

## Chapter 13

# Modeling the Water Column, Sediment and Biota Concentrations of the Detroit River

**C. C. Lin and Ralph H. Kummler**

Department of Chemical Engineering  
Wayne State University  
Detroit, Michigan, 48202

The International Joint Commission (IJC) has identified 43 Areas of Concern (AOC's) on the Great Lakes. The Detroit River, a binational waterway, is one such AOC with impaired uses documented in the Stage I Remedial Action Plan (RAP) submitted to the IJC under the Great Lakes Water Quality Agreement, including restrictions on fish and wildlife consumption due to mercury contamination, degradation of benthic communities, and restrictions on dredging activities because of several metals, including mercury.

The authors modeled the Detroit River as part of the Stage II RAP process. The study used the historical field data to develop a comprehensive transport and fate model, including contaminant source/sink rates among three compartments (air, water, and sediment) and multiple point source contaminant discharges (municipal and industrial sources, tributaries, stormwater, and combined sewer overflows).

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The Wayne State University's Atmospheric and Sediment Deposition Model (ASDM) is a generalized temporal and spatial transport and fate model for computing water, sediment, fish, suspended solid, plankton, porewater and benthos phase contaminant concentration profiles in the river.

Three compartment (air, water, and sediment) contaminant interaction source/sink rates, and contaminant sorption effects of water and porewater exposure to suspended solids, plankton, fish, sediment and benthos were calculated from this model and applied to the water and sediment equations of continuity in one, two and three dimensions for both steady-state and transient conditions. Two equations of continuity for the water column and surface sediments were solved by the finite difference method, Crank-Nicolson method (Roginski, 1981), and iteration method. The computer program USSMPX (Lin, 1994) is run on a SUN workstation and MTS utilizing databases.

## **13.1 Model Theory**

### **13.1.1 Partitioning Processes**

ASDM assumes well-mixed behavior in each water column segment, and in each thin, high porosity surface sediment segment. This mathematical model includes water column and surface sediment contaminant advection and dispersion, multimedia contaminant transport processes (air/water diffusion, water/sediment diffusion, particle dry deposition, wet deposition of vapor and particle, suspended solid settling, sediment resuspension and burial), intermedia contaminant partitioning processes (water/suspended solid sorption, porewater/sediment sorption, water/plankton sorption, porewater/benthos sorption, and fish sorption), and contaminant transformation processes (biolysis, hydrolysis, oxidation, and photolysis).

The partition coefficient is highly dependent on the characteristics and the relative amount of each particulate phase. In general, for a particulate phase with an organic carbon fraction  $> 0.5\%$ , the organic carbon appears to be the predominant influence on the partition coefficient; the increasing partition coefficient with increasing organic carbon fraction is due to the high cation exchange capacity (O'Connor, 1980). The partition coefficient also varies inversely with the concentration of the particulate phase because a solid-solid interaction may be mediating the

adsorption and desorption process (U.S. EPA, 1982; O'Connor, 1980). Other environmental variables such as pH, temperature, hardness, alkalinity, and redox potential also will affect the partition coefficient (U.S. EPA, 1982).

The partition coefficients are very highly correlated with the suspended solids concentration in most cases (U.S. EPA, 1982; O'Connor, 1980). Therefore the following regression equation is useful for estimating contaminant partition coefficients for specific river systems where actual field data are not available (U.S. EPA, 1982; O'Connor, 1980).

$$K_{WS} = K_{WSO} C_M^a = \frac{C_{SS}}{C_W} \quad (13.1)$$

where:

$K_{ws}$  = partition coefficient of contaminants between water and suspended solids (l/Kg).

$K_{wso}$  = partition coefficient constant which is dependent on pH, temperature, hardness, alkalinity, and redox potential.

$C_M$  = suspended solid concentration (mg/l).

$a$  = partition coefficient exponential constant.

$C_{SS}$  = conc. of contaminants in the suspended solid.

$C_W$  = conc. of contaminants in the water.

The partition coefficient in surface sediments is linearly related to the organic carbon fraction (U.S. EPA, 1982; O'Connor, 1980). The organic carbon fraction is the most important factor in determining the partition coefficient of contaminants between the porewater and the sediment (U.S. EPA, 1982; O'Connor, 1980). If the organic carbon content of the suspended solid and sediment, and the partition coefficient ( $K_{ws}$ ) of contaminants between water and suspended solid are known, the partition coefficient ( $K_{ps}$ ) of contaminants between porewater and sediment is estimated using a linear proration equation.

$$K_{PS} = K_{WS} \frac{f_{ocs}}{f_{ocss}} = \frac{C_{Sed}}{C_{Pw}} \quad (13.2)$$

where:

- $f_{ocs}$  = organic carbon fraction in the sediment.
- $f_{ocss}$  = organic carbon fraction in the suspended solid.
- $C_{Sed}$  = concentration of contaminants in the sediment.
- $C_{Pw}$  = concentration of contaminants in the porewater.

The partition coefficient is also used in modeling the uptake of toxic contaminants by plankton (phytoplankton and zooplankton) or benthos from water or porewater. The only difference is that excretion is temperature dependent (Halfon, 1990). The following equilibrium mass balance is assumed steady-state.

$$k_1 \left( K_{WS} \cdot \frac{f_{ocpb}}{f_{ocss}} \right) C_D - k_2 f(T) C_{PB} - A(\text{food}, C_{PB}) = 0 \quad (13.3)$$

where:

- $k_1$  and  $k_2$  = parameters with respective values  
4.56x10<sup>-7</sup> m<sup>3</sup>/hr - 1 and 1.14x10<sup>-4</sup> hr<sup>-1</sup> (for Lake St. Clair)
- $f_{ocpb}$  = organic carbon content in the plankton ( $f_{ocp}$ ) or benthos ( $f_{ocb}$ )
- $f(T)$  = 1.024<sup>T</sup>(T°C)
- $C_{PB}$  = concentration of contaminants in the plankton ( $C_{pl}$ ) or benthos ( $C_{Ben}$ )
- $A(\text{food}, C_{PB})$  = uptake of toxic contaminants in the plankton or benthos by the small and large fish

for the plankton:

$$W^{k_6} = \frac{d_w (W_{SF}^{k_6} + W_{LF}^{k_6})}{d_w + d_p}$$

or benthos:

$$W^{k_6} = \frac{d_p (W_{SF}^{k_6} + W_{LF}^{k_6})}{d_w + d_p}$$

$d_w$  = is the depth of the water column.  
 $d_p$  = depth of the surface sediment.

Fish absorb toxic contaminants both from water and porewater through the gills and from their food (plankton, benthos or small fish). Assuming steady-state, the following equilibrium mass balance is used to describe sorption (Halfon, 1990):

$$k_3 C_{DF} + A(\text{food}, C_{PBF}) - EC_F = 0 \quad (13.4)$$

where:

$$\begin{aligned}
 k_3 &= (0.07 \log K_{OW} - 0.02) RV/W \\
 K_{OW} &= B_{cf}/0.048 \text{ (octanol-water partition coefficient)} \\
 B_{cf} &= \text{bioconcentration factor of contaminants between} \\
 &\quad \text{the water and fish.} \\
 W &= 0.005 \text{ Kg (} W_{SF} \text{ for the small fish like smelt).} \\
 &= 3.180 \text{ Kg (} W_{LF} \text{ for the large fish like trout).} \\
 RV &= \text{filtration rate (} RV = k_4 TW^{0.8} \text{).} \\
 k_4 &= 6.45 \text{ m}^3/(\text{Kg}^{0.8} \text{ } ^\circ\text{C hr}) \text{ for the small fish} \\
 &= 10.3 \text{ m}^3/(\text{Kg}^{0.8} \text{ } ^\circ\text{C hr}) \text{ for the large fish} \\
 C_{DF} &= \text{fish intake concentration of contaminants from} \\
 &\quad \text{the water and porewater through the gills:} \\
 C_{DF} &= d_w C_w / (d_w + d_p) + d_p C_{pw} / (d_w + d_p) \\
 A(\text{food}, C_{PBF}) &= \text{assimilation rate from the plankton and benthos} \\
 &\quad \text{for the small fish, or from the plankton, benthos} \\
 &\quad \text{and small fish for the large fish} \\
 A(\text{food}, C_{PBF}) &= k_5 W^{k_6} e^{(k_7 T)} C_{PBF} \\
 &\quad k_5 (1/(\text{Kg}_{\text{predator}}^{k_6} \text{ hr}), k_6 \text{ (dimensionless), } k_7 \text{ (} ^\circ\text{C}^{-1} \text{)}) \\
 &\quad \text{have the relative values of:} \\
 &\quad k_5: 3.58 \times 10^{-5}; 1.33 \times 10^{-4}; 3.16 \times 10^{-3}, \\
 &\quad k_6: 0.769; 0.781; 0.764, \\
 &\quad k_7: 0.335; 0.129; -0.76 \\
 &\quad \text{for the three temperature ranges:} \\
 &\quad 0-6.7^\circ\text{C}; 6.7^\circ\text{C} - 14.9^\circ\text{C}; \text{ higher than } 14.9^\circ\text{C.} \\
 C_{PBF} &= d_w C_{pl} / (d_w + d_p) + d_p C_{Ben} / (d_w + d_p) \text{ for the small fish,} \\
 &= (1-0.2) d_w C_{pl} / (d_w + d_p) + (1-0.2) d_p C_{Ben} / (d_w + d_p) + 0.2 C_{SF} \\
 &\quad \text{for the large fish.}
 \end{aligned}$$

- $E$  = excretion rate ( $E=2.28 \times 10^3 W^{-0.75}/K_{ow}$ ).  
 $2.28 \times 10^3 (\text{g}^{0.75} \text{hr}^{-1})$  = empirical scaling constant  
 $C_F$  = concentration of contaminants in the small fish ( $C_{SF}$ ) or large fish ( $C_{LF}$ )

Finally, the concentration of contaminants in the plankton ( $C_{pl}$ ), the concentration of contaminants in the benthos ( $C_{Ben}$ ), the concentration of contaminants in the small fish ( $C_{SF}$ ) and the concentration of contaminants in the large fish ( $C_{LF}$ ) can be solved from four equations which include equation (13.3) for the plankton and benthos, and equation (13.4) for the small fish and large fish.

### 13.1.2 Air/Water and Water/Sediment Diffusion

#### *Air/Water Diffusion*

The air-water diffusion equations are developed from the two-film model. The two-film model assumes that the interfacial resistance is negligible and there is a sharp transition between a stagnant film and a well-mixed fluid in which concentration gradients are negligible with the main resistance to gas transfer coming from the gas and liquid phase interfacial layers (Liss, 1974).

Assuming that the transport of gas across the interface is a steady-state process, it follows that

$$F_{AW} = K_A (C_A RT - HC_W) = K_W \left( \frac{C_A RT}{H} - C_W \right) \quad (13.5)$$

where:

$$\frac{1}{K_A} = \frac{RT}{k_A} + \frac{H}{k_w} \quad (13.6)$$

$$\frac{1}{K_W} = \frac{1}{k_w} + \frac{RT}{Hk_A} \quad (13.7)$$

$F_{AW}$  = flux of air-water gas contaminant diffusion through each boundary layer

- $K_A$  and  $K_W$  = contaminant overall mass transfer coefficients in the air and water at the air-water interface, respectively.
- $k_A$  and  $k_W$  = contaminant mass transfer coefficients in the air and water at the air-water interface, respectively.
- $C_A$  and  $C_W$  = concentrations of contaminants in the air and water, respectively.
- $R$  = gas constant.
- $T$  = temperature.
- $H$  = contaminant Henry's law constant.

Because the overall mass transfer coefficient ( $K$ ) is dependent on Henry's constant ( $H$ ), a small value of  $H$  ( $<5 \times 10^{-6} \text{ atm-m}^3/\text{mole}$ ) results in gas phase controlled absorption, while large values of  $H$  ( $>5 \times 10^{-6} \text{ atm-m}^3/\text{mole}$ ) result in liquid phase controlled volatilization (Mackay, 1989).

#### *Water/Sediment Diffusion*

In addition, the water-sediment diffusion equation can be developed from the two-film model. The result is:

$$F_{WP} = K'_W (C_W - K_{WP} C_{Pw}) = K_{Pw} \left( \frac{C_W}{K_{WP} - C_{Pw}} \right) \quad (13.8)$$

where:

$$\frac{1}{K'_W} = \frac{1}{k'_W} + \frac{K_{WP}}{k_{Pw}} \quad (13.9)$$

$$\frac{1}{K_{Pw}} = \frac{1}{k_{Pw}} + \frac{1}{K_{WP} k'_W} \quad (13.10)$$

- $F_{WP}$  = flux of water-sediment contaminant diffusion.
- $K'_W$  and  $K_{Pw}$  = contaminant overall mass transfer coefficients in the water and porewater at the water-sediment interface.
- $k'_W$  and  $k_{Pw}$  = contaminant mass transfer coefficients in the water and porewater at the water-sediment interface.

$K_{WP}$  = partition coefficient of contaminant between water and porewater.

$C_{Pw}$  = concentration of contaminants in the porewater.

### 13.1.3 Particle Dry Deposition

The atmospheric flux of particle contaminants depends to a large degree on particle size and characteristics, wind speed, receptor surface and micrometeorological conditions. In a simplified case, the following equation is most commonly used to calculate particulate fluxes (Mackay, 1986).

$$F_D = V_D C_P \quad (13.11)$$

where:

$F_D$  = dry particle contaminant flux.

$V_D$  = dry deposition velocity.

$C_P$  = conc. of contaminants in the particle phase.

### 13.1.4 Wet Deposition of Vapor and Particle

The flux of contaminant wet deposition from the atmosphere to surface water by rain and snow can be determined from the equation (Mackay, 1986).

$$F_W = F_V + F_P = W_V C_A J + W_P C_P J = C_T W_T J = C_L J \quad (13.12)$$

where:

$F_W$  = flux of contaminant wet deposition

$F_V$  and  $F_P$  = fluxes of vapor and particle contaminant wet deposition, respectively.

$J$  = precipitation intensity.

$C_L$  = conc. of contaminants in the rain and snow.

$C_T = C_A + C_P$

$W_T = W_V(1-\psi) + W_P\psi = C_L/C_T$

$\psi = C_P/C_T$

$W_V$  = vapor washout ratio

$W_P$  = particle washout ratio.

### 13.1.5 Suspended Solid Settling and Sediment Resuspension

#### *Suspended Solid Settling*

The flux of suspended solid contaminant deposition at the water-sediment interface can be calculated by the following equation:

$$F_s = C_{SS} C_M V_s \quad (13.13)$$

where:

- $F_s$  = flux of suspended solid contaminant settling.
- $C_{SS}$  = conc. of contaminants in the suspended solid.
- $C_M$  = suspended solid concentration.
- $V_s$  = suspended solid settling velocity.

#### *Sediment Resuspension*

The flux of sediment contaminant resuspension at the water-sediment interface can also be computed by the following equation:

$$F_R = C_{Sed} F_{RS} \quad (13.14)$$

where:

- $F_R$  = flux of sediment contaminant resuspension.
- $C_{Sed}$  = concentration of contaminants in the sediment.
- $F_{RS}$  = flux of sediment resuspension.

### 13.1.6 Sediment Burial

The flux of contaminant burial is calculated by the following equation (Chapra, 1983).

$$F_B = C_{Sed} C_{MS} V_{BSed} + C_{Pw} V_{BPw} \quad (13.15)$$

where:

- $F_B$  = flux of contaminant burial.
- $C_{Sed}$  = concentration of contaminants in the sediment.
- $C_{MS}$  = sediment concentration.
- $V_{BSed}$  = sediment contaminant burial rate.

$C_{pw}$  = concentration of contaminants in the porewater  
 $V_{BPw}$  = porewater contaminant burial rate.

### 13.2 Model Application

The source/sink rates (air/water diffusion, water/sediment diffusion, particle dry deposition, wet deposition of vapor and particle, suspended solid settling, sediment resuspension and burial) and reaction rates can be calculated by the Atmospheric and Sediment Deposition Model (ASDM) and applied to the continuous equation. The concentration of contaminants in the suspended solid or sediment is expressed by the concentration of contaminants in the water or porewater from equation (13.1) or (13.2), and also applied to the continuous equation. Concentrations which are given at the head of the river from measured data are the boundary conditions for the continuous equation.

The continuous equation in orthogonal curvilinear coordinates for stream flow is (Roginski, 1981; Mackay, 1989):

$$\begin{aligned}
 \frac{\partial(C_D+C_B)}{\partial t} = & \frac{1}{A_x} \cdot \frac{\partial \left[ -Q_x(C_D+C_B) + E_x A_x \frac{\partial(C_D+C_B)}{\partial x} \right]}{\partial x} + \\
 & \frac{1}{A_y} \cdot \frac{\partial \left[ -Q_y(C_D+C_B) + E_y A_y \frac{\partial(C_D+C_B)}{\partial y} \right]}{\partial y} + \\
 & \frac{1}{A_z} \cdot \frac{\partial \left[ -Q_z(C_D+C_B) + E_z A_z \frac{\partial(C_D+C_B)}{\partial z} \right]}{\partial z} + r + s
 \end{aligned} \tag{13.16}$$

where:

$C_D$  = mean concentration of contaminants in the water ( $C_w$ ) or porewater ( $C_{pw}$ ).  
 $C_B$  = mean concentration of contaminants in the suspended solid ( $C_{ss}$ ) or sediment ( $C_{sed}$ ). ( $C_B = KC_D$ )  
 $A_x, A_y, A_z$  = local areas for the water column or surface sediment in a plane normal to the given axis at a point.

- $Q_x, Q_y, Q_z$  = flows for the water column or surface sediment in the x, y, z directions, respectively.
- $E_x, E_y, E_z$  = eddy diffusivities for the water column or surface sediment in the coordinate directions.
- $r$  = time-averaged reaction rate in the water column or surface sediment.
- $s$  = time-averaged source/sink rate in the water column or surface sediment.

The continuous equations for the water column and the surface sediment partial derivatives can be replaced by their finite difference representations using the finite difference method and solved by the Crank-Nicolson method. Then, these two equations for water column and surface sediment can be solved by using Gaussian elimination with partial pivoting and backsubstitution, and iteration method simultaneously.

## 13.3 Model Calibration and Verification

### 13.3.1 Water Column Mercury Mass Balance

First, let us consider an overall mercury mass balance for the Detroit River water column assuming a steady-state one-box model, considering long residence times (about 19 to 21 hours), and equated total sources/sinks and reactions of Mercury. The water and suspended solid mercury inflow (main flow, tributary, municipal discharge, industrial discharge, CSOs and stormwater) rates and outflow rates are known (Michigan Department of Natural Resources, 1991; U.S. EPA, 1988; Camp Dresser & McKee, 1993; Giffels/Black & Veatch, 1980; Environmental Science and Engineering, Inc., 1987). The mercury source/sink fluxes can be calculated from the Atmospheric and Sediment Deposition Model (ASDM). The reaction rates are assumed to be zero when considering a total mercury balance. The Detroit River water column mercury mass balance result (see Figure 13.1) suggests that in the steady state, the Detroit River water column is a potential source (volatilization > dry and wet deposition, suspended solid settling > sediment resuspension and sediment diffusion to water) of mercury. The total input is equal to the total output in the Detroit River water column mercury mass balance (See Figure 13.1). So the Atmospheric and Sediment Deposition Model (ASDM) is a mass conservation model.

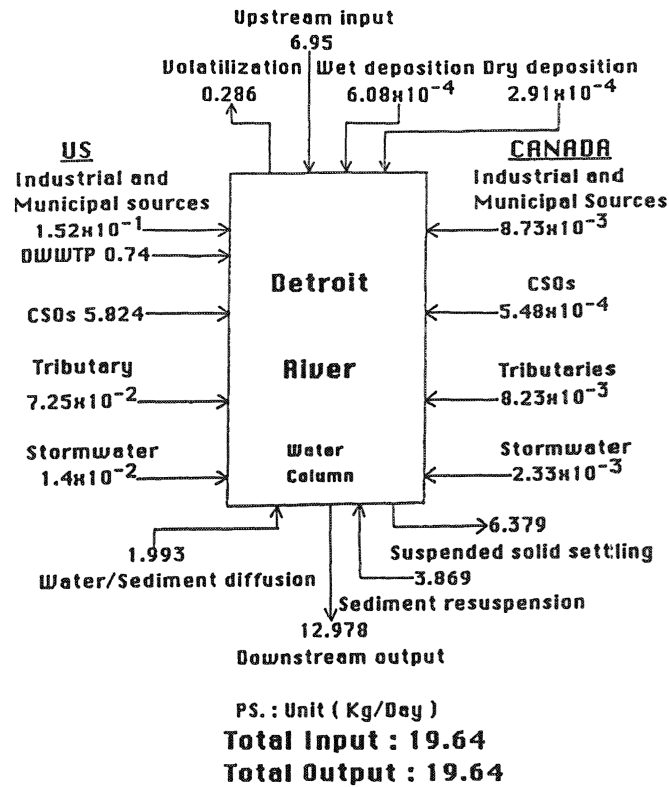


Figure 13.1  
 Detroit River water column mercury mass balance result.  
 (Sediment flow 1982-1991, computed CSO flow rates).

### 13.3.2 Steady State Mercury Concentration Profiles

The equation of continuity for the water column can be simplified to steady state when considering long residence times (about 19 to 21 hours). Because the Detroit River is well-mixed from top to bottom, and if we consider a source/sink transport model with no reaction, because we will consider a balance on total Hg, we can consider two dimensional flow (Environmental Science and Engineering, Inc., 1987):

$$\frac{1}{A_{Wx}} \cdot \frac{\partial \left[ -Q_{Wx}(C_W + C_{SS}) + E_{Wx} A_{Wx} \frac{\partial (C_W + C_{SS})}{\partial x} \right]}{\partial x} + \frac{1}{A_{Wy}} \cdot \frac{\partial \left[ -Q_{Wy}(C_W + C_{SS}) + E_{Wy} A_{Wy} \frac{\partial (C_W + C_{SS})}{\partial y} \right]}{\partial y} + s_W = 0 \quad (13.17)$$

#### *Water Mercury*

The UGLCC study using low detection levels, determined that all Detroit River water mercury concentrations exceed Michigan's Rule 57(2) Criteria (0.6 ng/l) (Michigan Department of Natural Resources, 1991). The model output computed that the entire Detroit River water mercury concentrations exceed 0.6 ng/l.

#### *Sediment Mercury*

The US EPA (1980-1987) reported that mercury concentrations in the Detroit River sediments were less than EPA Dredge Criteria (Heavily Polluted Value 1.0 mg/Kg) with the exception of the Michigan shoreline between Monguagon Creek and Elizabeth Park; most of the Ontario and mid-river sediments contained less than Toxicity Characteristic Rule (0.2 mg/Kg) (Michigan Department of Natural Resources, 1991). The regression analysis (see Figure 13.2) gives a good fit (Slope = 1.3, Intercept = 0, Regression Coefficient = 0.6) except at the upper Trenton Channel where simulation data are higher than measured data, at the middle Trenton Channel where simulation data are lower than measured data. For this regression analysis, the slope of the regression analysis line is over one, so the model simulation results are an underestimation due to lack of complete loading data.

#### *Fish Methyl Mercury*

Fish are highly migratory, so the trends of contaminants in the fish collected from the Detroit River area must relate to the contiguous water

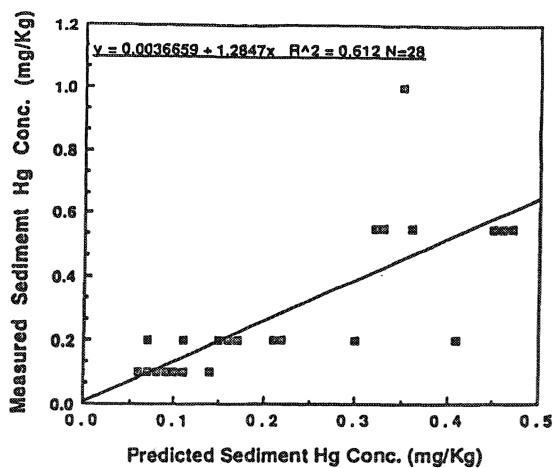


Figure 13.2  
Comparison of predicted and measured sediment mercury concentrations  
(Sediment flow, 1982-1991 computed CSO flow rates).

bodies of Lake Erie and Lake St. Clair. The Ontario MOE (1988-1989) (Michigan Department of Natural Resources, 1991) found that most of Lake St. Clair large walleye methyl mercury concentrations were over the OME Criterion (0.5 mg/Kg); similar results are computed in simulation results.

### 13.4 Conclusions

The ASDM model can be used to identify potential sources or sinks of contaminants among three compartments (air, water, and sediment), and to quantify contaminant loading rates from air/water diffusion, dry deposition, wet deposition, water/sediment diffusion, suspended solid settling, sediment resuspension and burial in the river system. The major sources for mercury in the Detroit River water column are upstream input (51%), CSOs (43%), and DWWTP (5%). The major sinks for mercury in the Detroit River water column are downstream output (94%), deposition to sediment (4%), and volatilization to air (2%). So the Detroit River water column is a source of mercury for Lake Erie, river sediment, and air. In addition, the Detroit River water column overall mercury mass balance showed that the total input is equal to the total output. So the ASDM model is a mass conservation model.

The ASDM can also be used to compute water, sediment, suspended solid, plankton, fish, porewater and benthos phase contaminant concentration profiles in the river aquatic and sediment systems. The steady state model results showed that all Detroit River water mercury concentrations exceed Michigan's Rule 57(2) Criteria (0.6 ng/l); the UGLCC study also found the same results. In addition, regression analysis for steady state sediment mercury give a general indication of goodness of fit (Regression Line Slope = 1.3, Regression Line Intercept = 0, Regression Coefficient = 0.6). The steady state model outputs also showed that most of large fish methyl mercury concentrations are above the OME Criterion, similar to the fish methyl mercury concentrations in Lake St. Clair.

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