CDM Camp Dresser & McKee

Report

Draft Report

MODEL-BASED ESTIMATES OF THE LOCAL CONTRIBUTION OF PCBs TO THE HAMILTON POND PORTION OF CEDAR CREEK

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MODEL-BASED ESTIMATES OF THE LOCAL CONTRIBUTION OF PCBs TO THE HAMILTON POND PORTION OF CEDAR CREEK

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Contents

List of Tables

List of Figures

1. SUMMARY

In September 1996, Camp Dresser & McKee (CDM) undertook a preliminary analysis of the available data on polychlorinated biphenyls (PCBs) in Cedar Creek, Cedarburg, WI (CDM, 1996). The area of interest for the Creek includes a series of ponds or impoundments: Ruck Pond, Columbia Pond, Wire and Nail Pond, and Hamilton Pond (listed in order of downstream flow). The objective was to determine if the data would support a determination of the relative contribution -- between Amcast Corporation and other potentially responsible parties (primarily Mercury Marine) -- of the sediment-bound PCBs present in the Hamilton Pond portion of Cedar Creek. The data in the reports reviewed generally indicated that the Amcast contribution to the PCBs of Hamilton Pond was a minor one. However, this initial review could only support a qualitative conclusion. To provide a quantitative estimate of the potential Amcast contribution, CDM recommended that a mathematical model be used (CDM, 1996). This report describes the creation and use of a model to supply the desired quantitative estimate.

The model created by CDM essentially uses a mass balance approach, following the PCB inputs and outputs to/from the sediments of each pond over time. The specific equations making up the model are based on a number of assumptions about the mechanisms and rates of PCB transfers. One key assumption in the model is that all of the PCBs in the Creek started out in two ponds that are upstream of Hamilton Pond: Ruck Pond and/or Columbia Pond. These assumptions and other physical features of the system are represented in a number of model input variables and equations. The model outputs calculated included the PCB mass and concentration in each pond over time. The model was calibrated to the existing data on PCB masses and concentrations in the three upstream ponds, including data from Blasland Bouck and Lee's sampling in 1998 (BBL, 1998). The calibration did not include use of data from Hamilton Pond in order to avoid any bias. The calibrated model was found to very closely reproduce the measured data with realistic values for all inputs.

The potential contribution of local dischargers of PCBs to Hamilton Pond (e.g., Amcast and the Cedarburg Publicly Owned Treatment Works [POTW]) is typically obtained by subtracting the model-predicted PCB mass in Hamilton Pond from the actual measured mass. For example, if the model predicted the presence of 63 kg of PCBs in Hamilton Pond due to inputs from upstream sources, and the actual measured mass was 64 kg, then 1 kg must have come from local sources. In this case the local contribution would be 1.6% of the total. If the model-predicted mass is greater than the actual mass, then no local PCB input needs to be invoked to account for the PCBs present in the Pond's sediments. This was commonly the case.

Two versions of the model were created, each representing a different hypothesis regarding the way in which the sediments in each pond are mixed over time. They are referred to as Options 1 and 2. The Option 1 model, which gave the best fit to the target data, always predicted 0% local contribution. The Option 2 model, which was not able to fit the target data as well, predicted up to a 40% local contribution.

Tests with the model created showed that it does not allow a single set of inputs (and related outputs) to be chosen as the best solution. Rather, a range of input values (all reasonable) and associated outputs is found to be possible. This is due to the fact that there are nine variables in the model and only three data points available for calibration. In addition, the computer program used in the model calibration, Solver in Excel®, was found to give variable solutions in different runs in which the same inputs were used. (This is likely due to a random function in the equations that seek to efficiently find the best fit to the target data.) Nevertheless, the different solutions were semiquantitatively consistent, i.e., the outputs did not vary significantly. In all Option 1 model runs, the predicted local contribution was 0%, irrespective of the above-mentioned model instability.

Based upon the above model results, it is concluded that there was a very low local contribution of PCBs to the PCB load in Hamilton Pond sediments. Due to the above-described model limitations, no specific numeric estimate can be listed and defended as the best overall estimate of the local contribution. However, based on the better fit (of predicted and measured data) with model Option 1, it is likely that the true local contribution is closer to 0% than to the values predicted by model Option 2 (15 to 40%).

This semiquantitative finding is consistent with the qualitative findings of CDM's preliminary review (CDM, 1996) which considered three different types of data: (1) data on PCB masses and concentrations in the four ponds (a focus of this report); (2) data on the PCB congener profiles for sediment samples taken above and below the point where Amcast had a discharge to Hamilton Pond; and (3) data on the relative concentrations of PCBs found in the storm sewers leading from Mercury Marine and Amcast to the Cedar Creek Ponds. All of these data had indicated that the Amcast contribution was relatively small.

2. MODEL DESCRIPTION

Objective

The objective of the model is to predict average PCB concentrations in the sediments of Cedar Creek near Cedarburg, WI. In particular, predictions are made for sediment PCB concentrations in Ruck Pond, Columbia Pond, Wire and Nail Pond and Hamilton Pond based on the primary assumption that all of the PCBs were initially released into Ruck Pond and Columbia Pond, and were thereafter carried downstream with portions being retained in the sediments of the downstream ponds. By comparison of predicted with measured PCB sediment concentrations, an estimate can be made of the local contribution (i.e., Amcast and the Cedarburg POTW) to the PCBs in Hamilton Pond.

Basic Modeling Approach

The portion of Cedar Creek of interest consists of a series of ponds or impoundments as shown in

Figure 1. The ponds of interest, listed in order of upstream to downstream, are: (1) Ruck Pond; (2) Columbia Pond; (3) Wire and Nail Pond; and (4) Hamilton Pond. The basic modeling approach treated this aquatic system as a connected series of impoundments containing water and sediments, as shown schematically in **Figure 2**. Figure 2 also shows the mass of sediments estimated by Westenbroek (1993) to be present in each Pond. The basic model developed may be considered a lumped parameter (box) model in which a mass balance is calculated for all PCBs entering and leaving each pond in a specified time interval, and over some total time period. The information on PCB mass is then combined with information on sediment mass in the pond to obtain an average PCB sediment concentration. The calculations are carried out in an iterative manner - one series of calculations for each year - starting at a hypothetical time (t = 0 or year 1) after the initial release of the PCBs into Ruck and Columbia Ponds.

The report by Strand (1992) indicates that one suspected PCB discharger, Mercury Marine, operated plants in this area from 1939 to 1982 (see Figure 1). Plant #2 (with a discharge to Ruck Pond) operated from 1951 to 1982, and Plant #1 (with a discharge to Columbia Pond via the Ruck Pond Raceway) operated from 1939 to 1981. Thus some PCB discharges could have started over 50 years ago. Other PCB dischargers could have released PCBs before or after this date. Thus, the iterative calculations can realistically consider a total time period of up to about 50 years for the redistribution of PCBs in the sediments. Data on the actual times of PCB release to Ruck and Columbia Ponds were not available for this study. While such data would have allowed the creation of a more accurate model, knowledge of the precise release times is not a critical parameter in the model. As described below (see Section 4), a redistribution time of 20 years was selected for most model runs based on sensitivity tests (which evaluated the quality of fit) and best judgement.

The model calculations are conducted in a Microsoft Excel® spreadsheet which provides results in yearly increments. There is no attempt in the model to make predictions for different sediment locations within a pond. Also, the calculations are carried out only for total PCBs; i.e., no attempt is made to provide separate results for individual PCB congeners or homolog groups. The restriction to total PCBs is due to the fact that the vast majority of the available measurements of PCBs in the sediments have been for total PCBs (by Aroclor).

The basic input parameters of the model are adjusted to give the best fit to measured data on PCBs in the three upstream ponds. (These data are summarized in the recent data compilation by Blasland Bouck & Lee [BBL, 1998]). This is referred to as model calibration. The data used to calibrate the model -- and to define the actual mass and concentration of PCB in Hamilton Pond -- come from several sampling events between 1986 and 1998. The number of samples in each event, and the sediment depths sampled, differed. Nevertheless the target data used in this program used simple averages of all data points; i.e., there was no attempt to obtain weighted averages of the data. Some of the data represent a time before the remediation of Ruck Pond (in 1994-1995) and the breaching of the Hamilton Pond dam in 1996. No Ruck Pond data from after its remediation were used. A simple comparison of the model-predicted PCB mass in Hamilton Pond and the measured mass (adjusted masses from those estimated by Westenbroek, 1993) is

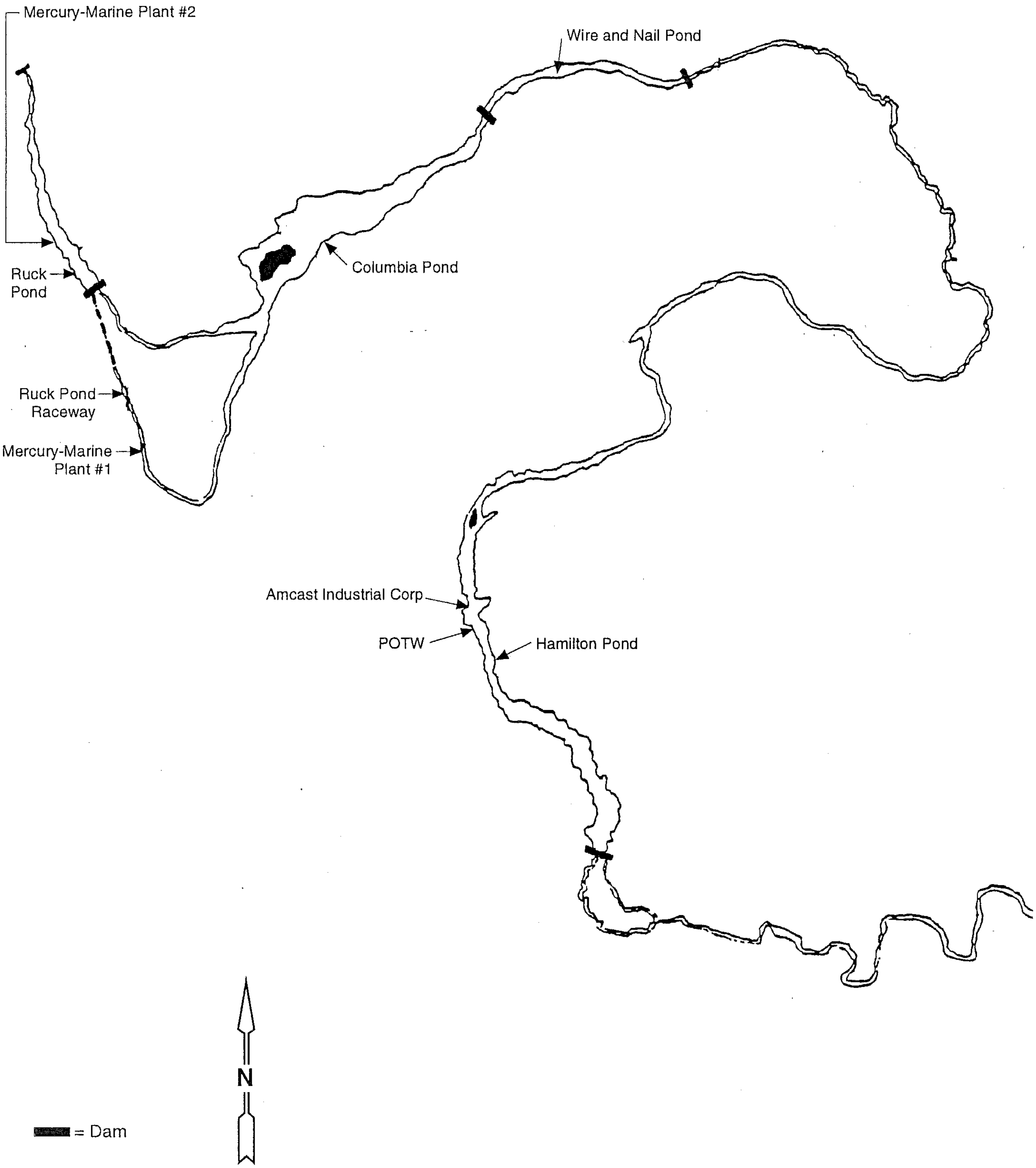


Figure 1
Location of the Cedar Creek Study Area in Vicinity of Cedarburg, Wisconsin

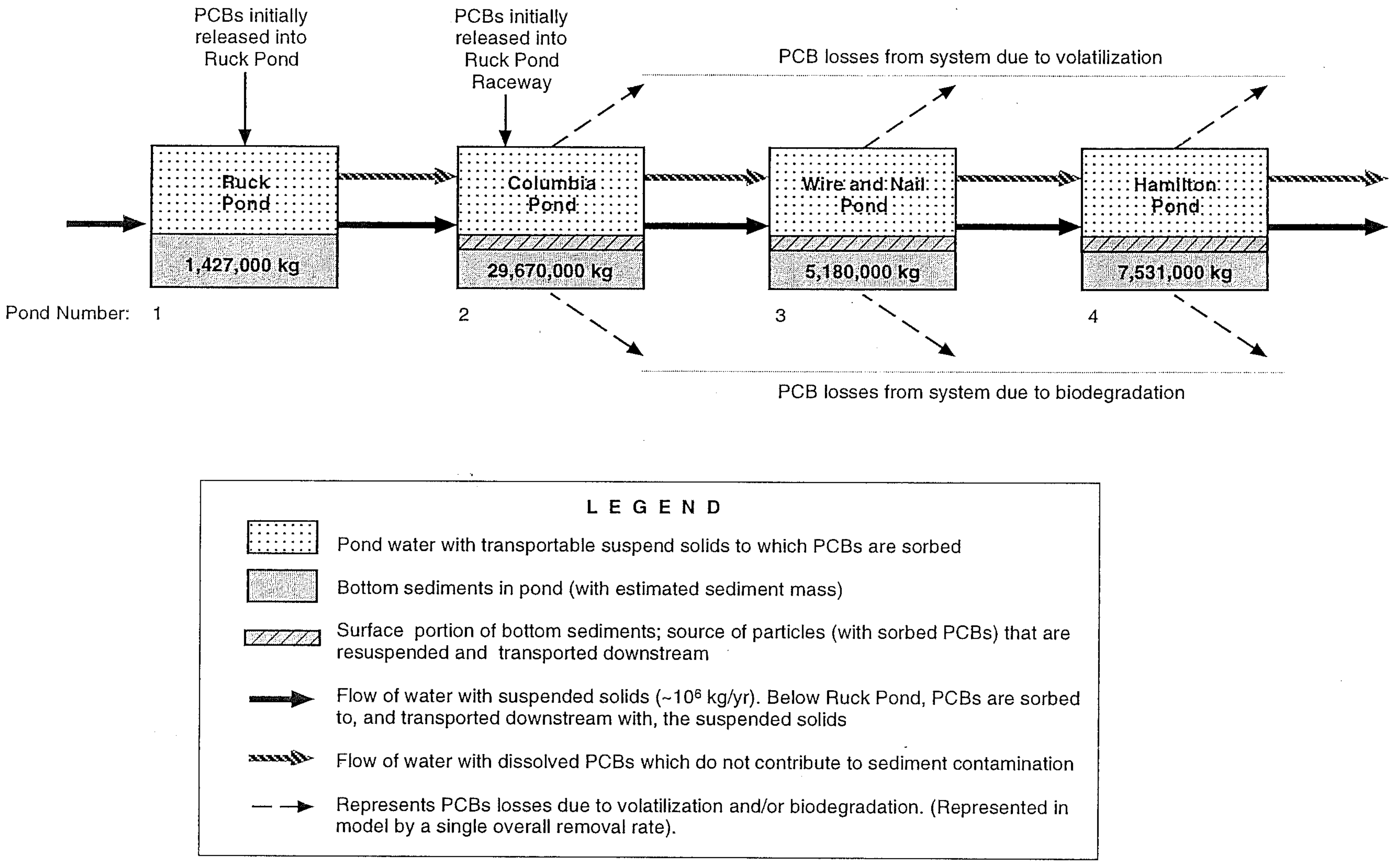


Figure 2
Schematic Diagram of Cedar Creek Impoundments and Elements of Mass Balance Model

used to estimate the mass of PCBs that may have entered the Hamilton Pond sediments as a local contribution, i.e., via the outfalls linked to Amcast's plant and/or the Cedarburg Publicly Owned Treatment Works (POTW).

Major Assumptions

Under normal operations, the model assumes the following:

- Initially (i.e., at time t = 0), one user-defined mass (M_1) of PCBs is present in Ruck Pond and a second used-defined mass (M_2) of PCBs is present in Columbia Pond; there are no PCBs present in Wire and Nail or Hamilton Ponds.

- The PCBs initially present in Columbia Pond are completely mixed with the sediments in the Pond. No assumption is made regarding the PCB distribution in Ruck Pond.

- PCBs leave Ruck Pond at a user-specified annual rate, which may be either: (1) a percentage of the amount present in the Pond (e.g., 2%/yr); (2) a constant mass removal rate (e.g., 10 kg/yr); or a combination of (1) and (2).

- Below Ruck Pond, the PCBs of interest are transported while sorbed to mobile suspended solids. The suspended solids that are entrained in one pond come from the surface sediments of that pond. The suspended solids carried from one pond to the next are deposited in the downstream pond and mixed, in a user-specified manner, with the sediments of that pond (see following bullet). (PCBs not of interest are those transported as dissolved solutes; see last bullet below.)

- There is a constant (user-specified) mass (TS) of sediments transported downstream in the study area each year. (Available data [Westenbroek, 1993] indicate the average is about 10^6 kg/yr.)

- The mixing of PCBs in the surface sediments considers two mixing options, both of which specify the manner in which the PCBs entering (with suspended solids) in the current year are mixed with the bottom sediments (containing PCBs from prior years) that were already in the pond. The two options are:

  Mixing Option 1: The mass of incoming sediments (TS) is mixed with a mass of existing sediments that is N times the value of TS (N is user specified).

  Mixing Option 2: The mass of incoming sediments (TS) is mixed with a mass (MS_n) of existing sediments that is available within a user-defined depth (D) of the pond's sediments. (Note: Subscript n refers to the pond number; see Figure 2.) This option requires an estimate of the sediment-water interface area (AP_n) for the three downstream ponds. The calculation also requires values an estimate of the bulk dry density of the sediments. (If the value of D selected results in MS < TS, then an adjustment is made to avoid anomalous mass transfers.)

- The PCBs that remain in a pond's sediments after the end of a calculational year are assumed to be completely mixed in those sediments.
- There is no change in the total mass of sediments present in each pond. (The constant sediment masses are those given by Westenbroek [1993]; see Figure 2.)
- PCBs may be lost from the system via volatilization and/or biodegradation; these processes are accommodated in the model by the incorporation of an overall first-order decay constant (expressed with a user-specified half-life). No such losses are considered for the PCBs that remain in Ruck Pond. This is reasonable given that the high concentrations present, and the likely presence of PCBs in the form of a non-aqueous phase liquid, would restrict or inhibit volatilization and degradation.
- Some PCBs are transported downstream as dissolved solutes and, as such, do not contribute to the accumulation of PCBs in the bottom sediments of the ponds. The fraction of PCBs present in the water column that are sorbed to suspended solids (i.e., not in solution) is specified by the user. (Data from Westenbroek [1993] indicate the fraction averages about 0.7- 0.8.)

Model Input Variables

Table 1 provides a summary of the eight input variables that must be specified each time the model is run with Mixing Option 1. In this table, only the parameter N relates to the assumptions of Mixing Option 1. The right-hand column of Table 1 shows the typical initial value used in the calibration runs. (The best fit values are provided in Tables 9 and 10, discussed below in Section 5.) If Mixing Option 2 is used, the parameter N is not required, but the additional parameters listed in **Table 2** are required. In both cases, the mass of sediments in Ruck, Columbia, Wire and Nail, and Hamilton Ponds are also required by the model, but are not considered to be variables. The values, shown in Figure 2, were derived by Westenbroek (1993) using sediment contour maps.

Mixing Option 2 requires estimates of the sediment water interfacial area for the three downstream ponds. CDM estimated these values using a planimeter and the sediment contour maps provided by Westenbroek (1993). For Hamilton and Columbia Ponds, the planimeter measurements used the contour for sediments greater that 1 foot depth; for Wire and Nail Pond, the planimeter measurements used the contour for greater that 2 feet. The calculations assume a flat sediment surface. The resulting interfacial areas are shown in Table 2. Mixing Option 2 also requires a value for the dry bulk density of the sediments. Based on data provided by Westenbroek (1993), an average value of 39.5 lbs/ft^3 was selected.

Table 1

Input Parameters for Mass Balance Model

Parameter	Definition (Units)	Initial Value*
M_1	Initial mass of PCBs in Ruck Pond (kg)**	1,000
M_2	Initial mass of PCBs in Columbia Pond (kg)***	200
FT	Fraction of PCB mass in Ruck Pond transferred to Columbia Pond each year (dimensionless)	0.02
M_C	Constant mass of PCBs transferred each year from Ruck Pond to Columbia Pond (kg)	0 or 10
FS	Fraction of transported PCBs that are sorbed to settleable solids (dimensionless)	0.8
$t_{1/2}$	Disappearance half-life for PCBs due to biodegradation and volatilization losses combined (yrs)	30
TS	Mass of bottom sediments transferred from pond to pond each year (kg)	10^6
N	Mixture ratio of (existing) bottom sediments to (new) transported-in sediments, used to define surface (transportable) sediments (dimensionless; N = 1 for 1:1 ratio, N = 2 for 2:1 ratio, etc.)	1
Y	Number of years for which simulation is run (yrs)	15-40 (Usually 20)

* Initial values used in model runs where calibration was being carried out.

** Mass presumed not to be subject to degradation.

*** Assumed to be completely mixed in the Pond's sediments and subject to degradation.

Table 2

Additional Input Parameters for Mass Balance Model Required for Mixing Option 2

Parameter	Definition (Units)	Values(s) Used
D	Mixing depth in sediments (ft)	1*
ρ	Bulk density of dry sediments (lbs/ft^3)	39.5
AP_2	Area of sediment-water interface in Columbia Pond (ft^2)	445,000
AP_3	Area of sediment-water interface in Wire and Nail Pond (ft^2)	38,000
AP_4	Area of sediment-water interface in Hamilton Pond (ft^2)	128,000
MS_2	Mass of surface sediments in Columbia Pond (kg)**	7,979,000
MS_3	Mass of surface sediments in Wire and Nail Pond (kg)**	681,000
MS_4	Mass of surface sediments in Hamilton Pond (kg)**	2,295,000

* Initial value used in model runs where calibration was being carried out.
** Values calculated as follows:

$$MS_2 = (AP_2)(D)(\rho)(0.4536 \text{ kg/lb})$$
$$MS_3 = (AP_3)(D)(\rho)(0.4536 \text{ kg/lb})$$
$$MS_4 = (AP_4)(D)(\rho)(0.4536 \text{ kg/lb})$$

Values listed in right-hand columm show result for D = 1 ft.

Model-Calculated Parameters

The parameters calculated by the model for each year are as follows:

- For Ruck Pond: the mass of PCBs present and the average concentration of PCBs in the pond's sediments (at the start of a calculational year);
- For Columbia, Wire and Nail, and Hamilton Ponds: (1) the mass of PCBs transferred into the pond; (2) the total mass of PCBs present in the pond's sediments; (3) the average concentration of PCBs in the pond's sediments; and (4) the average concentration of PCBs in the pond's surface sediments (i.e., those subject to entrainment and downstream transport);
- For Hamilton Pond: the mass of PCBs transported to downstream areas; and
- The total mass of PCBs present in the sediments of the four ponds (at the end of a calculational year).

Each of these parameters is a column header within the spreadsheet used for the model calculations. **Table 3** provides a summary list of the 16 parameters and the column indices.

The calculation of two PCB sediment concentrations for each pond, an overall average (C_{BS}) and a surface sediment value (C_{SS}), is related to the conceptual model that assumes that only the surface sediments in a pond can be entrained and transported downstream (see Model Assumptions).

Model Equations

The equations used in the model with Mixing Option 1 are listed in **Table 4**. Specifically, this table lists all of the equations for the calculations in years 1 and 2. The equations for subsequent years mirror those for year 2 with only the spreadsheet cell indices being incremented to reflect the current year. Note that the symbol $V_{i,j}$ is used to represent the value (V) of cell i,j in the spreadsheet. In this formulation, i = row (calculational year) and j = column (calculated parameter).

Table 5 lists the equations that are changed when Mixing Option 2 is used.

3. TARGET DATA

Measured values of sediment PCB concentrations and sediment masses are used to calculate average values of sediment PCB concentrations for each pond and the total mass of PCBs in each pond. These data are called target data in that they are the endpoints that the model is intended to

Table 3

List of Model-Calculated Parameters

Column Index	Parameter Symbol	Pond Location	Definition (units)
1	M_1	Ruck	Mass of PCBs present (at start of year) (kg)
2	C_{BS}	Ruck	Average PCB concentration in bottom sediments (mg/kg)
3	$M_{1,2}$	Columbia	Mass of PCBs transferred in (kg)
4	M_2	Columbia	Total mass of PCBs in bottom sediments (kg)
5	C_{BS}	Columbia	Average PCB concentration in bottom sediments (mg/kg)
6	C_{SS}	Columbia	Average PCB concentration in surface sediments (mg/kg)
7	$M_{2,3}$	Wire & Nail	Mass of PCBs transferred in (kg)
8	M_3	Wire & Nail	Total mass of PCBs in bottom sediments (kg)
9	C_{BS}	Wire & Nail	Average PCB concentration in bottom sediments (mg/kg)
10	C_{SS}	Wire & Nail	Average PCB concentration in surface sediments (mg/kg)
11	$M_{3,4}$	Hamilton	Mass of PCBs transferred in (kg)
12	M_4	Hamilton	Total mass of PCBs in bottom sediments (kg)
13	C_{BS}	Hamilton	Average PCB concentration in bottom sediments (mg/kg)
14	C_{SS}	Hamilton	Average PCB concentration in surface sediments (mg/kg)
15	$M_{4,5}$	Hamilton	Mass of PCBs transferred out (kg)
16	M_T	All 4	Total PCB mass in all 4 ponds at end of year (kg)

Table 4

Equations for Mass Balance Model - Mixing Option 1

Notes: 1) Time increment of 1 year is assumed for iterative calculations.
2) $V_{i,j}$ = value in spreadsheet cell i,j
3) See Tables 1 and 2 for parameter definitions and units
4) "10^6" in equations is units conversion factor, kg to mg
5) Equations only provided for year 1 (cells 1-1 to 1-16) and year 2 (cells 2-1 to 2-16)

Cell	Equation
1-1	$M_1 = M_1$ (Initial M_1 value input by user.)
1-2	$C_{BS} = (V_{1,1})(10^6)/(1{,}427{,}000) = (V_{1,1})/(1.427)$ where 1,427,000 = mass of sediments n Ruck Pond
1-3	$M_{1,2} = (FT)(V_{1,1}) + M_C$
1-4	$M_2 = (V_{1,3})(FS)(\exp\{-0.693/t_{1/2}\}) + M_2$ (Initial M_2 value input by user.)
1-5	$C_{BS} = (V_{1,4})(10^6)/(29{,}670{,}000) = (V_{1,4})/(29.67)$ where: 29,670,000 = mass of sediments in Columbia Pond (kg)
1-6	$C_{SS} = [(V_{1,3})(FS)(10^6)(\exp\{-0.693/t_{1/2}\})/(TS) + (N)(V_{1,5})]/(1 + N)$
1-7	$M_{2,3} = (V_{1,6})(TS)/(10^6)$
1-8	$M_3 = V_{1,7}$
1-9	$C_{BS} = (V_{1,8})(10^6)/(5{,}180{,}000) = (V_{1,8})/(5.18)$ where: 5,180,000 = mass of sediments in Wire and Nail Pond (kg)
1-10	$C_{SS} = (V_{1,7})(10^6)/[(TS)(1 + N)]$
1-11	$M_{3,4} = (V_{1,10})(TS)/(10^6)$
1-12	$M_4 = V_{1,11}$
1-13	$C_{BS} = (V_{1,12})(10^6)/(7{,}531{,}000) = (V_{1,12})/(7.531)$ where: 7,531,000 = mass of sediments in Hamilton Pond (kg)
1-14	$C_{SS} = (V_{1,11})(10^6)/[(TS)(1 + N)]$

(Continued)

Table 4

Equations for Mass Balance Model - Mixing Option 1(continued)

Cell	Equation
1-15	$M_{4,5} = (V_{1,14})(TS)/(10^6)$
1-16	$M_T = V_{1,1} - V_{1,3} + V_{1,4} - V_{1,15}$
2-1	$M_1 = V_{1,1} - V_{1,3}$
2-2	$C_{BS} = (V_{2,1})\ (10^6)/(1{,}427{,}000) = (V_{2,1})/(1.427)$
2-3	$M_{1,2} = (V_{2,1})(FT) + M_C$
2-4	$M_2 = [(V_{2,3})(FS) + (V_{1,4} - V_{1,7})](\exp\{-0.693/t_{1/2}\})$
2-5	$C_{BS} = (V_{2,4})(10^6)/(29{,}670{,}000) = (V_{2,4})/(29.67)$
2-6	$C_{SS} = [(V_{2,3})(FS)(10^6)(\exp\{-0.693/t_{1/2}\})/(TS) + (N)(V_{2,5})]/(1 + N)$
2-7	$M_{2,3} = (V_{2,6})(TS)/(10^6)$
2-8	$M_3 = V_{2,7} + (V_{1,8} - V_{1,11})(\exp\{-0.693/t_{1/2}\})$
2-9	$C_{BS} = (V_{2,8})(10^6)/(5{,}180{,}000) = (V_{2,8})/(5.18)$
2-10	$C_{SS} = [(V_{2,7})(10^6)/(TS) + (N)(V_{2,9})]/(1 + N)$
2-11	$M_{3,4} = (V_{2,10})(TS)/(10^6)$
2-12	$M_4 = V_{2,11} + (V_{1,12} - V_{1,15})(\exp\{-0.693/t_{1/2}\})$
2-13	$C_{BS} = (V_{2,12})(10^6)/(7{,}531{,}000) = (V_{2,12})/(7.531)$
2-14	$C_{SS} = [(V_{2,11})(10^6)/(TS) + (N)(V_{2,13})]/(1 + N)$
2-15	$M_{4,5} = (V_{2,14})(TS)/(10^6)$
2-16	$M_T = V_{2,1} - V_{2,3} + V_{2,4} - V_{2,7} + V_{2,8} - V_{2,11} + V_{2,12} - V_{2,15}$

Table 5

Revised Equations for Mass Balance Model - Mixing Option 2

Notes:
1) Time increment of 1 year is assumed for iterative calculations.
2) $V_{i,j}$ = value in spreadsheet cell i,j
3) See Tables 1, 2 and 3 for parameter definitions and units
4) "10^6" in equations is units conversion factor, kg to mg
5) Equations only provided for cells that are different for Mixing Option 2; see Table 4 for other equations.

Cell	Equation
1-6	$C_{SS} = [(M_2)(MS_2)/(29.67) + (V_{1,3})(FS)(\exp\{-0.693/t_{1/2}\})]/(MS_2)$
1-10	$C_{SS} = (V_{1,7})(10^6)/(MS_3)$
1-14	$C_{SS} = (V_{1,11})(10^6)/(MS_4)$
2-6	$C_{SS} = [(V_{2,3})(FS)(10^6)(\exp\{-0.693/t_{1/2}\}) + (V_{1,5})(MS_2)]/(MS_2)$
2-10	$C_{SS} = [(V_{2,7})(10^6) + (V_{1,9})(MS_3)]/(MS_3)$
2-14	$C_{SS} = [(V_{2,11})(10^6) + (V_{1,13})(MS_4)]/(MS_4)$

Furthermore, if $MS_n < TS$ for any pond (n = 2, 3 or 4), then use:

1-7	$M_{2,3} = [(V_{1,6} + V_{1,5})/(2)](TS)/(10^6)$	Only if $MS_2 < TS$
1-11	$M_{3,4} = [(V_{1,10} + V_{1,9})/(2)](TS)/(10^6)$	Only if $MS_3 < TS$
1-15	$M_{4,5} = [(V_{1,14} + V_{1,13})/(2)](TS)/(10^6)$	Only if $MS_4 < TS$
2-7	$M_{2,3} = [(V_{2,6} + V_{2,5})/(2)](TS)/(10^6)$	Only if $MS_2 < TS$
2-11	$M_{3,4} = [(V_{2,10} + V_{2,9})/(2)](TS)/(10^6)$	Only if $MS_3 < TS$
2-15	$M_{4,5} = [(V_{2,14} + V_{2,13})/(2)](TS)/(10^6)$	Only if $MS_4 < TS$

represent. Initial test runs with the model were made using as target data the PCB concentrations and masses in the four ponds shown in **Table 6**. These data are taken from the report by Westenbroek (1993); they reflect conditions around 1990. Subsequently, model runs were conducted using the complete set of data available on PCBs in the four ponds. The updated target data are shown in the right hand columns of **Table 7** (marked "Combined"). Other columns in Table 7 show what the available data were if only pre-1998 data are considered, or if only the most recent data from the 1998 sampling are considered (middle columns). It should be understood that the target data values have a significant amount of uncertainty associated with the heterogeneity of the PCB contamination in the sediments and the limited number of samples that were collected in each pond.

4. MODEL CALIBRATION

The model was fit to (i.e., calibrated with) the target data by minimizing a goodness-of-fit parameter similar to that used in common least-squares programs. This selected goodness-of-fit parameter involves a comparison of the measured and predicted PCB concentrations in the three upstream ponds; i.e., Ruck, Columbia and Wire and Nail. The fitting parameter, F, is calculated as follows:

$$F = [(C_{1P} - C_{1M})/(C_{1M})]^2 + [(C_{2P} - C_{2M})/(C_{2M})]^2 + [(C_{3P} - C_{3M})/(C_{3M})]^2$$

where: C = concentration of PCBs present in pond
$_{1,2,3}$ = subscripts representing, respectively, Ruck, Columbia and Wire & Nail Ponds
$_{M,P}$ = subscripts representing, respectively, measured and predicted values

In the above equation, the difference in the measured and predicted values is divided by the measured value before being squared. The use of such a normalized version of a least-squares fitting routine is to prevent any one target point from dominating the value of the goodness-of-fit parameter (F). This is especially important in this application since the largest target values are associated with Ruck Pond, and these values have a high uncertainty.

The Solver utility in Microsoft Excel® was used to calibrate the model, i.e., to find those values of the model inputs that gave the smallest value of the goodness-of-fit parameter, F. The Solver solution process involves successive trials, or iterations. During each iteration, a new set of changing input parameter values is used to recalculate the worksheet (i.e., calculate the output values listed in Table 3), considering any user-specified constraints and initial values specified. The process stops when a solution is found with acceptable precision, when no further progress is possible, or when the maximum time or number of iterations is reached. In all cases for the model created, a solution was found with acceptable precision.

For the model inputs listed in Tables 1 and 2, the following constraints were used in all fitting runs:

Table 6

Initial Target Data Used to Compare with Model Results*

	Pond				
Parameter	Ruck	Columbia	Wire & Nail	Hamilton	Total All Four
Total PCB Mass (kg)	370	308	54	52	784
Avg. PCB Conc. (mg/kg)	257	10.4	10.4	6.9	--
Number of Cores Taken	12	8	4	9	33
Number of PCB Analyses	60	28	13	26	127

* Source: Westenbroek , 1993. Data from Table 17 in this source, using solids mass calculated from sediment contour maps.

Table 7
Summary of Average PCB Concentrations for Cedar Creek Impoundments

Summary of PCB Concentration Data (mg/kg)						
	Pre-1998		1998		Combined[3]	
Cedar Creek Impoundments	Average PCB Concentration	N	Average PCB Concentration	N	Average PCB Concentration	N
Ruck Pond[1]	329	83	**	**	329	83
Columbia Pond[2]	25.9	88	23.6	87	24.8	175
Wire and Nail Pond[2]	18.5	13	21	22	20.1	35
Hamilton Pond[2]	7.07	52	9.8	54	8.5	106

Notes:

1. Combined data from Westenbroek (1993) and BBL (1998).
2. Pre-1998 and 1998 data from letter report from BBL to M. Thimke and T. Hoffman, dated 7/24/98.
3. Weighted average. Average weighted by number of samples in each data set.

** Not pertinent.

N = Number of samples in data set.

- All values > 0
- $0.5 < FS < 0.9$ (based on measurements reported by Westenbroek, 1993)
- 10 years $< t_{1/2} <$ 100 years
- 600,000 kg < TS < 1,500,000 kg (based on measurements reported by Westenbroek, 1993)

As indicated above, the following parameters were considered to be fixed at user-defined values:

- Sediment mass in each pond (see Figure 2)
- Sediment-water interfacial area for 3 downstream ponds (see Table 2)
- Sediment bulk density (see Table 2)

Currently, the model does not directly fit the data to find the best value of Y, the number of years since the initial release of the PCBs. Thus, an initial series of runs was made in which the value of Y was manually varied from 15 to 40 years in 5-year increments. Runs at all values of Y could result good fits of the data (i.e., produced low F values). There was a slight preference for Y = 20 years. In some previous trial runs, a slight preference was shown for Y = 25 years.

Following the selection of Y = 20 years, a number of tests were run to evaluate the model's sensitivity to various model options (e.g., Mixing Options 1 and 2) and to the initial values that had to be specified for each input for the Solver utility. Low values of F were almost always obtained (i.e., the model was able to predict the measured PCB concentrations and masses quite closely), although some solutions were considered to be preferred because of lower F values. In addition, when the F value was low, the resulting best-fit values of the model inputs were all within reasonable ranges. Generally, a unique solution would be expected regardless of the initial values specified. Due to limitations of the model algorithm, slightly different results were obtained using different initial values for several parameters, including M_C, FT, $t_{1/2}$ and N. In these cases, it appears that the Solver found a localized minimum of the goodness-of-fit parameter. However, the subsequent model-based calculation (described below) of the local input of PCBs to Hamilton Pond did not fluctuate significantly with varying initial conditions. Therefore, best judgement was used to select appropriate initial conditions for the model runs described below.

5. MODEL RESULTS

Calculation of Local Input into Hamilton Pond

For each of the model runs made after the initial testing and calibration, a calculation was made of the percentage of the mass of PCBs in Hamilton Pond that did not come from the upstream ponds, per the model's prediction. The percent was calculated as follows:

$$\%L = [(M_{4M} - M_{4P})/(M_{4M})]\times 100$$

where: %L = % of PCB mass added locally to Hamilton Pond
M_{4M} = measured mass of PCBs in Hamilton Pond (kg)
M_{4P} = predicted mass of PCBs in Hamilton Pond (kg)

If M_{4P} exceeded M_{4M}, the value of %L was set equal to 0. In this case, the model predicts that all of the PCBs in Hamilton Pond can be accounted for by upstream sources.

Values of M_M for all ponds were derived from the masses estimated by Westenbroek (1993) as follows. The Westenbroek estimates were multiplied by the ratio of the Combined PCB concentration (Table 7) to the Westenbroek concentration (Table 6), on a pond-by-pond basis. For example, the estimated mass of PCBs in Hamilton Pond, 64.1 kg, was obtained from:

52 kg [Table 6] × (8.5 mg/kg [Table 7] ÷ 6.9 mg/kg [Table 6]) = 64.1 kg

Similarly, the mass of PCBs in Ruck, Columbia and Wire and Nail Ponds was estimated to be 474 kg, 734 kg and 104 kg, respectively.

Presentation of Results

Table 8 lists the results from 11 model runs which illustrate the findings. The input (fitted) values of the model parameters for each run are provided in **Table 9**, and the model outputs (i.e., predicted PCB masses and concentrations in each pond) are shown in **Table 10**. The first 6 runs under model Option 1 show the results for different values of Y, the number of years during which downstream transport and mixing of PCBs is assumed to take place. Model run 7 is intended to show the impact of changing the initial (user-specified) value of one model variable, M_C (the mass of PCBs transferred from Ruck to Columbia Ponds each year [see Table 1]).

As also indicated above, changing the initially-specified value for some other parameters (i.e., FT, $t_{1/2}$ and N) also yielded somewhat variable best-fit values, but did not significantly change the resulting values of %L.

As previously indicated, the model developed does not provide a unique best fit to the measured PCB data, and thus there is no unique or best estimate of the percent of PCB mass in Hamilton Pond that came from local sources (i.e., the parameter %L). There is, however, a fairly strong basis for selecting Mixing Option 1 as the preferred model based on significantly lower goodness-of-fit parameter values. The goodness-of-fit values (F) for Mixing Option 1 were typically in the range of 10^{-10} to 10^{-13}. By contrast, F values with Mixing Option 2 were on the order of 1. As shown in Table 8, all Mixing Option 1 runs resulted in a 0% local PCB contribution. For Mixing Option 2, the predicted local contribution ranged from 15% to 40%. The results with Mixing Option 2 are considered less reliable that those with Mixing Option 1 because of the significantly higher values of F for Option 2.

To illustrate the quality of fit that the model achieved, **Figure 3** plots both the measured and

Table 8
Model Run Summary

Mixing Option	Run #	Run Features[1]	Local PCB Contribution (%L)
Option 1	1	$M_C = 10$; $Y = 15$	0.0%
	2	$M_C = 10$; $Y = 20$	0.0%
	3	$M_C = 10$; $Y = 25$	0.0%
	4	$M_C = 10$; $Y = 30$	0.0%
	5	$M_C = 10$; $Y = 35$	0.0%
	6	$M_C = 10$; $Y = 40$	0.0%
	7	$M_C = 0$; $Y = 20$	0.0%
Option 2	8	$M_C = 10$; $Y = 20$	15.1%
	9	$M_C = 0$; $Y = 20$	39.9%
	10	$M_C = 10$; $Y = 25$	15.1%
	11	$M_C = 0$; $Y = 25$	39.9%

1. User-specified initial values. Optimum value of M_C is determined by Solver. Value of Y remains fixed.

Table 9
Inputs / Fitted Values for Model Runs

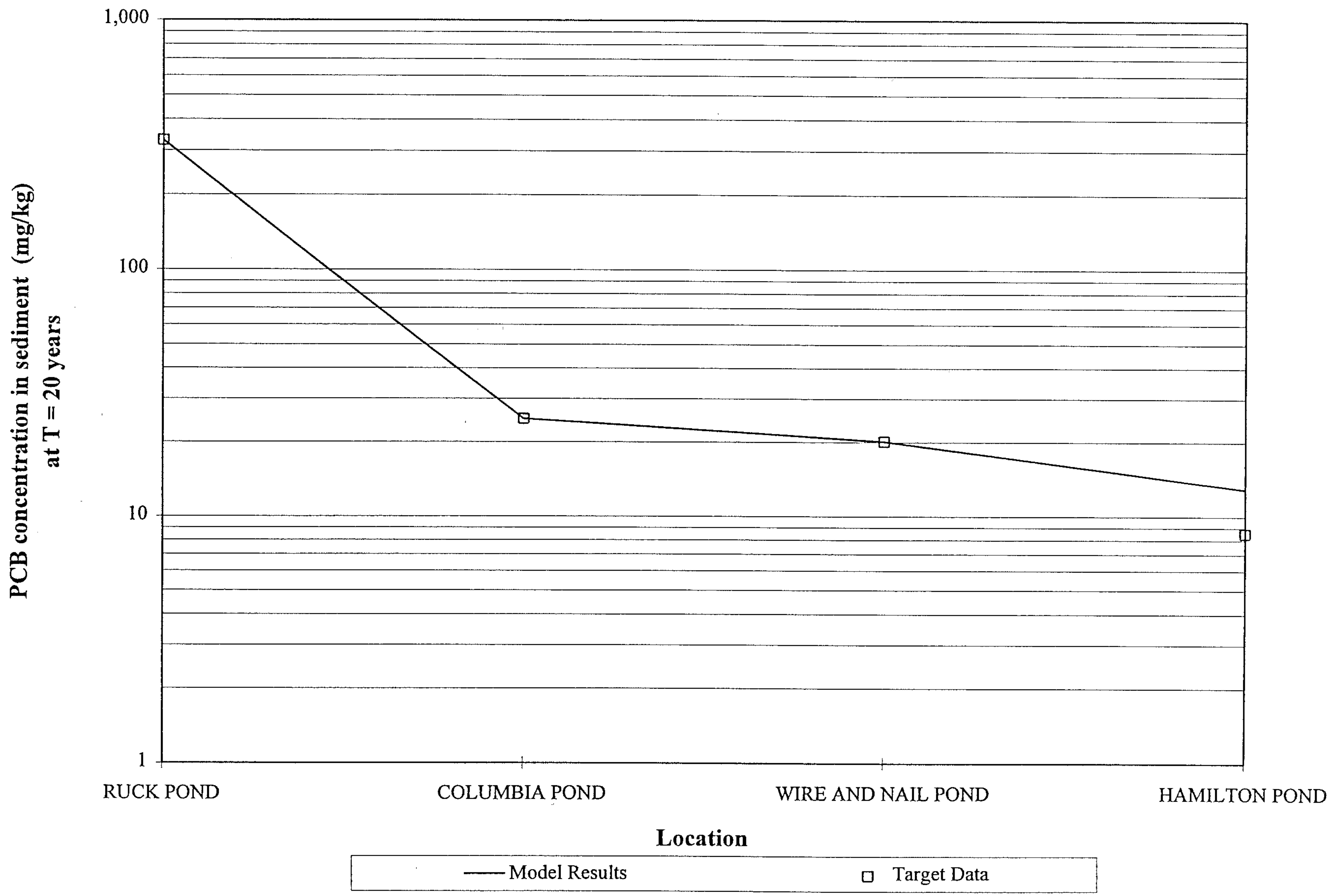
Mixing Option	Run #	Initial mass of PCBs in Ruck Pond (kg) M_1	Initial mass of PCBs in Columbia Pond (kg) M_2	Fraction of PCB mass in Ruck Pond transferred to Pond 2 each year (dimensionless) FT	Constant mass of PCBs transferred each year from Ruck pond to Pond 2 (kg) M_C	Fraction of transported PCBs that are sorbed to settleable solids (dimensionless) FS	Disappearance half-life for PCBs due to biodegradation and volatilization losses combined (years) $t_{1/2}$	Mass of bottom sediments transferred from pond to pond each year (kg) TS	Mixture ratio of (existing) bottom sediments to (new) transported-in sediments used to define surface (transportable) sediments (dimensionless) N	Number of years to be simulated (years) Y
Option 1	1	609	942	0.00	9.99	0.90	71.2	600,000	9.18	15
	2	668	1,006	0.00	10.5	0.9	71.9	600,000	3.62	20
	3	707	1,108	0.000	9.89	0.90	69.5	600,000	2.51	25
	4	775	1,113	0.000	10.5	0.90	84.1	600,000	1.87	30
	5	858	1,158	0.000	11.4	0.90	83.9	600,000	1.46	35
	6	837	1,454	0.000	9.42	0.90	66.9	600,000	1.58	40
	7	469	1,212	0.000	0.000	0.90	74.7	600,000	4.96	20

Mixing Option	Run #	Initial mass of PCBs in Ruck Pond (kg) M_1	Initial mass of PCBs in Columbia Pond (kg) M_2	Fraction of PCB mass in Ruck Pond transferred to Pond 2 each year (dimensionless) FT	Constant mass of PCBs transferred each year from Ruck pond to Pond 2 (kg) M_C	Fraction of transported PCBs that are sorbed to settleable solids (dimensionless) FS	Disappearance half-life for PCBs due to biodegradation and volatilization losses combined (years) $t_{1/2}$	Mixing Depth in sediments (ft) D	Dry Bulk density of sediments (lbs/ft^3) ρ	Mass of bottom sediments transferred from pond to pond each year (kg) TS	Mixture ratio of (existing) bottom sediments to (new) transported-in sediments used to define surface (transportable) sediments (dimensionless) N	Number of years to be simulated (years) Y
Option 2	8	1,042	213	0.022	10.9	0.90	32.1	1.00	39.5	681,344	1	20
	9	788	217	0.026	0.0	0.90	32.3	1.00	39.5	681,344	1	20
	10	1,042	213	0.022	10.9	0.90	32.1	1.00	39.5	681,344	1	25
	11	788	217	0.026	0.0	0.90	32.3	1.00	39.5	681,344	1	25

Table 10
Model Outputs

Mixing Option	Run #	RUCK POND (Pond 1)		COLUMBIA POND (Pond 2)		WIRE AND NAIL POND (Pond 3)		HAMILTON POND (Pond 4)		ALL 4 PONDS
		Mass of PCBs present (kg) M_1	Avg PCB conc. in all bottom sed. (mg/kg) C_{BS}	Mass of PCBs present (kg) M_2	Avg PCB conc. in all bottom sed. (mg/kg) C_{BS}	Mass of PCBs present (kg) M_3	Avg PCB conc. in all bottom sed. (mg/kg) C_{BS}	Mass of PCBs present (kg) M_4	Avg PCB conc. in all bottom sed. (mg/kg) C_{BS}	Total PCB Mass in sediments of 4 ponds (kg) M_T
Option 1	1	469	329	735.8	24.8	104.1	20.1	83.2	11.1	1,349
	2	469	329	735.8	24.8	104.1	20.1	96.8	12.8	1,361
	3	469	329	735.8	24.8	104.1	20.1	106.6	14.2	1,371
	4	469	329	735.8	24.8	104.1	20.1	113.1	15.0	1,376
	5	469	329	735.7	24.8	104.1	20.1	117.2	15.6	1,379
	6	469	329	735.8	24.8	104.1	20.1	125.7	16.7	1,390
	7	469	329	735.8	24.8	104.1	20.1	102.0	13.5	1,378
Option 2	8	506	355	388	13.1	34.5	6.7	54.4	7.2	933
	9	480	337	262	8.8	23.6	4.6	38.5	5.1	773
	10	400	280	387	13.1	35.1	6.8	58.8	7.8	832
	11	421	295	252	8.5	23.2	4.5	40.1	5.3	707

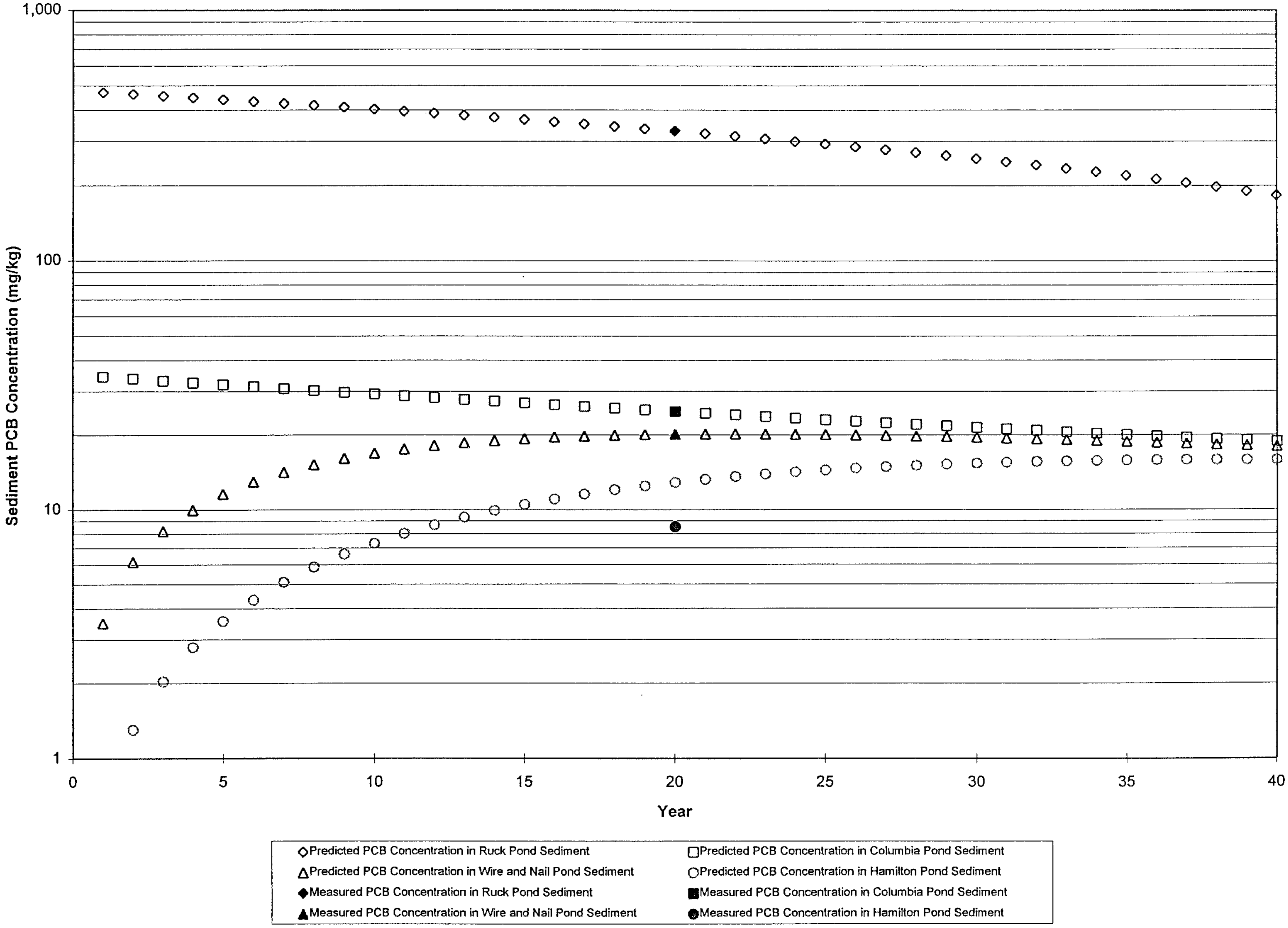
Figure 3
PCB Concentration vs. Location (Run 2)



predicted PCB concentrations for the four Cedar Creek ponds using the data from Run 2. Note that the model predictions (solid line) pass precisely through the measured values ("target data," symbolized by squares) for the three upstream ponds, but over-predict the PCB concentrations in Hamilton Pond.

Figure 4 shows the model's prediction of PCB concentrations over time (extending out to 40 years) if the Run 2 calibrated model is used. The measured (or target) values are also shown at the 20 year mark, showing close agreement with the predicted values at least for the three upstream ponds which are used in model calibration.

Figure 4
Sediment PCB Concentration over Time (Run 2)



6. REFERENCES

BBL, 1998. "Cedar Creek - Sediment Characterization Data." Letter, with data attachments, from Kendrick Jaglal, Blasland Bouck & Lee, to Mark Thimke (Foley & Lardner) and Timothy Hoffman (Coolidge, Wall, Womsley & Lombard), dated July 24, 1998.

Camp Dresser & McKee (CDM), "Initial Review of Data Relevant to Source Allocation of PCBs in Cedar Creek Sediments," report prepared for Katten Muchin & Zavis, Chicago, IL, September 1996.

Strand, "Cedar Creek PCB Investigation, Final Report, Volume 1 of 2," Wisconsin Department of Natural Resources, report by Strand Associates, Inc. Madison, WI, May 1992.

Westenbroek, "Cedar Creek PCB Mass Balance - Part 1: Data Summary and Analysis," Final Draft, June 18, 1993.