



## IMPORTANCE OF DOC IN SEDIMENTS FOR CONTAMINANT TRANSPORT MODELLING

Byung-Gi Hwang\*, Kwan-Soo Jun\*\*, Young-Dae Lee\*\*\*  
and Wu-Seng Lung†

\* *Department of Environmental Engineering, Sang Myung University, Chonan,  
Chung Nam, 330-720, Korea*

\*\* *Department of Environmental Engineering, Yeung Nam University, Kyongsan,  
Kyung Buk, 712-749, Korea*

\*\*\* *Environment Research Centre, Korea Institute of Science and Technology,  
Cheongyang, Seoul, 130-650, Korea*

† *Department of Civil Engineering, University of Virginia, Charlottesville, VA 22901,  
USA*

### ABSTRACT

Contaminants in the interstitial waters are not only dissolved but also associated with a filterable colloidal phase such as DOC. The DOC plays an important role regulating the distribution of chemicals between particulate and dissolved phases since it binds chemicals and makes them unavailable for vertical diffusive exchange. A three-phase partitioning model that consists of free-dissolved, DOC-bound, particulate-bound components of the chemicals involved is used for the contaminant transport model in order to include the effect of DOC on the partition coefficient. The contaminant model is linked to WASP modeling framework to predict remobilization of PCBs in sediments and the fate and transport of the contaminant in overlying waters of the New Bedford Harbor where the harbor has been contaminated with PCBs and heavy metals released from electronic capacitor manufacturers. Simulation of remedial controls indicates that if no action is taken, PCB concentrations will continue to be at elevated levels. Several scenarios for the removal of contaminated sediments have been performed to reduce the elevated PCB concentrations to background levels. © 1998 Published by Elsevier Science Ltd on behalf of the IAWQ. All rights reserved

### INTRODUCTION

Sediment contamination is one of major end results of pollutant discharges into estuarine aquatic environments. These contaminant discharges have resulted in highly contaminated sediments in the industrialized ecosystem. For toxic chemicals, sediments represent the primary repository and the principal source of contamination to the food chain (Landrum and Robbins, 1990). Among estuarine and coastal waters, New Bedford Harbor in Massachusetts has been contaminated with industrial and municipal waste, principally PCBs, released into the river and harbor areas shown in Figure 1. The main sources of contamination were from electronic capacitor manufacturers such as Aerovox, Inc. and Cornell Dubilier, which used PCBs during the years 1947–78. Although direct discharges of PCBs to the harbor were stopped in 1978, the PCB concentration in overlying waters remains high and has resulted in closure of fisheries in the harbour and adjacent areas of Buzzards Bay since contaminated sediments of the upper estuary continuously release the PCBs to the water column and act as a source of contaminant PCBs for the next several decades.

A number of water quality management questions have been raised:

1. What is the fate of PCBs associated with the bottom sediments? Are they permanently buried?, or, do they reach to overlying waters? That is, what are the main pathways of the movement, both in downward and upward directions? How much are they remobilized to the water column from the contaminated bed?

- Once they reach the water column, how will they be transported and dispersed through harbor and surrounding waters, both spatially and temporally? That is, what are the key processes in the fate of the toxicants in the water column?
- It is known that suspended solids regulate the toxicant concentrations in water by sorbing the chemicals, making them not bioavailable. What is the role of suspended solids distribution of the PCBs between the dissolved and particulate phases?
- What is the long-term fate of PCBs in water if no remedial action is taken? What would happen with the removal of contaminated sediments in hot spots?

Accordingly, to understand what mechanisms are important in the fate of a chemical, and to be able to make a projection of the expected change in concentration of the chemical, both in spatial and in temporal dimensions, there is a growing need for models to predict the transport of cohesive sediment associated with sediment-bound organic chemicals. In this paper we present a contaminant transport model using two partitioning coefficients in sediments to address complex sorption / desorption phenomena between DOC-bound and particulate-bound PCBs. We will focus on the development of a three-phase partitioning model in sediments: details of transport and calibration of the contaminant model are presented in Hwang (1995).

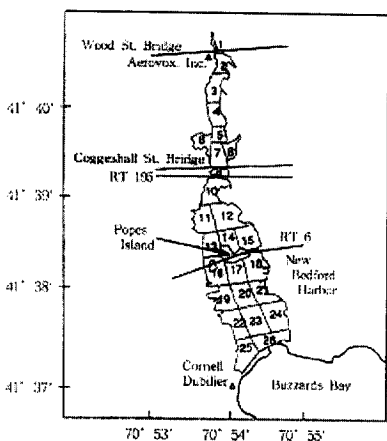


Fig.1 Map of New Bedford Harbor

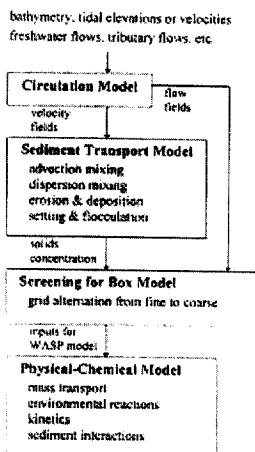


Fig.2 Schematics of modeling procedures

## MODELING APPROACH

To quantify interactions between sediments and sediment-bound chemicals, a three-phase partitioning model in sediments has been considered since contaminants in the pore water are not only dissolved but are also associated with a filterable colloidal phase such as dissolved organic carbon (DOC). A kinetic subroutine for the contaminant transport model was developed for the study area and linked to the EPA's WASP modeling framework since a quantitative understanding of rates of chemical reactions and interphase exchanges is critical in predicting the fate and transport of contaminants since many toxic chemicals are strongly sorbed to the sediments.

A modeling framework, including a hydrodynamic model, a sediment transport model and a contaminant transport model, has been developed in order to reflect those complex phenomena. The depth-averaged two-dimensional hydrodynamic model that successfully provides the circulation pattern for the Maryland Coastal Bay (Lung and Hwang, 1994) is used to derive velocity fields for the sediment transport model

and the contaminant model. Then, the sediment model is developed to predict spatial and temporal distribution of suspended solids. Next, the dynamic results obtained from those models are adopted for the toxic model through interfacing procedures, including the temporal and spatial averaging processes from fine grids in hydrodynamic work to coarse grids in box model. A series of modeling procedures are shown in Figure 2. Details of developing and calibrating the hydrodynamic and the sediment transport model are presented in Hwang (1995).

## MODEL DEVELOPMENT

### Model equation

Assuming that the sorption/desorption kinetics between the particulate and dissolved toxicant forms are rapid and lead to a local equilibrium, the mass balance equation of the contaminant model is written for the total toxicant concentration  $C_{T,i}$  in sediments for segment  $i$ .

$$V_{2i} \frac{dC_{T,i}}{dt} = -K_{f,i}^{12} \left( \frac{f_{d2,i} C_{T2,i}}{\Phi_{2,i}} - f_{d2,i} C_{T2,i} \right) + v_{s,i} A_s f_{p1,i} C_{T1,i} - v_{s,i} A_s f_{p2,i} C_{T2,i} - v_{d,i} A_s f_{p2,i} C_{T2,i} + K_{f,i}^{23} A_s \left( \frac{f_{d3,i} C_{T3,i}}{\Phi_{3,i}} - \frac{f_{d2,i} C_{T2,i}}{\Phi_{2,i}} \right) \quad (1)$$

in which (1) indicates the water column, (2) the upper-most sediment layer, and (3),(4) the underlying sediment layers, respectively. The definition of all terms are as follows:  $V_i$  = volume of segment  $i$  ( $m^3$ );  $K_{f,i}$  = sediment diffusive exchange rate (m/day);  $A_s$  = sediment area ( $m^2$ );  $v_{s,i}$ ,  $v_{u,i}$ , and  $v_{d,i}$  = settling velocity, resuspension velocity, and sedimentation velocity, respectively (cm/yr);  $\Phi_i$  = porosity (L in water/L in bulk volume);  $f_p$  and  $f_d$  = fractions of particulate and dissolved forms for the toxicant, respectively.

The total chemical concentration,  $C_T$  can be written as:

$$C_T = C_p + C_d \quad (2)$$

The results from several investigators (Di Toro et al., 1991) support that for certain chemicals such as PCBs in addition to partitioning to particulate organic carbon associated with sediment particles, there exists an additional partitioning to sorbing third phase which is not removed by conventional filtration. The third phase is identified as being either dissolved organic carbon (DOC), which is in colloidal-sized particles that are too small to be removed by the particle separation techniques.

Taking the DOC into consideration in sediments, the dissolved chemical concentration in pore water can be expressed as a sum of the dissolved free chemical,  $C_d^f$ , and DOC-complexed chemical,  $C_d^{DOC}$ , concentrations as follows:

$$C_d = C_d^f + C_d^{DOC} \quad (3)$$

The particulate chemical concentration,  $C_p$ , can be related to free-dissolved chemical concentration and sediment concentration  $m$  using the partition coefficient,  $K_p$ , as  $C_p = mK_p C_d^f$  and the DOC-bound chemical concentration,  $C_d^{DOC}$ , can be related to free-dissolved chemical concentration and colloid concentration  $m_{DOC}$  using the partition coefficient,  $K_{DOC}$ , as  $C_d^{DOC} = m_{DOC} K_{DOC} C_d^f$ . That is, the total chemical concentration can be written as:

$$C_T = mK_p C_d^f + C_d^f + m_{DOC} K_{DOC} C_d^f = (mK_p + 1 + m_{DOC} K_{DOC}) C_d^f \quad (4)$$

The three forms of the chemical concentration can be formulated as the fractions of the total chemical as follows:

$$C_p = f_p C_T \quad C_d^f = f_d^f C_T \quad C_d^{DOC} = f_d^{DOC} C_T \quad (5)$$

Then, the fractions are given by:

$$\begin{aligned} f_p &= \frac{mK_p}{mK_p + 1 + m_{DOC} + K_{DOC}} \\ f_d^f &= \frac{1}{mK_p + 1 + m_{DOC} + K_{DOC}} \\ f_d^{DOC} &= \frac{m_{DOC}K_{DOC}}{mK_p + 1 + m_{DOC} + K_{DOC}} \end{aligned} \quad (6)$$

(Also note that  $f_p + f_d^f + f_d^{DOC} = 1$ )

### Specification of model parameters

Water column partition coefficients are found as a function of the fraction of organic carbon  $f_{oc}$ , suspended solids concentration  $m$ , and the octanol/water partition coefficient  $K_{ow}$ . In the sediment, a three-phase equilibrium model involving the colloidal phase as well as the dissolved and particulate phases is used to evaluate the diagenetic processes and remobilization of sediment-bound PCBs in sediments. The PCBs in sediments for the New Bedford Harbor are mainly composed of Aroclors 1242 and 1254, for which the values of  $K_{ow}$  are  $10^{5.58}$  and  $10^{6.03}$  L/kg, respectively. The apparent partition coefficient in sediments  $K_p'$ , which is the ratio of the sediment chemical concentration to the total pore water chemical concentration, is given to be  $10^3$  to  $10^4$  L/kg by Brownawell and Farrington (1985a). The partition coefficient between the colloidal phase and the free dissolved phase  $K_{DOC}$  is given approximately to be equal to the value of  $K_{ow}$  (Di Toro *et al.*, 1991; Brownawell and Farrington, 1985b). The DOC concentration in sediments  $m_{DOC}$  is given to be 10 to 30 mg/L, which is extrapolated from the results of a sediment core study in the harbor (Brownawell and Farrington, 1985a).

Table 1. Parameters for the contaminant transport model

Notation	Description	Value
$K_p$	Sediment partition coefficient	$10^3 - 10^4$ L/kg
$K_{DOC}$	DOC partition coefficient	$10^3$ L/kg
$K_{ow}$	Octanol/water partition coefficient	$10^6$ L/kg
$M$	Solids concentration in sediments	500 - 700 g/L
$m_{DOC}$	DOC concentration in sediments	10 - 30 mg/L
$f_{oc}$	Fraction organic carbon in the water column	0.07
$f_{oc}^s$	Fraction organic carbon in sediments	0.02
$K_f$	Sediment diffusive exchange rate	$10^{-4} - 10^{-3}$ cm <sup>2</sup> /s
$k_l$	Volatilization rate constant	1.0 - 3.0 m/day
$v_d$	Net deposition rate	0.05 - 0.5 cm/year
$v_s$	Settling velocity	1.5 - 2.5 m/day

### Input Loading Estimation

Based on the results of many studies (Metcalf and Eddy, 1983; Battelle New England, 1985; Brown and Wagner, 1990), spatial variation of PCB concentrations in the bottom sediment has been estimated. The estimated values are about 800 ppm in the region of Wood Street (Segment 1), 2000 ppm in nearby sites of Aerovox, Inc. (Segments 2 and 3), and decrease linearly to the value at Coggeshall Street Bridge of 300 ppm. Concentrations sharply decrease to the lower estuary (north of Popes Island and Rte 6 Bridge) to 10 ppm and then increase slightly to 20 ppm toward the Hurricane Barrier, where is near the place at which Cornell Dubillier released PCBs into the Buzzards Bay.

MODEL RESULTS

The water column of the study area is divided into 26 segments. One hundred and four segments in the sediment system, consisting of four layers, underlie water column segments and thus a total of one hundred and thirty segments are configured as shown in Figure 1. The sediment layers have depths of 4, 8, 8 and 12 cm, respectively. The delineation of sediment layers is based on the vertical gradient of the PCB data (Metcalf and Eddy, 1983).

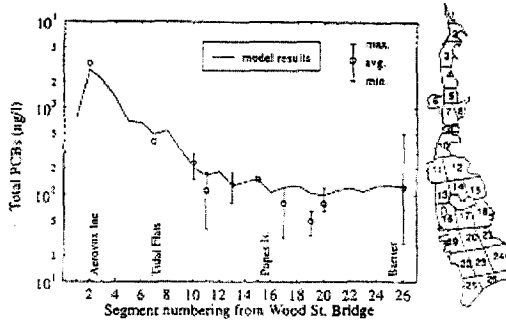


Fig. 3 Model calibration for the total PCB concentrations in water

Fig. 3 Model calibration for the total PCB concentrations in water

The contaminant transport model is calibrated for the data collected during the sample cruises (Battelle, 1985). The field data is represented by the mean values and the ranges of concentration. A comparison between observed and calculated concentration is presented in Figure 3. The model calculation adequately estimates the average values of the observed data, although the data are spread over a wide range. Generally, the spatial distribution of PCBs in the water column is well reproduced by the model. The extensive data from Battelle cruises, as analysed by ASA (1986), indicated mean ratios of filterable (particulate) to unfilterable (dissolved) PCBs of 1.44 for the average of three surveys. The model also calculates the ratio of the particulate to the dissolved PCBs as 1.56 and reproduces the ratio well.

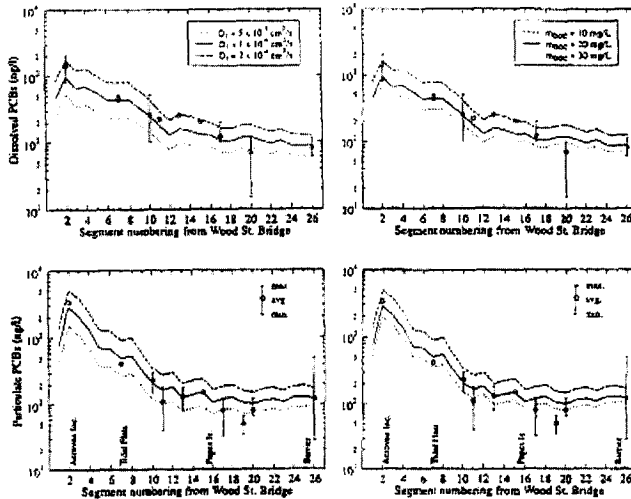


Fig.4 Model sensitivity analyses for vertical diffusive coefficients and DOC concentrations

### Model sensitivity

Before using the model for a long-term projection, in order to test the degree of sensitivity to the variations of the controlling parameters, sensitivity analysis has been conducted for vertical exchange coefficients between the overlying water and the pore water, and DOC concentrations in the interstitial waters (Figure 4).

As the coefficient is increased to  $2 \times 10^{-4} \text{ cm}^2/\text{s}$ , the increased dispersion coefficient enhances the diffusive flux from the interstitial water to the overlying water, resulting in the increased amount of PCBs in the water. As expected, higher water column PCB concentrations were obtained from the increased coefficient. Similarly, the decreased vertical coefficient results in decreased concentrations of PCBs in the water column. To quantify the effect of DOC concentrations, the model was tested at three different DOC concentrations. As can be seen, the model result with the highest DOC value (30 mg/L) provides the lowest water column concentrations since the toxicant preferentially adsorbed to the dissolved organic matter such as DOC, binding by the DOC reduces the freely dissolved toxicant concentration, which is available for vertical diffusive exchange according to concentration gradient. The reduced toxicant concentration in pore waters lessens the gradient, thereby reducing the transport of the contaminant. The model matches the observed data well with the DOC concentration of 20 mg/L.

### Long-term simulations

Long-term projection has been performed with the "no action" alternative, which assumes that the current trends arrived at from the model calibration effort will continue, indicated by solid line in Figure 5. That is, no remedial action such as dredging will be undertaken over the projected year period. Based on the model-calibrated year, 1985, a twenty-year simulation of the total PCB concentration in the water column has been attempted. The model results show little change over the period, which means without any remedial action an elevated PCB concentration in the water column will remain at least for the next several decades.

In this research, two remediation scenarios have been studied. As shown in the model projection, the first indicated by dense dotted line does not significantly reduce the amount of PCBs in water. Loading from the most contaminated area (Segment 2) will continuously release the PCBs and discharge to downstream, causing the contaminant concentration of the harbor to remain high. The second remediation scenario represented by sparse dotted line significantly reduces the PCB concentrations in overlying waters. However, it should be noted that dredging in this region should be carefully examined since turbation would probably impact the ecological system due to material released during dredging.

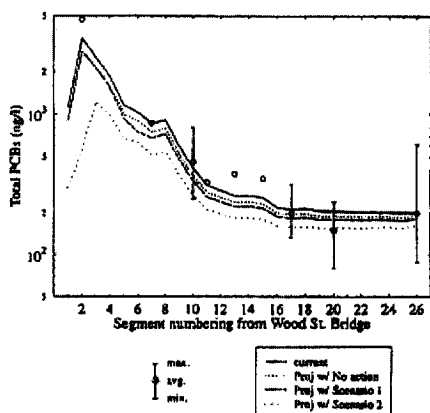


Fig. 5 Long-term projection of total PCB concentrations

## SUMMARY AND CONCLUSIONS

In order to predict the long-term fate of PCBs, and to provide a tool for assessing the PCBs management in the New Bedford Harbor, a series of modeling procedures have been developed. To quantify the effect of DOC concentration, the contaminant model incorporates a three-phase partitioning model in the sediments. A good agreement between the model result and the observed data indicates that the estimation of toxicant loading was reasonable and that key parameters controlling the physical-chemical processes were appropriately quantified.

It is concluded that as long as the sediment remains contaminated, the water column PCB concentrations will not be reduced. The amount of PCBs released through the interstitial dispersion process is relatively small. To reduce the amount of PCBs in overlying waters, and to improve the health of the ecological system, it is essential to remove the contaminated sediment from the harbor.

## REFERENCES

- Applied Science Associates (1986). Circulation and Pollutant Transport Model of New Bedford Harbor, ASA86-18, Narragansett, Rhode Island, 119p.
- Battelle New England (1985). Report on June 1985 Sampling for New Bedford Harbor Superfund Project, Duxbury, Massachusetts.
- Brown, J.F. and Wagner, R.E. (1990). PCB Movement, Dechlorination, and Detoxication in the Acushnet Estuary. *Environmental Toxicology and Chemistry*, 9, 1215-1233.
- Brownawell, B.J. and Farrington, J.W. (1985a). Biochemistry of PCBs in Interstitial Waters of a Coastal Marine Sediment. *Geochimica et Cosmochimica Acta*, 50, 97-120.
- Brownawell, B.J. and Farrington, J.W. (1985b). Partitioning of PCBs in Marine Sediment. In: *Marine and Estuarine Geochemistry*, A.C. Sigleo and A. Hattori (Ed.), 89-131.
- Di Toro, D.M. et al. (1991). Technical Basis for Establishing Sediment Quality Criteria for Nonionic Organic Chemicals Using Equilibrium Partitioning, *Environmental Toxicology and Chemistry*, 10, 1541-1583.
- Hwang, B.G. (1995). Modeling Remobilization of Sediment-Bound Contaminants in Sediments and Their Fate and Transport in Overlying Waters, Ph.D. Dissertation, University of Virginia, Department of Civil Engineering, Charlottesville, Virginia, 178p.
- Landrum, P.F. and Robbins, J.A. (1990). Bioavailability of Sediment-Associated Contaminants to Benthic Invertebrates. In: *Sediments: chemistry and toxicity of in-place pollutants*, R. Bando and H. Muntau (Ed.), 237-263.
- Metcalf & Eddy, Inc. (1983). Acushnet Estuary PCBs Data Management Final Report, EPA Region I Library, Boston, Massachusetts, 137p.