum depth of erosion during big events. A better analysis of Sedflume results as suggested in the attached report will determine a higher and more reasonable value for  $n$ . The coefficients in Eqs. (3), (4), and (5) should vary throughout the river as required by the data.

In the present model, deposition rates are also too low. Deposition rates are essentially a calibrated parameter and are determined such that the suspended solids concentration is calculated properly. If erosion rates are increased, deposition rates must also be increased in order to maintain good agreement between calculated and observed suspended solids concentrations.

Equilibrium partitioning is not a valid assumption. Desorption rates are relatively slow such that, when bottom sediments are resuspended, the sorbed PCBs do not desorb sufficiently rapidly for equilibrium partitioning to be approached before particle deposition occurs. The result is that PCBs sorbed to the suspended solids are not in equilibrium with the PCBs dissolved in the water. The sediment-water flux of PCBs due to resuspension/deposition is therefore much lower than that predicted by equilibrium partitioning, as is assumed in the present model. A finite sorption rate between the PCBs sorbed to the solids and the dissolved PCBs needs to be added to the model and will replace the equilibrium assumption.

The sediment-water flux of PCBs due to "diffusion" as calculated by the present model is too low. The formulation of this flux and its parameters are also incorrect. The mass transfer coefficient,  $k$ , was given a value of 1.5 cm/day, constant throughout the river; this value was chosen on the basis of calibration, not on the basis of any field or laboratory measurements.

Since the PCB flux due to resuspension/deposition should be smaller than that predicted by the present model, the PCB flux due to “diffusion” must increase, strictly on a calibration basis, to compensate for this; it must also increase on the basis of a more fundamental investigation of molecular diffusion and bioturbation (Deane et al. 1999, Lick et al. 2006, Luo et al. 2006). In these articles, it is shown that  $k$  due to “diffusion” of HOCs has a lower limit of 1.2 cm/day (no organisms) and increases to 10 cm/day ( $10^4$  oligochaetes/m<sup>2</sup>) and even greater for larger numbers of organisms, i.e., the sediment-water flux due to “diffusion” may be significantly greater than that predicted by the present model. A realistic value for  $k$  should be determined on the basis of the concentrations and types of benthic organisms. When this is done,  $k$  will be significantly larger on the average than it is now and will be relatively low upstream but will increase in the downstream direction.

The numerical gridding can be improved by increasing the number of grid cells across the river and decreasing the number of grid cells in the floodplain. The calculations of the hydrodynamics, sediment transport, and PCB transport should be separated.

The higher than predicted PCB concentrations in Woods Pond as well as much of the variability seen in the sediment PCB concentrations can be explained by finite PCB sorption rates as well as by the variability in the PCB sources and the hydrodynamics. The improved model should be able to predict some of this and at least suggest the reasons for the remaining variability if finite sorption rates are assumed and a finer grid is adopted.

These suggested modifications to the model are relatively simple (except possibly for the re-gridding) and should be able to be accomplished in a year.

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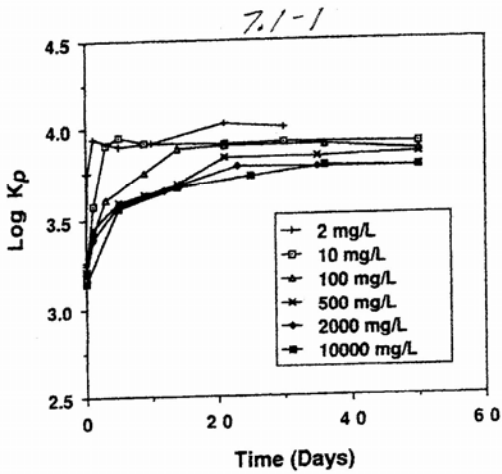
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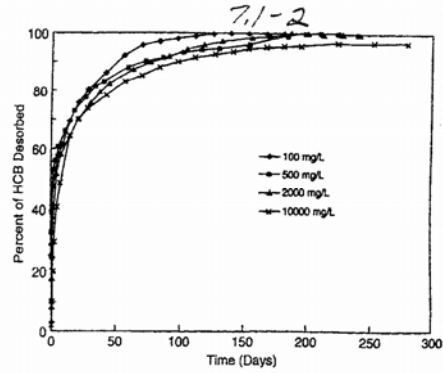
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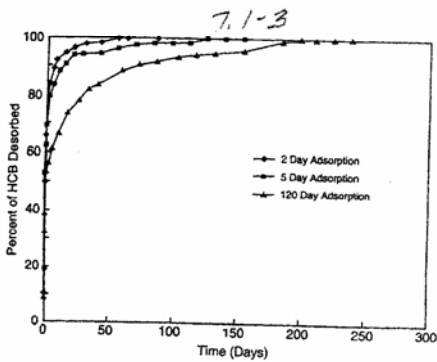
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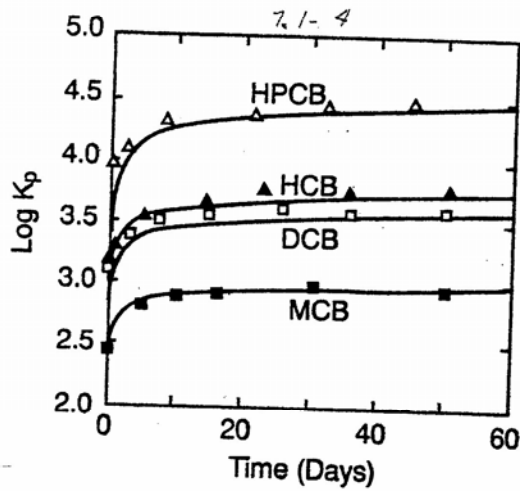
Adsorption experiments with hexachlorobenzene (HCB) and pure water.  $\text{Log } K_p$  as a function of time for sediment concentrations of 2, 10, 100, 500, 2,000, and 10,000 mg/L [8].



Desorption experiments with hexachlorobenzene (HCB) and pure water. Percent of the initially sorbed HCB which has desorbed is shown as a function of time. Sediment concentrations are 100, 500, 2,000, and 10,000 mg/L [10].



Hexachlorobenzene (HCB) short-term adsorption followed by desorption experiments. The sediment concentration is 500 mg/L. The HCB was first adsorbed to sediments for either 2 d or 5 d and then desorbed. Also shown is long-term adsorption (120 d) followed by desorption, i.e., the standard desorption experiment [10].



Partition coefficients for the adsorption of HCB and three PCB congeners (MCB, DCB, and HPCB) to sediments from the Detroit River.  $\text{Log } K_p$  is shown as a function of time. Experimental data is shown as open and closed symbols while the modeling results are shown as solid lines.

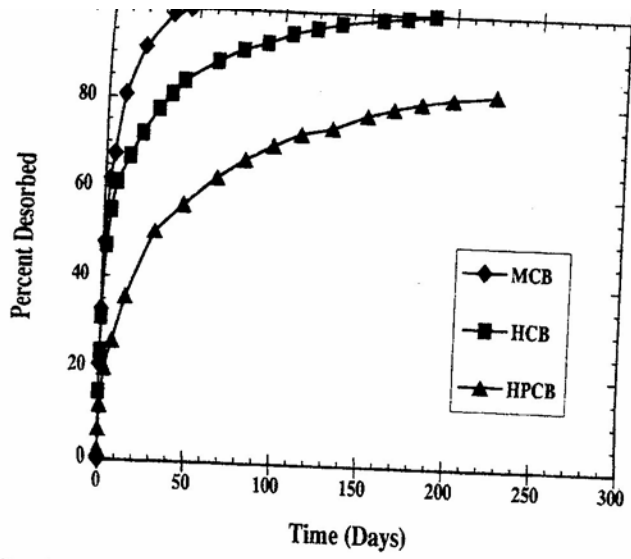


Fig. 8. Desorption experiments with HCB, a monochlorobiphenyl (MCB) and a hexachlorobiphenyl (HPCB). Sediment concentration of 2,000 mg/L.