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FATE AND TRANSPORT OF PCBS AT THE NEW BEDFORD HARBOR SUPERFUND SITE

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Abstract—A unique, holistic modeling approach, combining theoretical, empirical, and deterministic elements, was developed to define the ambient background transport of polychlorinated biphenyl (PCB) from New Bedford Harbor, to provide a baseline for remediation assessment of this Superfund site. Both empirical and deterministic elements characterized sediment processes. The deterministic section employed experimental data to describe flocculation through fluid shear, differential settling, and Brownian motion mechanisms, yielding a sediment settling velocity. The empirical portion of the model used this settling velocity, along with suspended solids, and flow field data to characterize sediment action. The remaining PCB transport mechanisms (volatilization and sorption) are theoretically considered to give a complete contaminant transport assessment. The PCBs in New Bedford Harbor tend to volatilize at the rate of 5.9 g/d; or sorb, with sorption coefficients increasing with percent chlorination from $10^{-2.2}$ to $10^{-0.4}$ m^3/g for Aroclors 1016 and 1260, respectively, rather than stay in solution. The deterministic model showed that fluid shear was the most significant flocculation mass removal mechanism contributing to the settling velocity calculation. From the empirical model, the dominant sediment action mechanisms, resuspension and deposition, were driven by the change in suspended solids concentration and tides. The cycling of PCB-laden sediment, indicated by the PCB sorption tendency and the presence and dominance of resuspension, and subsequent transport from the site, can lead to PCB contamination of the water column, atmosphere, or downstream (marine) areas.

Keywords—Modeling PCBs Contaminant transport Sediments

INTRODUCTION

New Bedford Harbor is an estuary in southern Massachusetts bounded on the north by the Acushnet River and on the south by a hurricane barrier leading to Buzzards Bay. The cities of Fairhaven, New Bedford, and Acushnet border the harbor to the east and west (Fig. 1). It has long been a prosperous fishing port of the Atlantic. More recently, it served as an industrial center for electronics manufacturers, such as Aerovox and Cornell Dubilier. This industrial expansion resulted in contamination of New Bedford Harbor through point (e.g., effluent discharges) and nonpoint (e.g., landfills) sources of contamination. The water column, sediment, and biota are contaminated with polychlorinated biphenyls (PCBs) and heavy metals. Total sediment PCB concentrations detected were as high as 30,000 μg/g in the upper estuary, 5–50 μg/g in the harbor, and up to 5 μg/g in Buzzards Bay and other downstream areas [1]. This may indicate that the point of highest concentration, the hot spot (Fig. 1), in the upper estuary has begun to spread and move out of the harbor. The U.S. Environmental Protection Agency (EPA) water quality criteria for PCBs are 0.014 ng/ml in freshwater and 0.030 ng/ml in saltwater [2]. Total water column PCB concentrations in New Bedford Harbor are in the 0.2-μg/ml range [3]. These high PCB concentrations in both the water column and sediment possibly pose a risk to human populations in the New Bedford area, as well as marine life within the harbor, Buzzards Bay, and the Atlantic Ocean.

In 1982, New Bedford Harbor was added to the Superfund Priority List for cleanup due to PCB contamination. Polychlorinated biphenyls are chemically stable, nonflammable, nonconductive compounds with high boiling points and low solubilities. Their stability or resistance to degradation contributes to their bioconcentration potential that can cause hazards for biota [4]. Considering New Bedford Harbor manufacturers use of PCBs, and that environmental persistence increases with chlorine content, it follows that the congeners detected most resembled a mixture of Aroclors 1242 and 1254 [5]. These Aroclors each contain some of the most toxic PCB coplanar congeners [6,7]. Suggested dredging will resuspend contaminated sediments, either at the sediment surface or as a result of dredge overflow water entering the system [8]. Reduced suspension of dredge solids has been achieved at some operations, such as the Sheboygan River, Wisconsin [9]. However, Palermo and Pankow [10] cite resuspended contaminated sediments from dredging activities as a major source of increased New Bedford Harbor water column contamination. In one way, the success of a dredging operation depends on the extent of environmental reexposure and toxicity of effects. Consequently, our work defines steady-state PCB controlling phases and quantifies potential baseline PCB fate and transport. We assumed a steady-state completely mixed condition for the preremediation New Bedford Harbor site because the hurricane barrier severely restricts tidal perturbations, average freshwater inflows are very low, suspended solids concentrations are constant throughout the region of consideration (upper estuary), and contaminants have been present for a sufficient length of time to eliminate unpredictable changes in concentration due to contaminant addition or relocation.

We combined theoretical, empirical, and deterministic approaches to predict the fate and transport of PCBs in New Bedford Harbor under worst case (high contaminant concentration) scenarios. Volatilization and sorption were characterized theoretically, sediment processes empirically, and sediment settling velocity deterministically from experimental data. Gaseous PCB escape was theoretically quantified using a combination of Fick's and Henry's Laws to produce PCB flux values of 5.9 g/d. Partition coefficients represent sorption characteristics, and

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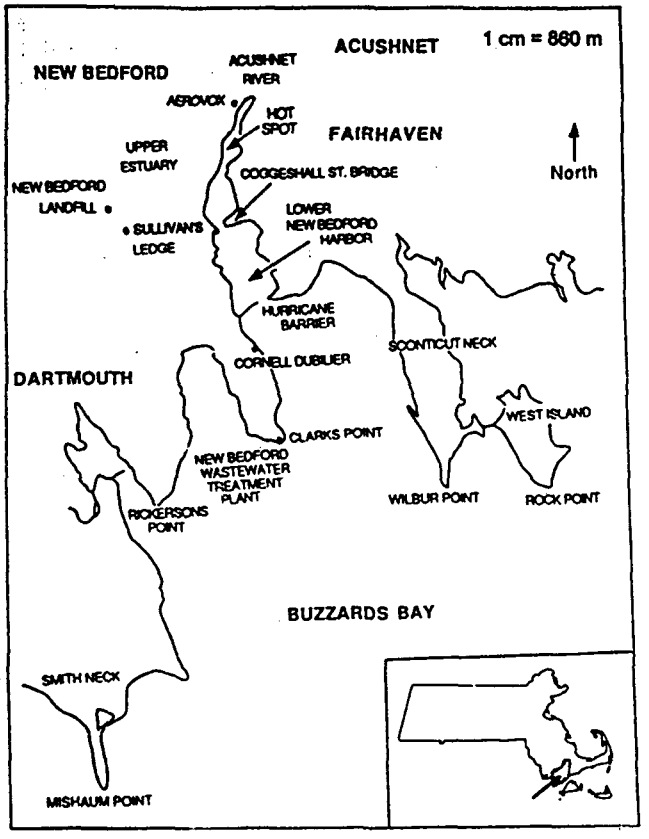

Fig. 1. Map of New Bedford Harbor, Massachusetts (adapted from Ikalainen and Hall [1]).

were found to be $10^{-2.3}$–$10^{-0.4}$ m³/g for Aroclors 1242 and 1260, respectively. These values correspond to compounds tending to sorb to solids rather than remain in solution.

Emphasis was placed on sediment processes through an empirical model using solids sources and sinks, flow, and suspended solids concentration data. Experimental settling column studies and a deterministic model were used to calculate settling velocity values for the empirical model. The deterministic model was also used to characterize flocculation mechanisms affecting settling, indicating fluid shear as the dominant flocculation process. Empirical model results yielded notable sediment recycle, with deposition dominant over resuspension. Combining the deterministic and empirical approaches produced a fate and transport assessment for New Bedford Harbor. The PCBs are not very soluble, volatilizing or sorbing to sediment rather than staying in solution. This allows PCB transport from the harbor, as either sorbed to sediments or transferred to mobile sediments during resuspension activity. As well as assessing PCB fate and transport, this approach shows the feasibility of coalescing various analysis techniques. This takes advantage of as much experimental and field data as possible and uses theoretical principles where data are lacking.

APPROACH

Overall model framework

This modeling effort consists of three main elements: empirical, deterministic, and theoretical. Both empirical and deterministic elements characterize sediment processes. The deterministic section employs experimental data to describe flocculation through fluid shear, differential settling, and Brownian motion mechanisms, yielding a sediment settling velocity. The empirical portion of the model uses this settling velocity, along with suspended solids, and flow field data to characterize sediment action. The remaining PCB transport mechanisms (volatilization and sorption) are theoretically considered to give a complete contaminant transport assessment. Each of the model parts will be considered individually in the following sections. The empirical and deterministic models assume steady-state and completely mixed conditions. These simplifications were deemed reasonable because of hurricane tidal damping, low freshwater inflows, and suspended solids concentrations the same at the hot spot (Fig. 1) and at Coggeshall St. Bridge (the limits of the modeling region). The overall modeling scheme was developed to make the best use of all available data. The simple empirical suspended solids mass balance model employed is not ultimately complete nor absolutely accurate. Steady state and completely mixed are assumed, food chain accumulation, bioturbation, and runoff are not considered, but a more complex model would require more data, in this case, unavailable data. Introduction of numerous unknown parameters to such a modeling effort would increase the degrees of freedom and thus the uncertainty of the model results.

Gas/liquid

Atmospheric transport of PCBs in the vapor-phase or on particulate matter can be a major source of PCBs to some areas [11]. Therefore, minimizing potential losses via these processes is important. The amount of PCBs available for vaporization depends on the water column concentration of the dissolved species, as well as hydrodynamic mixing phenomena. For a long-term time frame and an unremediated quiescent harbor such as New Bedford Harbor [12], the PCB water column concentration and subsequent vaporization will be assumed to reach a dynamic equilibrium.

The evaporative transfer process defined by Whitman's two-film theory, describes both liquid and gas-phase boundaries at the gas/liquid interface as the resistant mechanisms of transfer [13]. The basis of this theory relies on the supposition of Henry's Law, describing an equilibrium between gas and liquid phases as

$$p_i = Hc_i \tag{1}$$

where p_i is the partial pressure of the gas constituent at the interface, H is the contaminant specific distribution coefficient, and c_i is the constituent liquid concentration at the interface. For any particular contaminant, H can be approximated as the ratio of vapor or partial pressure, P, to aqueous solubility, S,

$$H = \frac{P}{S} \tag{2}$$

A useful representation of PCB transfer between gas and liquid phases is flux, as defined by Fick's first law,

$$J = k_l(c_i - c_l) \tag{3}$$

or

$$J = \frac{k_g}{RT_a}(p_g - p_i) \tag{4}$$

where J is flux; k_l, k_g are the mass transfer coefficients in the gas (g) or liquid (l) phases; c_i, c_l are the liquid concentrations at the interface (i) or in the bulk fluid (l); R is the gas constant; T_a is the absolute temperature; and p_g, p_i are the partial pressures of the gaseous phase (g) and at the interface (i).

Flux, J, is calculated by combining Henry's Law and Fick's first law [14], to yield

$$J = K_l\left(\frac{p_g}{H} - c_l\right) \tag{5}$$

or

$$J = \frac{K_g}{RT_a}(p_g - Hc_l) \tag{6}$$

where

$$\frac{1}{K_l} = \frac{RT_a}{Hk_g} + \frac{1}{k_l} \tag{7}$$

and

$$\frac{1}{K_g} = \frac{H}{RT_a k_l} + \frac{1}{k_g} \tag{8}$$

where $1/K_l$ is the total resistance of contaminant removal from liquid as the sum of resistance in the gas layer (RT_a/Hk_g) and resistance in the liquid layer ($1/k_l$), and $1/K_g$ is the total resistance of contaminant removal from gas as the sum of resistance in the gas layer ($1/k_g$) and resistance in the liquid layer ($H/RT_a k_l$). The above formulations are more meaningful when a resistance factor for the liquid phase is determined [15], as

$$R_l = \frac{\textit{liquid resistance}}{\textit{total resistance}} = \frac{1/k_l}{1/K_l} = \frac{1/k_l}{RT_a/Hk_g + 1/k_l} = \frac{H}{H + RT_a(k_l/k_g)} \tag{9}$$

This quantity, a percentage value, specifies whether the gas or liquid concentration of contaminant in the system controls transfer to the gas phase. Low R_l values indicate gas-phase concentration controls transfer; high R_l values indicate liquid-phase concentration controls transfer; and intermediate R_l values indicate control by both gas and liquid concentrations.

Actual mass transfer coefficients, k_l and k_g, for New Bedford Harbor depend on the amount of turbulence in the gaseous and liquid phases on either side of the interface and also on the chemical reactivity of the gas [16,17]. The effects of these physical factors on k_l and k_g, in m/d, are empirically defined by Chapra and Reckhow [14] from summarized data in Mackay [18], accounting for wind and compound specificity, as

$$k_l = \frac{0.5W^{3/2}}{\sqrt{M}} \tag{10}$$

and

$$k_g = \frac{1{,}200W}{\sqrt{M}} \tag{11}$$

where W is wind speed (m/s) and m is molecular weight.

Sorption/desorption

Sorption/desorption are processes at the liquid–solid interface where contaminants are either assimilated on, into, or removed from particles either physically or chemically. Contaminants sorbed to particles in the water or released from the particles are the only processes considered in this discussion, not specific mechanisms. Karickhoff et al. [19] linearly define the extent of sorption and desorption for hydrophobic compounds spanning a solubility range of 1 μg/mL to 1,000 μg/mL. These studies used sorbents from clay through sand with a fraction organic carbon up to 0.035. Empirically determined, this particle distribution coefficient (m^3/g) is

$$K_{PD} = 6.3 \times 10^{-7} f_{oc}(K_{ow}) \tag{12}$$

where f_{oc} is the fraction particulate organic carbon (g-org C/g) and K_{ow} is the octanol:water distribution coefficient ([mg octanol/m³]/[mg water/m³]). K_{PD} represents the ratio of the contaminant concentration sorbed onto sediment (mg/g) to the contaminant concentration in solution (mg/m³). K_{PD} for all organic chemicals ranges in magnitude from 10^{-10} to 10^2, with higher values indicating a greater affinity for contaminant sorption [20]. This indicates more contaminant will sorb to sediment as the organic content of the sediment increases.

Sediment processes

Sediment processes considered included physical mechanisms such as settling, flocculation, resuspension, advection, and dispersion. These processes are important because they control the transport of sediment-bound contaminants from or buried within the sediment environment. Settling is the deposition or falling out of particles from the water column. Flocculation mechanisms affect settling, in that the aggregation and breakup of particles can occur as settling occurs. Aggregation will increase settling rates due to greater particle size, as represented in Stokes' equation:

$$V_{ss} = \frac{g(\rho_p - \rho_l)d_p^2}{18\mu} \tag{13}$$

where V_{ss} is the settling velocity, g is the gravitational acceleration, ρ_p, ρ_l are the particle (p) and liquid (l) densities, d_p is the particle diameter, and μ is the fluid viscosity. Resuspension resembles reverse settling at the sediment–water interface, in that particles are transferred from the sediment layer to the water. Advection transports particles in water flow and dispersion is the spreading out of particles toward a spatial concentration equilibrium. Tidal influences can affect a system through all these mechanisms, but most measurably by advection as tidal flows change from flood to ebb. The PCBs present in aqueous systems are predominantly particle bound because of their hydrophobicity. The solid-bound phase dominates the transport and fate of PCBs in aqueous systems. For this study, we focused special attention on particle processes (particle transport and potential interactions), reflecting both empirical and mechanistic approaches.

An empirical model for the upper New Bedford Harbor estuary, north of Coggeshall St. Bridge, was developed to relate the change in suspended solids over time to the flow in and out of the system, as well as within the system, through the following dynamic mass balance relationship

$$\frac{\textit{mass loss}}{\textit{accumulation}} = \textit{solids sources} - \textit{solids sinks} + \textit{flow loading} \tag{14}$$

or

$$\forall\frac{dSS}{dt} = \forall r - \forall d + QSS \tag{15}$$

where SS is suspended solids concentration in the water column, t is time, r is the rate of solids influx by sources, d is the rate of solids removal by sinks, Q is the net discharge, where positive flow indicates flood tide (in) and negative flow indicates ebb

tide (out), and $\forall$ is the volume of the estuary above Coggeshall St. Bridge. The upper estuary system was assumed to be completely mixed. This was deemed a valid assumption because concentrations of suspended solids at the hot spot (Fig. 1) and at the bridge were approximately equal, an indication of complete mixing [22]. With this assumption, Equation 15 becomes

$$\left.\frac{dSS}{dt}\right|_{HS} = r - d + \left.\frac{QSS}{\forall}\right|_{b} \tag{16}$$

where HS indicates calculation at the hot spot and b indicates calculation at the bridge.

Considering each term in Equation 16, dSS/dt is the change in suspended solids over the change in time and was approximated according to a central difference scheme

$$\left.\frac{dSS}{dt}\right|_{HS} \approx \left.\frac{\Delta SS}{\Delta t}\right|_{HS} = \frac{(SS_{HS})_{i+1} - (SS_{HS})_{i-1}}{t_{i+1} - t_{i-1}} \tag{17}$$

where SS_{HS} is suspended solids at the hot spot and i indicates the time step. The base mass loading, QSS/V, represents the net horizontal particle movement caused by flow in and out. Flow was calculated according to

$$Q(t) = v(t)[\bar{A} + h(t)w] \tag{18}$$

where $v(t)$ is the current velocity as a function of time, $\bar{A}$ is the constant minimum cross-sectional area at the bridge, $h(t)$ is the change in depth above a minimum level as a function of time (approximated as a sine curve, $h[t] = 1 + 0.75\sin[t]$), and w is the average width of the harbor at Coggeshall St. Bridge, each determined from preliminary studies at New Bedford Harbor [22]. This determination assumes constant harbor bathymetry. Integration of Equation 18 yields the incremental volume, represented as

$$\forall = \forall_m + \int_{t-1}^{t} Q\,dt \tag{19}$$

where $\forall_m$ is the constant minimum volume of water upstream from the bridge (determined from bathymetry of upper harbor [23]), and the integration of Qdt is approximated numerically using a trapezoidal method [24].

The particle sinks, d, assumed to be settling dominant [25], can be quantified as

$$d = \frac{V_{ss}}{h(t)}SS \tag{20}$$

where V_{ss} is the experimentally verified deterministic settling velocity. Determination of V_{ss} involved the synthesis of settling column experiment results [25,26] by a vertical transport model [27]. The model specifically defined and accounted for the flocculation processes according to fluid shear, differential, and Brownian motion collision frequency functions. These can cause changes in V_{ss}. The values within these equations can reflect changing conditions within the system caused by weather or other external sources and thus lead to a V_{ss} value that accurately describes the system being considered. Solution of the differential equation that considered sink terms for the dispersive dominant, completely mixed column [25], as was the case for the experimental column

$$\frac{\partial SS}{\partial t} = \frac{V_{SS}}{h}SS \tag{21}$$

where $V_{ss}/h = m$,

$$\ln\frac{SS}{SS_0} = -mt + 0 \tag{22}$$

where SS_0 is the initial suspended solids concentration at the beginning of the tidal cycle being considered. From Equation 22 the slope of the regression of $\ln SS/SS_0$ vs. t from deterministic model results enables calculation of V_{ss}, the average flocculated particle settling velocity. The average value for m was $2.78 \times 10^{-5}\ s^{-1}$, which produced $V_{ss} = 5.6 \times 10^{-5}$ m/s at 2 m depth. Particle sources for the harbor were determined by solving equation 15 for r, resulting in

$$r = \frac{dSS}{dt} - \frac{Q}{\forall}SS + d \tag{23}$$

All components for r are as determined above (Eqns. 17–20).

Resuspension and deposition can be further described by another term, C_r, often called a recycle ratio, defined as,

$$C_r = \frac{k_u}{k_u + k_b} \tag{24}$$

where k_u is the mass-transfer coefficient of solids due to sources or "scour" [L/T] and k_b is the burial velocity or "accumulation" [L/T]. This term serves to describe the sediment action characteristics of a system. C_r can range from no recycle at $C_r = 0$, when $k_b \gg k_u$ to total recycle at $C_r = 1$, when $k_u \gg k_b$.

Relating Equation 24 and a net contaminant loss rate [20], L_w, to previous empirical sediment determinations allowed for calculation of k_u and k_b. The water column was used as the frame of reference for the steady-state net contaminant loss rate, L_w, as

$$L_w = K_1c_d + (1 + C_r)V_{ss}c_s \tag{25}$$

where K_1 is the mass transfer coefficient of solids due to volatilization; V_{ss} is the experimentally verified deterministic settling velocity; c_d is the fraction of contaminant dissolved in water, as $1/(1 + K_{PD}SS)$; and c_s is the fraction of contaminant sorbed to suspended particulates in water, as $1 - c_d$. To calculate the transfer of solids to the water column, k_u was determined from the resuspension term (Eqn. 23) to be,

$$k_u = \frac{rh(t)}{SS} \tag{26}$$

To account for the sinks within the system and determine how quickly particles are actually leaving the water column and being buried, k_b was determined from the deposition term (Eq. 20) to be

$$k_b = \frac{d\forall}{SSA_s} \tag{27}$$

where $\forall$ is the volume of the upper estuary and A_s is the surface area of the upper estuary. k_b encompasses all sedimentation, both resuspendable sediment and deeply buried sediment.

FIELD DATA

Flow considerations for Acushnet River inflows to the estuary are negligible, with river flow being less than 2% of tidal flow [5]. The model used suspended solids, velocity, and harbor depth data as a function of time to extract the necessary parameters from a pilot study performed on July 8 and 9 and September 24 and 28, 1987 by the EPA for the U.S. Army Corps of Engineers [28–30]. In these studies, samples were taken each hour at the Coggeshall St. Bridge, with sampling times beginning 1 h after both slack (high) tide and low tide.

Table 1. Suspended solids data and standard deviations for data for July 8, July 9, September 24, and September 28, 1987

Date	Suspended solids reading (mg/L)	Standard deviation (SD)
July 8 (ebb)	7.9	±1.9
July 8 (flood)	10.2	±1.7
July 9 (ebb)	7.8	±0.8
July 9 (flood)	9.4	±1.1
September 24 (ebb)	7.5	±1.1
September 24 (flood)	6.8	±1.1
September 28 (ebb)	6.4	±0.4
September 28 (flood)	7.0	±1.1

Suspended solids data were collected at three depths and composited for hourly samples. For each composite, the samples were filtered, rinsed, dried, and weighed to the nearest 0.01 mg. InterOceans S-4 and Niel Brown direct reading (DRCM) current meters were used to determine current speed and direction for 4-min periods and 2-min intervals, with measurements taken every 2 s. Results were then averaged over each hour for the reported values. Standard deviations (SD) of suspended solids data are reported in Table 1 as mean ± SD. Current meter error data were reported graphically, with no sample average varying by more than 8 cm/s.

RESULTS AND DISCUSSION

Gas/liquid

The gas/liquid concepts and formulas presented were applied to New Bedford Harbor, using literature and EPA field study values, with results summarized in Table 2. The air and water PCB concentrations used were maximum reported values to allow determination of worst possible exposure via these pathways. The PCB air concentrations used were 1.27×10^{-11} and 0.10×10^{-11} atm for Aroclors 1242 and 1254, respectively [31]. The PCB water concentrations used were 1.48×10^{-6} and 3.3×10^{-7} mol/m³ for Aroclors 1242 and 1254, respectively [22]. An annual sea surface temperature range of 0–30°C was determined from data in Signell [32]. A temperature range is considered because Burkhard et al. [33] show that flux rates can vary with variations in temperature. Flux is defined as a mass quantity per area and time. A minus sign on the flux values in Table 2 indicates a loss of contaminant from the aqueous phase to the air phase. The J_T value in Table 2 accounts for the molecular weight of the PCB and the surface area of the upper estuary to give more applicable units of mass per time. Temperature varying flux was only slight, but increased with increasing temperature. At present concentrations, 5.85–5.93 g of total PCBs/d escape to the atmosphere from the upper estuary, for 30°C and 0°C, respectively. Envoking required significant figures, these values become the same and translate into almost 2.2 kg/year of PCBs leaving the harbor water column to the atmosphere. This release directly exposes either New Bedford or Fairhaven, with the average wind speed in this area being 3 m/s [32]. These winds are predominantly northwesterly (toward New Bedford) in the winter and southwesterly (toward Fairhaven) in the summer. During dredge operations in the harbor, resuspended sediments potentially release PCBs to the water column. The PCB water concentrations up to four orders of magnitude less than solubility limits (9.86×10^{-5} mol/L for Aroclor 1242, 2.95×10^{-6} for Aroclor 1254 [34,35]) support this transfer of PCBs to the water column upon sediment mixing. These calculations indicate that additional atmospheric releases of PCBs may subsequently occur.

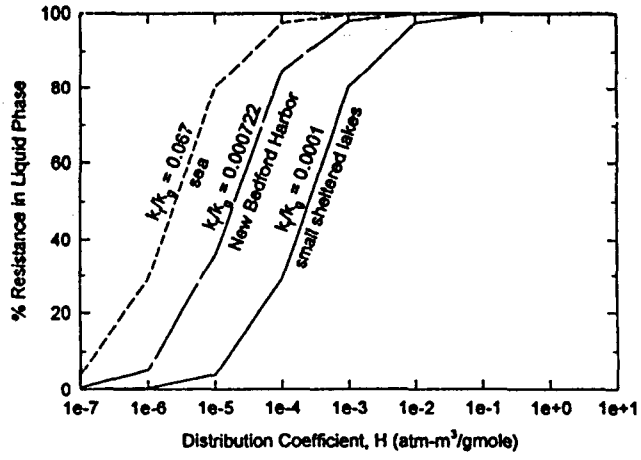

Fig. 2. Percent resistance (R_l) versus distribution coefficient. New Bedford Harbor lies between the oceanic and lake conditions [14–16].

The high values for R_l indicate that the vaporization of PCBs at the given liquid/gas concentrations will be liquid controlled, implying that the liquid phase concentration controls whether transfer will occur. Figure 2 shows the relationship between R_l, H, and k_l/k_g. Because New Bedford Harbor is an estuary, it has its own characteristic R_l versus H curve that lies between oceanic and lake conditions. Thus it appears New Bedford Harbor experiences enough ocean current turbulences to keep the gas transfer rate at the surface from stagnating, as would occur in very calm surface water environments. This figure also indicates that compounds with low aqueous solubility (high R_l) and high H are quickly removed from water, while those with high aqueous solubility (low R_l) and low H stay in solution. The PCBs

Table 2. Summary of calculated values for vaporization of PCBs from New Bedford Harbor

	0°C Aroclor 1242	Aroclor 1254	30°C Aroclor 1242	Aroclor 1254
k_l (m/d)	0.1619	0.1438	0.1619	0.1438
k_g (m/d)	224.3	199.2	224.3	199.2
k_l/k_g ($\times 10^{-4}$)	7.217	7.217	7.217	7.217
K_l (m/d)	0.144	0.122	0.142	0.120
K_g (m/d)	24.6	29.7	27.0	32.5
J (gmol/m²·d)($\times 10^{-7}$)	−2.00	−0.390	−2.00	−0.390
J_T (g/d)	−4.75	−1.18	−4.69	−1.16
R_l (%)	0.890	0.851	0.879	0.837

Table 3. Particle distribution coefficients for selected PCBs in New Bedford Harbor

Aroclor	K_{PD}	Source
1016	$10^{-2.2}$	[38]
1242	$10^{-2.3}$	[39]
1254	$10^{-2.3}$	[39]
1260	$10^{-0.4}$	[38]

fall within the range of compounds that are nearly insoluble, and thus if water column concentrations increase (i.e., as a result of dredge activity), PCB volatilization will also increase. For Aroclors 1242 and 1254, solubilities are 9.86×10^{-5} and 2.95×10^{-6} mol/L, respectively [36,37].

Another indicator of liquid/gas control is comparison of K_l and K_g to corresponding k_l and k_g as defined by Equations 7, 8, 10, and 11, respectively. Mackay [18] shows that if the liquid-phase controls, $k_l = K_l$ and if gas-phase controls, $k_g = K_g$, each indicating that the resistance across the liquid or gas layer, respectively, equals the total resistance. From Table 2, $k_l \approx K_l$ and $k_g \gg K_g$, so PCB gas–liquid transfer depends on the liquid concentration.

Sorption/desorption

K_{PD} values for all toxicants generally range from 10^{-10} to 10^2, with higher values indicating a greater affinity of the contaminant for the solid phase [20]. K_{PD} values for PCBs range from 10^{-2} to 10^0. Table 3 shows K_{PD} values determined for PCBs in New Bedford Harbor using Equation 12 and data from Wood et al. [38] when actual values were not available from Myers and Brannon [39]. Values range from $10^{-2.3}$ to $10^{-0.4}$. A value of 2.6% was determined for f_{oc} from New Bedford Harbor TOC data [19]. The K_{PD} values indicate compounds that will sorb to particulates with the sorption tendency increasing as K_{PD} increases. As sediment particles become available, free contaminant will sorb to the particles. The contaminant will have a greater area on which to sorb if more particles are present. As will be discussed, particle concentrations are high enough in New Bedford Harbor to promote sorption of contaminants to sediment particles. This is a potential concern when these contaminated sediment particles are transported to previously uncontaminated areas.

Sediment processes

Using data from the pilot study [30], Table 1 shows the change in suspended solids concentration over time at Coggeshall St. Bridge for two sampling periods. Summer (July) data revealed a high suspended solids load with greater ranges of total suspended solids between ebb and flood tides. The suspended solids increased during ebb tide and decreased during flood tide. This increase in suspended solids could be caused by several sources, most significantly biological growth, seasonal effects, horizontal processes, or physical mechanisms such as settling and resuspension. Our empirical model uses a combination of the latter two processes to describe suspended solids changes, as described in the following text.

First, to determine the significance of the biological growth contribution to suspended solids increase, we implemented some simple assumptions. Assuming bioactivity was responsible for suspended solids increase during ebb tide, the following mass balance expression was developed.

$$\frac{dSS}{dt} = -\frac{Q}{\forall}SS + a_g SS - a_d SS \tag{28}$$

The sink/source terms here include growth and death rates as, $a_g SS$ and $-a_d SS$, respectively. a_g and a_d are expressed in units of one over time, in this case, 1/d. Representing growth in this way assumes that SS represents all biological materials, as a worst case test. We conservatively assumed that a_d, as well as other sink terms, were negligible in determining a_g, which can be determined by rearranging Equation 26 as

$$a_g = \frac{\frac{dSS}{dt} + \frac{Q}{\forall}SS}{SS} \tag{29}$$

Using the empirical model to solve for a_g components during extreme shifts in suspended solids, yielded an a_g of approximately 7.7 per d. This calculated a_g is still too large to represent a reasonable growth rate for estuarine phytoplankton [40]. Even if all suspended solids activity at points of extreme shifts in suspended solids were caused by biological activity, the turnover rate is still too large to represent biological growth. Also a DOC of 4.6 mg/L [30] cannot support heterotrophic bacteria at the observed suspended solids concentrations. Therefore we assumed biological activity was negligible.

Next, seasonal effects on suspended solids and flow into and out of the harbor (i.e., measurements taken at Coggeshall St. Bridge [Fig. 1]) were considered. The average flow for each season (50 m^3/s for summer, 75 m^3/s for fall) was not constant, either as a reflection of wet and dry seasons or as a result of a different portion of the spring-neap cycle being considered. $QSS/\forall$ versus time is included in Figure 3 and shows the same cyclic pattern of tidal response as flow alone, but variation between seasons was not present. This means that the base mass loading, $QSS/\forall$, had a constant cycle and did not vary with seasons, verifying that seasonal effects are negligible for increase of suspended solids considerations. But it does seem like particles were less stable in summer with a wider range in total suspended solids values between tidal cycles.

Horizontal processes alone were considered by elimination of the sink/source terms from Equation 26 to yield,

$$\frac{dSS}{dt} = -\frac{Q}{\forall}SS \tag{30}$$

This equation assumes dSS/dt depends only on the base mass loading, which accounts for horizontal transfer of sediments. If this were correct, a positive correlation would exist between dSS/dt and $QSS/\forall$ over all cycles. There is no significant correlation between dSS/dt and $QSS/\forall$ with an r^2 of only 0.06. The lack of correlation indicates that some other sink/source terms must be present to account for the change in suspended solids concentration.

Aquatic organisms did not appear to account for increases and decreases of suspended solids on a tidal or seasonal basis nor did horizontal processes alone. Neither have winds been shown to cause appreciable resuspension. The upper estuary averages 3–5 m deep and the lower estuary depths closer to the hurricane barrier are up to 20 m. This supports the notion that physical processes such as settling and resuspension of particles control changes in the suspended solids concentration. This further supports the approach to use a deterministic V_{ss} based on experimental tests, considering only physical processes, and performed with sediments from New Bedford Harbor [25].

Equation 16, the basis for the empirical model, included r

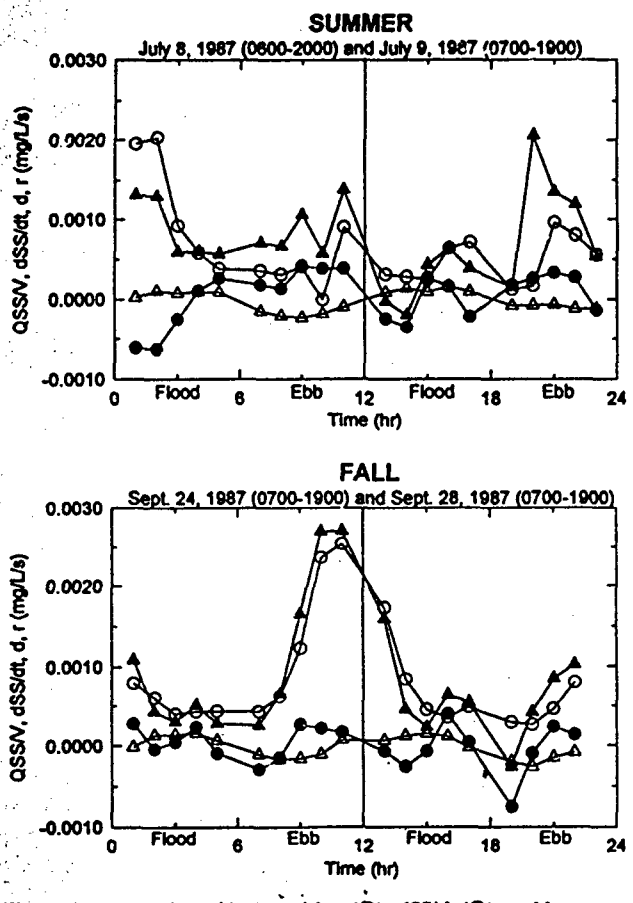

Fig. 3. Resuspension (▲), deposition (○), *dSS/dt* (●), and base mass loading (△) versus time from the empirical model. The resuspension and deposition track on one another, indicating a correlation and dependence on one another.

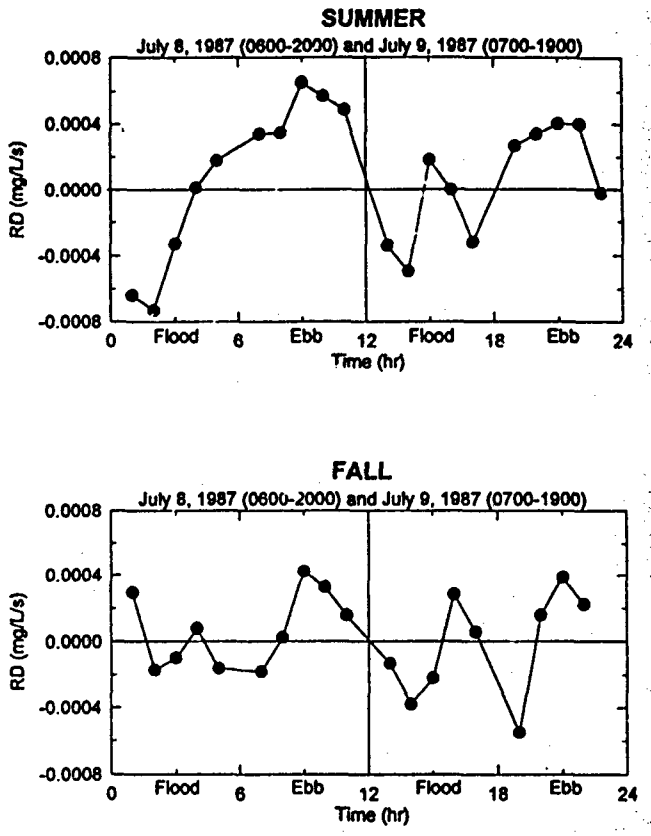

Fig. 4. Net resuspension and deposition versus time. Negative values correspond to deposition and positive values to resuspension, with deposition greater during flood tide and resuspension greater during ebb tide.

and d as sink/source terms in addition to $QSS/\forall$. For the model, r represented sediment resuspension and d represented sediment deposition. Figure 3 presents r, d, dSS/dt, and $QSS/\forall$ versus time, for comparison of suspended solids contributors. All of the terms are of the same magnitude. The r, d, and dSS/dt values tracked on one another, indicating positive correlation. For dSS/dt versus r, r^2 was 0.30 and for dSS/dt versus d, r^2 was 0.40. This means that resuspension and deposition were more driven by the change in suspended solids concentration than other factors considered. The fact that the values of r and d were noticeably greater than $QSS/\forall$ further reinforces this conclusion. Resuspension and deposition were the dominant processes considered in this system.

The recycle ratio, C_r, defined in Equation 22, further explained the relationship between r and d. Calculation of k_a and k_s from Equations 24 and 25, allowed determination of C_r. The maximum C_r value was 0.6, but the average was nearer to 0.25. This means that much recycle was taking place but deposition dominated resuspension as the net effect. Net deposition occurred in the New Bedford Harbor upper estuary. The settling dominance as reported by Sanders [25] further supports this observation.

An attempt to comprehend the interaction between r and d more fully was made by considering a net deposition term, RD, from the empirical model, where

$$RD = r - d \tag{31}$$

The result is presented in Figure 4. In this figure, positive values of RD are for resuspension and negative values are for deposition. The first half of each tidal cycle is flood tide and the last half is ebb tide, showing on the average, that deposition was greater during flood while resuspension was greater during ebb. Parts of the cycle (20 h) for September 28, 1987 varied from this trend. This could be caused by an unrecorded weather or tidal event. It is also possible this is an experimental artifact from smaller sample volumes taken for the 16-h and 20-h records [30]. The trends can be partly explained by considering that flood tide brings in water and sediments to the system; with the additional sediment, deposition must occur to maintain equilibrium. A similar, inverse phenomenon occurred during ebb tide when the water and suspended solids were removed. Resuspension adjusts the suspended solids concentration to account for the transport loss of sediments.

The deterministic model [27] provided a means for determining deposition in the empirical model, through V_{ss} (Eqn. 20). This was useful and necessary, but much more can be ascertained through the flocculation mechanisms that drive V_{ss} in the deterministic model. Using this approach, V_{ss} is a function of upper harbor weather conditions through the G term, which varies the hydrodynamic power dissipation. Using the G term is especially useful for representing wind-driven currents, a significant source of hydrodynamic effects [32]. This model considered three vertical transport mechanisms (Brownian motion, fluid shear, and differential settling). The results (Fig. 5) indicate that the dominant particle contact mechanism of those considered is driven by fluid shear. The volume fraction of particles

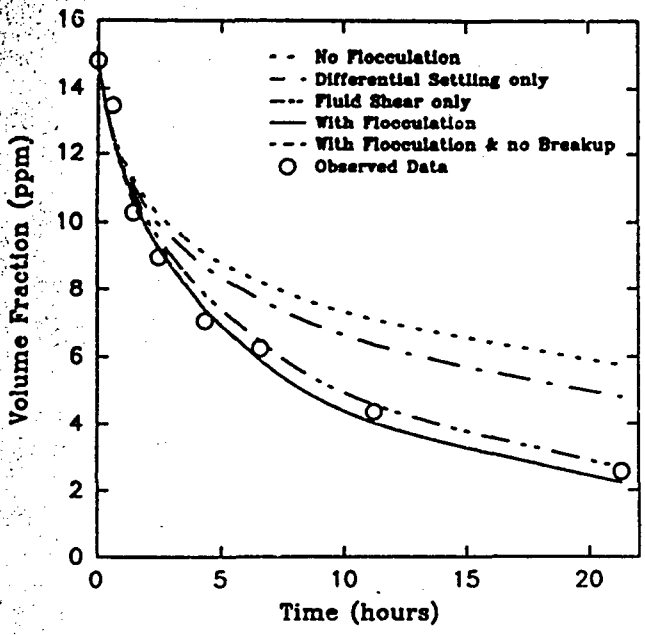

Fig. 5. Deterministic model particle column fraction versus time. The inclusion of differential settling and fluid shear as flocculation mechanisms gives the result closest to the observed value.

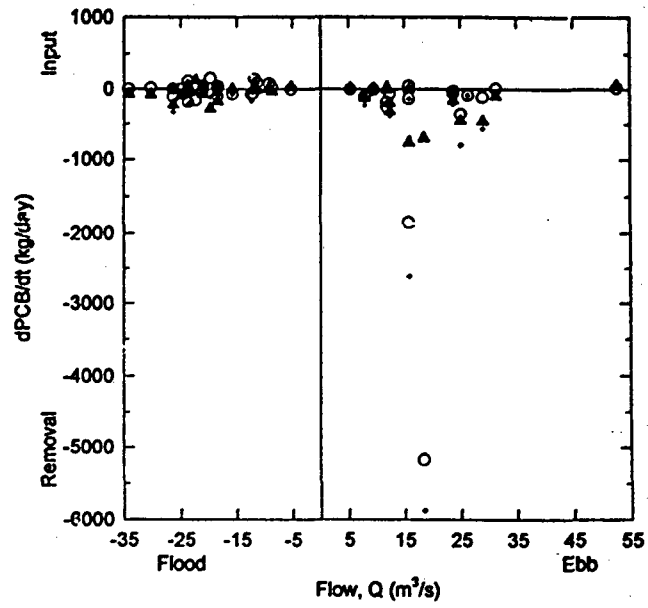

Fig. 6. Release of PCB as soluble (▲), particulate (○), and total (+) water concentration and its relationship to flow into and out of New Bedford Harbor at Coggeshall St. Bridge.

remaining decreased most rapidly when only fluid shear was considered. Brownian motion effects were negligible, as the curve with only Brownian motion considerations coincided with the response without flocculation occurring. By visual observation, differential settling alone accounted for approximately 30% of the mass removal. Fluid shear alone accounted for approximately 90% of the mass removal. When considering these mechanisms together, they account for 100% mass removal. Strict addition of these mechanisms was not possible because the fluid shear mechanism works more quickly than the differential settling mechanism. With both mechanisms at work, particle removal via fluid shear occurs before differential settling.

Overall

Gas and liquid interface processes are represented by air transport. The net result of this was up to 5.9 g/d PCB release from the harbor. Having average K_{PD} values near 10^{-2} m³/g, sorption/desorption processes showed that in the high particle concentration areas PCBs will sorb to the sediment, thus increasing concentration in the sediment. In Table 3, K_{PD} values increase with increase in percent chlorine, thus indicating greater sediment affinity with increase in percent chlorine. Physical properties of PCBs drive them toward sorption or volatilization. Their preferred phases are sediment and air due to their hydrophobicity. The influx of cleaner suspended solids to the upper estuary mixes with PCB-sorbed sediments. The dominant process depends on the specific PCBs or PCB mixtures present. Sediment affinity appears to decrease as percent chlorine or molecular weight decreases. This means the most toxic PCBs with greater chlorine percent will attach to sediments, allowing for greater ease in transport from the system.

Every model has uncertainties associated with it, arising from either numerical formulations or input data. Uncertainty and sensitivity of parameters in the deterministic model used are discussed in Bonner et al. [26]. The empirical model is based on field data, except for the settling velocity gleaned from the deterministic model. Uncertainty of the field data is discussed in that section of this document, with standard deviations of suspended solids data presented in Table 1. The experimentally verified deterministic settling velocity is incorporated into the deposition term of the empirical model. As such, when this value changes, both the resuspension and deposition results are affected. An order of magnitude increase in settling velocity will cause the deposition value to approach the resuspension value, while an equal decrease will cause the deposition value to approach zero. Sorption/desorption formulations are presented in Karickhoff et al. [19]. The K_{PD} calculation using this formulation resulted in values comparable to actual values for New Bedford Harbor (Table 3). The K_{PD} formulation is much less sensitive to f_{oc} changes than to K_{ow} changes. Even with a 100% organic carbon input value, the K_{PD} result is within an acceptable value range for K_{PD}.

Experimental tests reveal that the sediments of New Bedford Harbor will flocculate rapidly in the water column [25], settle out, and thus be exposed to PCBs present in the existing sediment. Data from the EPA support this PCB transfer process [22]. These data are presented in a diagram of flow versus *dPCB/dt* measured at Coggeshall St. Bridge (Fig. 6). Negative flow values represent flood tide and positive flow values ebb tide. Negative *dPCB/dt* values indicate PCB removal from the system. Removal of PCB from the system increases as flow out (during ebb tide) increases. Ebb tide was previously shown also to be the time of greatest solids input to the hot spot water column and when resuspension and deposition were greatest. As seen by the greater *dPCB/dt* removal values during ebb flow in Figure 6, up to 537.6 kg/d of soluble PCB is removed from the water. The particulate phase PCB, with 336 kg/d change, was more affected than soluble PCB by changes in flow. Rapid settling characteristics of the New Bedford Harbor sediments cause particles to fall out in the upper harbor before being horizontally transported from the hot spot at Coggeshall St. Bridge. Together these results describe the upper estuary as a depositional environment, in which particles entered, many particles flocculated out, others resuspended, and others were re-

moved by tidal currents. The PCB flux is a variable quantity dependent on many constantly changing factors.

CONCLUSIONS

Removal of PCBs from the upper estuary of New Bedford Harbor occurs by volatilization, sorption to sediment, and subsequent transport from the system by resuspension and tidal flows. From theoretical considerations PCBs volatilized at the rate of up to 5.9 g/d or 2.2 kg/year from New Bedford Harbor, this being immediately available in the atmosphere. Other theoretical properties of PCBs (K_{PD} range $10^{-2.3}$–$10^{-0.4}$ m³/g for Aroclor 1242 to Aroclor 1260; sediment affinity increases with increasing percent chlorine) and New Bedford Harbor conditions (high concentration of suspended sediments) showed that sorption to sediments is a preferred state for PCBs in water environments. An empirical model showed that sediments in the harbor are undergoing continuous resuspension to the water column and corresponding deposition, with deposition being dominant. Further study through a deterministic model with experimentally verified settling velocity revealed that the dominant mass removal mechanism involved in this sediment movement was fluid shear-driven flocculation. This was verified by field data demonstrating total particulate and soluble PCB removal at up to 873.6 kg/d during ebb flow, the greatest removal period. Combining these empirical and deterministic modeling efforts to take advantage of available experimental and field data is a unique approach that can be applied to other situations of limited field and experimental data. Under present conditions, PCBs are leaving the harbor, either by transport on the sediments or by volatilization to the atmosphere.

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REFERENCES

1. **Ikalainen, A.J. and L.H. Hall.** 1986. Project management plan for New Bedford Harbor, Massachusetts. U.S. Environmental Protection Agency, EPA Contract 68-01-7250, EPA Work Assign. 04-1L43. Narragansett, RI, USA.
2. **U.S. Environmental Protection Agency.** 1980. Ambient water quality criteria for polychlorinated biphenyls. EPA 440/5-80-068. Washington, DC.
3. **Averett, D.E.** 1988. New Bedford Harbor Superfund project Acushnet River estuary engineering feasibility study of dredging and dredged material disposal alternatives; report 3: Characterization of elutriate testing of Acushnet River estuary sediment. Technical Report EL-88-15. U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS, USA.
4. **National Research Council.** 1979. *Polychlorinated Biphenyls.* National Academy of Sciences, Washington, DC.
5. **Teeter, A.M.** 1988. New Bedford Harbor Superfund project Acushnet River estuary engineering feasibility study of dredging and dredged material disposal alternatives; report 2: Sediment and contaminant hydraulic transport investigations. Technical Report EL-88-15. U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS, USA.
6. **Amdur, M.O., J. Doull and C.D. Klassen, eds.** 1991. *Cassarett and Doull's Toxicology: The Basic Science of Poisons,* 4th ed. McGraw-Hill, Inc., New York, NY, USA, p. 600.
7. **Kannan, N., S. Tanabe, T. Wakimoto and R. Tatsukawa.** 1987. Coplanar polychlorinated biphenyls in Aroclor and Kanechlor mixtures. *J. Assoc. Off. Anal. Chem.* 70:451–454.
8. **Francingues, N.R., Jr., D.E. Averett and M.J. Otis.** 1988. New Bedford Harbor Superfund project, Acushnet River estuary engineering feasibility study of dredging and dredged material disposal alternatives; report 1: Study overview. Technical Report EL-88-15. U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS, USA.
9. **Sonzogni, W., L. Maack and T. Gibson.** 1991. Toxic polychlorinated biphenyl congeners in Sheboygan River (U.S.A.) sediments. *Bull. Environ. Contam. Toxicol.* 47:398–405.
10. **Palermo, M.R. and V.R. Pankow.** 1988. New Bedford Harbor Superfund project, Acushnet River estuary engineering feasibility study of alternatives for dredging and dredged material disposal; report 10: Evaluation of dredging and dredging control technologies. Technical Report EL-88-15. U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS, USA.
11. **Macdonald, C.R. and C.D. Metcalfe.** 1991. Concentration and distribution of PCB congeners in isolated Ontario Lakes contaminated by atmospheric deposition. *Can. J. Fish. Aquat. Sci.* 48:371–381.
12. **U.S. Department of Commerce.** 1991. Tidal current tables 1992: Atlantic coast of North America. National Oceanic and Atmospheric Administration, Rockville, MD, p. 108.
13. **Whitman, W.G.** 1923. The two-film theory of gas absorption. *Chem. Metal. Eng.* 29:146–148.
14. **Chapra, S.C. and K.H. Reckhow.** 1983. *Engineering Approaches for Lake Management,* Vol. 2. Mechanistic Modeling. Butterworth Publishers, Boston, MA, USA.
15. **Mackay, D.** 1978. Volatilization of pollutants from water. In O. Hutzinger, I.H. Lelyveld and B.C.J. Zoetman, eds., *Aquatic Pollutants: Transformations and Biological Effects.* Pergamon, Elmsford, NY, USA, pp. 175–186.
16. **Liss, P.S. and P.G. Slater.** 1974. Flux of gases across the air–sea interface. *Nature* 247:181–184.
17. **Cohen, Y., W. Cocchio and D. Mackay.** 1978. Laboratory study of liquid-phase controlled volatilization rates in presence of wind waves. *Environ. Sci. Technol.* 12:553–558.
18. **Mackay, D.** 1980. Solubility, partition coefficients, volatility, and evaporation rates. In O. Hutzinger, ed., *The Handbook of Environmental Chemistry: Reactions and Processes,* Vol. 2, Part A. Springer-Verlag, New York, NY, USA, pp. 31–46.
19. **Karickhoff, S.W., O.S. Brown and T.A. Scott.** 1979. Sorption of hydrophobic pollutants on natural sediments. *Water Res.* 13:241–248.
20. **Chapra, S.C.** 1991. Toxicant-loading concept for organic contaminants in lakes. *J. Environ. Eng.* 117:656–677.
21. **Brannon, J.M., T.E. Myers, D. Gunnison and C.B. Price.** 1991. Nonconstant polychlorinated biphenyl partitioning in New Bedford Harbor sediment during sequential batch leaching. *Environ. Sci. Technol.* 25:1082–1087.
22. **U.S. Environmental Protection Agency, Environmental Response Team.** 1983. Aerovox PCB disposal site, Acushnet River and New Bedford Harbor, Massachusetts: Tidal cycle and PCB mass transport study, January 10–12, 1983. Environmental Response Center, New Bedford Harbor archives, Edison, NJ.
23. **U.S. Department of Interior Geological Survey.** 1977. Map of New Bedford North Quadrangle, Massachusetts, 7.5 minute series. Reston, VA.
24. **Chapra, S.C. and R.P. Canale.** 1988. *Numerical Methods for Engineers.* McGraw-Hill, New York, NY, USA.
25. **Sanders, S.C.** 1990. Vertical transport and dynamic size distribution of New Bedford Harbor sediments. M.Sc. thesis. Texas A & M University, College Station, TX, USA.
26. **Bonner, J., A. Ernest, S. Sanders and R. Autenrieth.** 1994. Parameterizing models for contaminated sediment transport. In J.V. DePinto, W. Lick and J.F. Paul, eds., *Transport and Transformation of Contaminants Near the Sediment–Water Interface.* CRC, Boca Raton, FL, USA, pp. 281–306.
27. **Ernest, A., J. Bonner and R. Autenrieth.** 1995. Determination of inter-particle collision efficiencies for flocculent transport models. *J. Environ. Eng.* 121:320–331.
28. **Tracey, G. and T. Gleason.** 1988a. New Bedford Harbor pilot study, pre-operational monitoring—Progress report: Current meter studies at the Coggeshall Bridge during July 1987. EPA 68-03-

3528. U.S. Enviromental Protection Agency, Narragansett, RI. Appendix I.
29. Tracey, G. and T. Gleason. 1988. New Bedford Harbor pilot study, pre-operational monitoring—Progress report: Current meter studies at the Coggeshall St. bridge during September 1987. EPA 68-03-3528. U.S. Environmental Protection Agency, Narragansett, RI. Appendix II.
30. Scott, K.J. 1988. New Bedford Harbor pilot study, pre-operational monitoring—Progress report: Suspended solids measurements in New Bedford Harbor. EPA 68-03-3528. U.S. Environmental Protection Agency, Narragansett, RI, Appendix III.
31. Metcalf and Eddy, Inc. 1983. Acushnet River estuary PCB's data management, final report. EPA 68-04-1009. U.S. Environmental Protection Agency, Boston, MA.
32. Signell, R.P. 1987. Tide-/and wind-forced currents in Buzzards Bay, Massachusetts. Technical Report WHOI-87-15. Woods Hole Oceanographic Institute, Woods Hole, MA, USA.
33. Burkhard, L.P., D.E. Armstrong and A.W. Andren. 1985. Henry's Law constant for the polychlorinated biphenyls. *Environ. Sci. Technol.* 19:590–596.
34. Schulz, D.E., G. Petrick and J.C. Duinker. 1989. Complete characterization of polychlorinated biphenyl congeners in commercial Aroclor and Clophen mixtures by multidimensional gas chromatography-electron capture detection. *Environ. Sci. Technol.* 23:852–859.
35. Dunnivant, F.M., A.W. Elzerman, P.C. Jurs and M.N. Hasan. 1992. Quantitative structure–property relationship for aqueous solubilities and Henry's Law constants of polychlorinated biphenyls. *Environ. Sci. Technol.* 26:1567–1573.
36. Schulz, D.E., G. Petrick and J.C. Duinker. 1989. Complete characterization of polychlorinated biphenyl congeners in commercial Aroclor and Clophen mixtures by multidimensional gas chromatography-electron capture detection. *Environ. Sci. Technol.* 23:852–859.
37. Dunnivant, F.M., A.W. Elzerman, P.C. Jurs and M.N. Hasan. 1992. Quantitative structure–property relationship for aqueous solubilities and Henry's Law constants of polychlorinated biphenyls. *Environ. Sci. Technol.* 26:1567–1573.
38. Wood, L.W., G.-Y. Rhee, B. Bush and E. Barnard. 1987. Sediment desorption of PCB congeners and their bio-uptake by dipteran larvae. *Water Res.* 21:875–884.
39. Myers, T.E. and J.M. Brannon. 1988. New Bedford Harbor Superfund project, Acushnet River estuary engineering feasibility study of alternatives for dredging and dredged material disposal; report 5: Evaluation of leachate quality. Technical Report EL-88-15. U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS, USA.
40. Furnas, M.J. 1991. Net in situ growth rates of phytoplankton in oligotrophic, tropical shelf ecosystem. *Limnol. Oceanogr.* 36:13–29.