

Multimedia fate model of organic contaminants in Massachusetts Bay

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**MULTIMEDIA FATE MODEL OF ORGANIC CONTAMINANTS
IN MASSACHUSETTS BAY**

submitted to

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Executive Summary

We have developed a simple, multimedia contaminant fate model for Massachusetts Bay that is based on fugacity and intermedia-transfer concepts developed by Mackay (1991). We consider four bulk environmental compartments: air, water, soil, and bottom sediment, each consisting of subcompartments of air, water, inorganic matter, and organic carbon. This is a steady-state model and equilibrium is assumed to apply within each bulk compartment but not between bulk compartments. Contaminant input (source loading), output (advective flows and degradation reactions), and intermedia transport processes (both diffusive and non-diffusive) are included. Physical-chemical properties specific for each contaminant and environmental properties specific to Massachusetts Bay were used. This approach yields a relatively simple algebraic solution to the mass balance expression.

The model is applied to six organic chemicals that have a wide range of physical-chemical properties: benzene, naphthalene, benzo(a)pyrene, hexachlorobenzene, dieldrin, and 2,2',4,4',5,5' hexachlorobiphenyl (PCB 153). Each of these contaminants are discharged into Boston Harbor by the Massachusetts Water Resources Authority and each also has other sources to Massachusetts Bay. We present the model results for each contaminant in Massachusetts Bay under present conditions and calculate a mass balance.

We predict contaminant concentrations in each bulk compartment and compare these values with recent observations. We also calculate the relative importance of each transport and loss process and the mass-distribution of contaminants in the bulk compartments. Our results represent average steady-state conditions throughout a homogeneously-mixed Massachusetts Bays region. No site-specific or time-variant calculations were made, though relatively simple modifications to our model would allow estimates of these as well.

All of our calculated concentrations in water, sediment, and biota are in the range of reported observations, though for sediment and water, our calculations are consistently at the lower end of these ranges. This could result from an underestimate of the emission rates, but we suspect that it is more likely to result from a combination of errors in our assumed reaction and advection rates.

The calculated concentrations and the general fate and mass distribution profiles follow our intuitive understanding of these contaminants. The fate of the more water-soluble and volatile contaminants (benzene and naphthalene) are controlled by water and air processes. The more hydrophobic contaminants (benzo(a)pyrene, hexachlorobenzene, dieldrin, and PCB-153) are mostly bound to solid phases.

Atmospheric processes dominate the predicted fate for benzene, with reaction and advection in air accounting for nearly one-half and one-quarter of the total benzene loss, respectively. Water processes dominate the predicted fate for naphthalene with reactive loss about 40% and advective loss about 20% of the total. Solid phase processes are of greatest importance to the fate of benzo(a)pyrene and include soil reactions (36%), sediment burial (19%), and sediment reactions (11%). Nearly half of the hexachlorobenzene losses are through advection in the air. Dieldrin is lost almost equally through air advection (27%), water advection (28%), and soil reaction (27%). The PCB-153 congener is primarily lost through reactions in soil (42%), air advection (24%) and water advection (13%).

Predicted contaminant mass distributions indicate that nearly all the benzene is found in the water (72%) or the air (22%). Naphthalene is found in the soil (52%) and water (39%). Solid phases contain nearly all of the benzo(a)pyrene (soil: 68% and sediment: 30%), hexachlorobenzene (sediment: 78% and soil 19%), dieldrin (sediment 59% and soil:36%), and PCB-153 (soil: 66% and sediment: 32%).

The primary purpose of this study was to determine whether a simple multimedia fate model could reasonably describe the fate of contaminants in Massachusetts Bay. We believe that our model not only provides a reasonable evaluation of the relative importance of various fate processes, but that it also provides a reasonable (order of magnitude) approximation of concentrations in environmental media. The results indicate that our model can be used to evaluate the relative importance of various environmental fate processes and can provide approximate estimates of contaminant concentrations in water, sediment, and biota in Massachusetts Bay.

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1.0 INTRODUCTION

An important consideration in the management of the Boston Harbor — Massachusetts Bay — Cape Cod Bay (Massachusetts Bays) ecosystem is an understanding of the fate of toxic contaminants that enter the region. The major source of many contaminants to this region has been the municipal sewage and sewage sludge discharged in Boston Harbor by the Massachusetts Water Resources Authority (MWRA). By the middle of 1998, the MWRA is expected to begin discharging sewage through a new offshore outfall in Massachusetts Bay. The fate of contaminants that will be discharged through this new outfall has been the subject of several previous studies and reviews (MWRA, 1988; EPA, 1988; Shea and Kelly, 1992; EPA, 1993; Shea, 1994). The general consensus has been that discharge through the new outfall will cause little harm to the environment, but that very near the outfall diffuser there could be violations of human-health based water quality criteria and there likely will be a changed benthic environment. These predictions were based on conservative models that did not explicitly include numerous physico-chemical fate processes that could be very important in controlling the fate of contaminants discharged by the MWRA. In addition, there has been no rigorous attempt to develop a mass balance of contaminants in Massachusetts Bays, an accounting of the mass of contaminants that enter, leave, and become stored in the Bays. If we can develop a better understanding of the importance of the various fate processes and if we can account for the mass of contaminants in the Bays, we will likely have more accurate estimates of the exposure of marine organisms to effluent contaminants and we will be able to focus future efforts (modeling, monitoring, and interpreting) on obtaining more accurate site-specific or chemical-specific assessments. In this report, we present a multimedia contaminant fate model that can form the basis for these assessments.

The primary objective of this study was to determine whether a simple multimedia fate model could be used to establish the general fate profile expected for selected organic contaminants that are known to be discharged in the present MWRA effluent. Thus, the primary objective is evaluative. A secondary objective was to estimate order of magnitude concentrations of these organic contaminants in the major environmental media in the Massachusetts Bay ecosystem. We compare the estimated concentrations to measured concentrations to assess the accuracy of the model. We also summarize the relative importance of each contaminant removal process and the mass distribution of contaminants in various environmental compartments or media. This report focuses primarily on the concepts behind the model and we regard the predicted concentrations as more illustrative and speculative than definitive.

2.0 MODEL DESCRIPTION

We have developed a relatively simple steady-state contaminant fate model for Massachusetts Bay based on the Level III fugacity model developed by Mackay and co-workers (Mackay, 1991; Mackay and Patterson, 1991; Mackay *et al.*, 1992a, 1992b, 1993). Detailed descriptions of these models are given in these references; we only provide a brief summary of the model in this section.

We include four environmental media or bulk compartments — air, water, soil, and sediment. These compartments are treated as assemblies of subcompartments, which can consist of air, water, solid non-living matter, and living biotic matter. We assume that equilibrium (or equifugacity) is attained within each compartment (e.g., between sediment particles and porewater), but not between compartments (e.g., between sediment and overlying water). Thus, equilibrium partitioning processes and non-equilibrium reaction kinetics are explicitly considered. Intermedia transfer processes include both diffusive-transfer processes (e.g., volatilization) and nondiffusive or "one-way" transfer processes (e.g., wet deposition). In total, the model considers partitioning between 10 subcompartments, four separate compartment-specific reaction (degradation) rates, 13 intermedia-transfer processes, and advection in air and water.

Transfer processes are expressed in terms of "D" values as described by Mackay (1991). Each D value is a function of two terms: (1) a "Z" value which is the fugacity capacity and is derived from physico-chemical data for a specific chemical and (2) kinetic or transport rate terms such as a pseudo-first-order rate constant, a mass-transfer coefficient, or an advective flow rate. Partitioning of chemicals between phases is described by the equilibrium criterion of fugacity, f (Pa), which is a measure of the tendency (or driving force) of a chemical to escape a phase and can be considered to be the partial pressure of a chemical in a phase. Chemicals will spontaneously move from a phase of high fugacity to an adjacent phase of lower fugacity until the fugacities are equal (equilibrium between bulk phases is attained) unless, as we assume here, that equilibrium is not (necessarily) attained between phases. Fugacity is related to concentration (C) by the expression

$$C = fZ.$$

The fugacity capacity, or Z value, defines the capacity of a phase to accumulate a chemical, analogous to how heat capacity defines the capacity of a phase to accumulate heat. Chemicals will tend to accumulate in phases of higher fugacity capacity (e.g., hydrophobic chemicals will accumulate in fish tissue or sediment organic carbon). All chemical transport and transformation rates can be expressed as products of fugacities and D values. D values are summed and compared when the processes apply to the same source-phase fugacity.

Chemicals move between phases by both diffusive and non-diffusive processes. The diffusive flux, N, between two phases, 1 and 2, is described by

$$N = D (f_1 - f_2)$$

where D is a transfer coefficient and f_1 and f_2 are the fugacities for phases 1 and 2, respectively. The difference between f_1 and f_2 determines the direction of diffusive flux, moving from high fugacity to low fugacity. D is a function of Z values, interfacial areas, and diffusive properties in adjacent phases. Nondiffusive processes such as sediment deposition or resuspension also are described by a transport parameter

$$N = GC = GZf = Df$$

where G is the volumetric flow rate of the transported material (e.g., sediment). Diffusive and nondiffusive D values are then summed for all transfer processes from phase 1 to phase 2 (D_{12}) and phase 2 to phase 1 (D_{21}). The net flux from phase 1 to 2 is

$$N = D_{12} f_1 - D_{21} f_2$$

First order reactions in a phase (e.g., decay rates) can be described by

$$N = k_R VC = k_R VZf = D_R f$$

where k_R is a first order rate constant and V is the phase volume.

The reason that we are using the equilibrium criterion of fugacity is that we can simplify the algebraic solution to a chemical mass balance compared to that obtained using traditional concentration-based mass balance equations. The two alternative approaches yield identical results (Mackay, 1991). The conceptual approach of our model is illustrated in Figure 1. Properties of each environmental compartment are listed in Table 1. For each subcompartment in Table 1, a Z value is calculated and then combined with the volume fractions to give an overall Z value for the compartment as described by Mackay (1991). The physico-chemical properties of the chemicals we have selected are listed in Table 2.

We have made several assumptions in this model. We assume that equilibrium exists within each compartment, but not between compartments. Air consists of air and particulate matter (or aerosols) and these particles occupy the equivalent of $50 \mu\text{g}/\text{m}^3$. Water consists of seawater containing suspended sediment and fish with octanol-like organic carbon or lipid fractions of 0.2 and 0.05, respectively; and volume fractions equivalent to 5 mg/L and 1 ppm, respectively. The volume fraction of fish (1 ppm) is unrealistically high, but represents a rough maximum total biota and has no effect on the overall mass balance. Soil is a mixture of a solid phase (volume fraction of 0.5), air (volume fraction of 0.2), and water (volume fraction of 0.3). The fraction of organic carbon in the solid phase is 0.02 and the density is 2.4 kg/L. Sediment is a mixture of solids (volume fraction of 0.3, organic carbon fraction of 0.04, density of 2.4 kg/L) and pore water (volume fraction of 0.7).

Two loss processes are considered, advection and irreversible decay reactions. Air and water advective flow rates correspond to residence times of 1 and 30 days, respectively. Three pseudo-advective processes are air transfer to higher altitude (0.01 m/h), leaching from soil to groundwater (at 40% of rain rate on soil), and sediment burial or net sedimentation (at 0.75 mm/y solids) which is equal to the difference between sediment deposition and resuspension rates. These velocities are listed in Table 3. Reaction rates are included as pseudo-first-order decay constants derived from chemical-specific rates of biodegradation, photolysis, oxidation, and hydrolysis (Mackay, 1991; Mackay *et al.*, 1992a, 1992b, and 1993). Intermedia transport parameters are listed in Table 3 and are derived or taken directly from Mackay (1991) and Mackay *et al.* (1992a, 1992b, and 1993). These parameters are converted to D values as described above and by Mackay (1991). Emission rates are from Alber and Chan (1994), Bigornia-Vitale and Sullivan (1993), Golomb *et al.* (1994), Hunt (pers. comm., 1995), Mackay (1991), Menzie-Cura & Associates (1991), Shea (1994), and Uhler and West (1994).

Steady-state mass balance equations were established for each of the four bulk compartments including terms for contaminant loading, advection, reaction, and transfer between adjacent compartments. These equations were solved as described by Mackay (1991).

Our model was validated for comparability with the fugacity models developed by Mackay and coworkers by using input data from generic, evaluative models published by Mackay (1991) and Mackay and Patterson (1991), and comparing our model results with the published values. Model results were identical for benzene, naphthalene, benzo(a)pyrene, and hexachlorobenzene; there are no published results for dieldrin or PCB-153. Thus, our model is mathematically comparable to that developed by Mackay (1991). However, our model of Massachusetts Bay uses input values specific for this region and the only way to "validate" this model is to compare the model results to recent observations and/or conduct specific studies to verify assumed parameter values (e.g., mass-transfer coefficients).

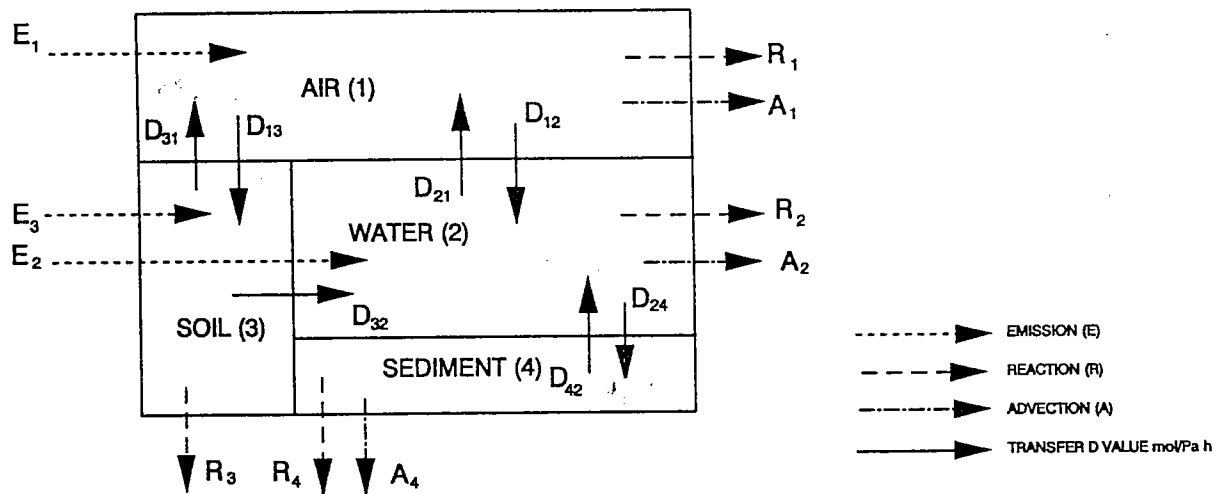


Figure 1. Illustration of the multimedia contaminant fate model for Massachusetts Bay.

| Table 1. Properties of the Environmental Compartments | | | | | | |
|--|--|--------------|---------------------|------------------|----------------------------------|-----------------------|
| Bulk Compartment | <u>Subcompartment Volume Fraction</u> | | | | Areas (m²) | Depths (m) |
| | Air | Water | Solids | Biota | | |
| Air | 1.0 | 0.0 | 2x10 ⁻¹¹ | 0.0 | 7.6x10 ⁹ | 1000 |
| Water | 0.0 | 1.0 | 5x10 ⁻⁶ | 10 ⁻⁶ | 3.6x10 ⁹ | 40 |
| Soil | 0.2 | 0.3 | 0.5 | 0.0 | 4.0x10 ⁹ | 0.1 |
| Sediment | 0.0 | 0.7 | 0.3 | 0.0 | 9.0x10 ⁸ | 0.01 |

¹ Density (kg/m³) of bulk compartments: air (1.19), water (1000), soil (1500), sediment (1420).

² Density (kg/m³) of subcompartments: air (1.19), water (1000), solids (2400), biota (1000).

³ Fraction of organic carbon in solids: water (0.2), soil (0.02), sediment (0.04)

⁴ Area for soil represents an arbitrary land mass adjacent to the water.

| Table 2. Physical-Chemical Properties of Selected Contaminants | | | | |
|---|-----------------------------------|--------------------------------|---|---------------------------|
| Contaminant | Molecular Mass (g/mol) | Vapor Pressure (Pa) | Solubility (g/m³) | log K_{ow} |
| benzene | 78.11 | 1.3x10 ⁴ | 1.8x10 ³ | 2.13 |
| naphthalene | 128.18 | 1.0x10 ¹ | 3.1x10 ¹ | 3.37 |
| benzo(a)pyrene | 252.32 | 7.0x10 ⁻⁷ | 3.8x10 ⁻³ | 6.04 |
| hexachlorobenzene | 284.8 | 1.5x10 ⁻³ | 5.0x10 ⁻³ | 5.47 |
| dieldrin | 380.9 | 4.0x10 ⁻⁴ | 2.0x10 ⁻¹ | 4.85 |
| PCB-153 | 360.88 | 1.2x10 ⁻⁴ | 1.0x10 ⁻³ | 6.90 |

| Table 3. Multimedia Transport Parameters | |
|--|--|
| Parameter | Value |
| air-side MTC ¹ over water | 3 m/h |
| water-side MTC | 0.03 m/h |
| transfer rate to higher altitude | 0.01 m/h (90 m/y) |
| rain rate (m ³ rain/m ² area x h | 9.7 x 10 ⁻⁵ m/h (0.85 m/y) |
| scavenging ratio | 2.0 x 10 ⁵ |
| dry deposition velocity | 10.8 m/h (0.003 m/s) |
| air-side MTC over soil | 1 m/h |
| diffusion path length in soil | 0.05 m (half of assumed soil depth) |
| molecular diffusivity in air | 0.04 m ² /h |
| molecular diffusivity in water | 4.0 x 10 ⁻⁶ m ² /h |
| water runoff rate from soil | 3.9 x 10 ⁻⁵ m/h (0.34 m/y) |
| solids runoff rate from soil | 2.3 x 10 ⁻⁸ m ³ /m ² h (0.0002 m/y) |
| water-side MTC over sediment | 0.01 m/h |
| diffusion path length in sediment | 0.005 m (half of sediment depth) |
| sediment deposition rate | 0.001 m/y |
| sediment resuspension rate | 0.00025 m/y |
| sediment burial rate | 0.00075 m/y |
| leaching rate to groundwater | 0.44 m/y (40% of rain rate) |

¹ MTC: mass-transfer coefficient

3.0 MODEL RESULTS AND IMPLICATIONS

Calculated concentrations are compared to recently-observed compartment concentrations in Table 4 for water and sediment. All of our calculated concentrations are in the range of reported values, though they are consistently at the lower end of this range for water and sediment. This could result from an underestimate of the emission rates, but we suspect that it is more likely to result from a combination of errors in our assumed reaction and advection rates (Table 3). Given the intended purpose of this preliminary modeling effort, the agreement in Table 4 is actually quite good. Our low sediment estimates could be reflecting the lower emission rates into Massachusetts Bays relative to historical emissions. This would not be evident in recent measurements of surface sediments because mixing of older (i.e., 10 years) sediments with less-contaminated, recent sediments would mask the lower concentrations. This would not be true in the water column, where the residence time is much shorter. However, our calculated values for water are in very good agreement with some of the most recent measurements in Massachusetts Bay (Menzie-Cura, 1993).

| Table 4. Comparison of calculated (calc) and observed (obs) concentrations in Massachusetts Bays¹ | | | | | | |
|---|---------------------|------------|---------------------------------|------------|------------------------|------------|
| Contaminant | Water (ng/L) | | Biota (ng/g)² | | Sediment (ng/g) | |
| | calc | obs | calc | obs | calc | obs |
| benzene | 0.01 | <5-50 | NA ³ | NA | 0.02 | <1 |
| naphthalene | 0.2 | <0.1-20 | NA | NA | 8 | 2-280 |
| benzo(a)pyrene | 0.05 | <0.01-3 | NA | NA | 22 | 4-680 |
| hexachlorobenzene | 0.09 | <0.01-1 | 1.3 | 0.25-2 | 0.28 | 0.03-8 |
| dieldrin | 0.03 | <0.01-1 | 0.11 | 0.1-0.5 | 0.19 | 0.07-3 |
| PCB-153 | 0.04 | <0.01-1 | 16 | 2-20 | 0.12 | 0.10-12 |

- ¹ Observed values are from MWRA (1988), Shea *et al.* (1991), Shea and Kelly (1992), Shea and Seavey (1995), Shea (unpublished data).
- ² Biota was calculated using $C_f = C_w \times 0.05 \times K_{ow}$, where C_f is the conc. in the fish, C_w is the conc. in the water, and 0.05 is the fraction of lipid in the fish.
- ³ NA: not applicable because these contaminants are readily metabolized by biota.

The relative importance of the various reaction and advection processes are summarized in Figure 2. Atmospheric processes dominate the predicted fate for benzene, with reaction and advection in air accounting for nearly one-half and one-quarter of the total benzene loss, respectively. Advective (12%) and reactive (14%) losses in water account for the remainder of the benzene loss in the Massachusetts Bays region.

Water processes dominate the predicted fate for naphthalene with reactive loss about 40% and advective loss about 20% of the total. Advective (15%) and reactive (22%) losses in air account for most of the remainder of the naphthalene loss, with reactive loss in soil (7%) the only other process of significance.

Solid phase processes are of greatest importance to the fate of benzo(a)pyrene and include soil reactions (36%), sediment burial (19%), and sediment reactions (11%). Water advection (17%) and water reaction (9%) are also significant. Advective (5%) and reactive (3%) losses in air account for the remaining loss processes.

Nearly half of the hexachlorobenzene losses are through advection in the air. The remaining losses are through water advection (17%), water reaction (4%), soil reaction (15%), sediment burial (8%), sediment reaction (3%), and air reaction (5%).

Dieldrin is lost almost equally through air advection (27%), water advection (28%), and soil reaction (27%). The remaining losses are through sediment reaction (5%), sediment burial (8%), air reaction (3%), and water reaction (1%).

The PCB-153 congener is primarily lost through reactions in soil (42%), air advection (24%) and water advection (13%). Sediment processes are significant with reaction (9%) and advection (7%) losses.

Predicted contaminant mass distributions are shown in Figure 3. Nearly all the benzene is found in the water (72%) or the air (22%). Naphthalene is found in the soil (52%) and water (39%). Solid phases contain nearly all of the benzo(a)pyrene (soil: 68% and sediment: 30%), hexachlorobenzene (sediment: 78% and soil 19%), dieldrin (sediment 59% and soil:36%), and PCB-153 (soil: 66% and sediment: 32%).

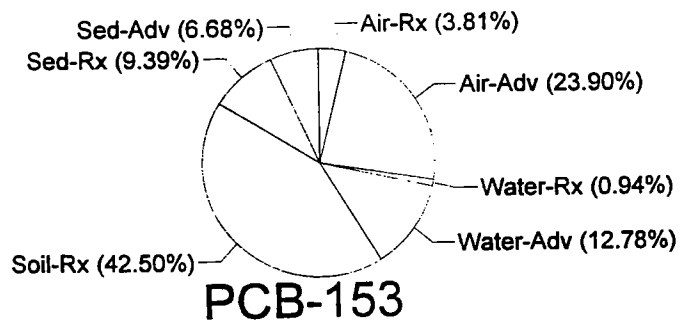
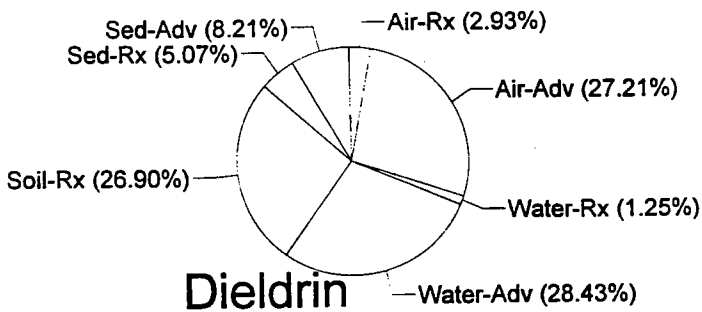
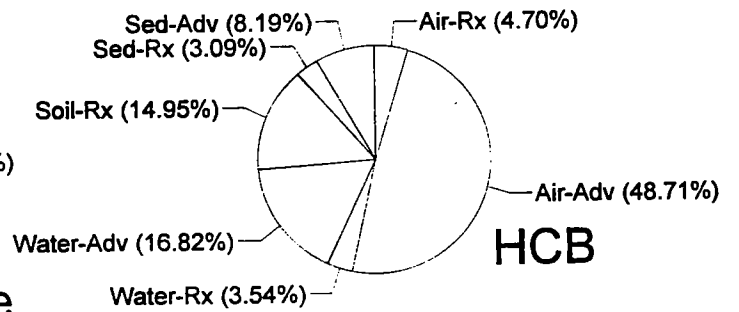
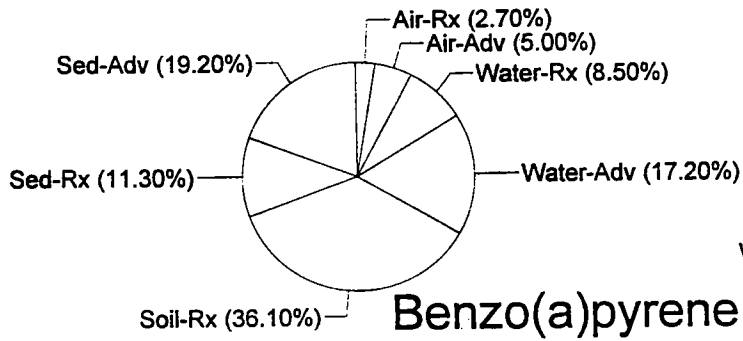
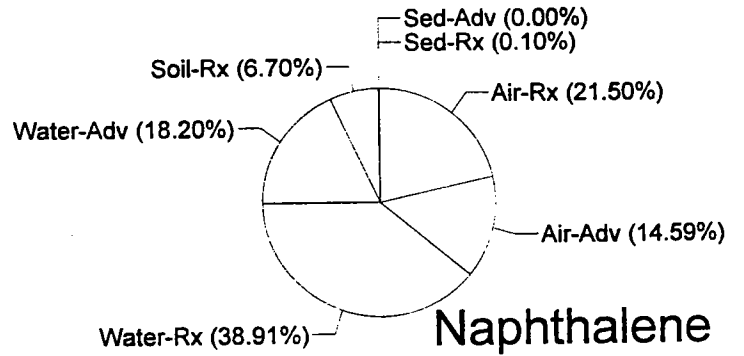
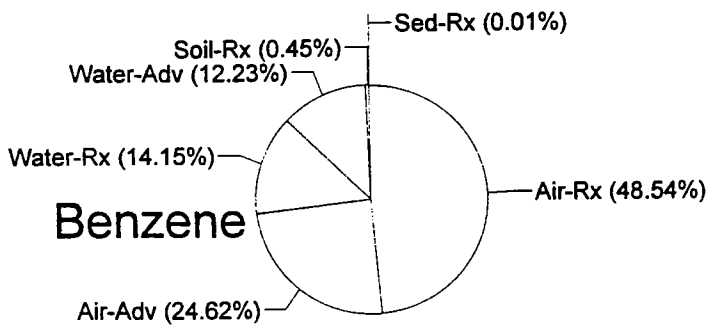


Figure 2. Contaminant removal distributions for the Massachusetts Bays region.

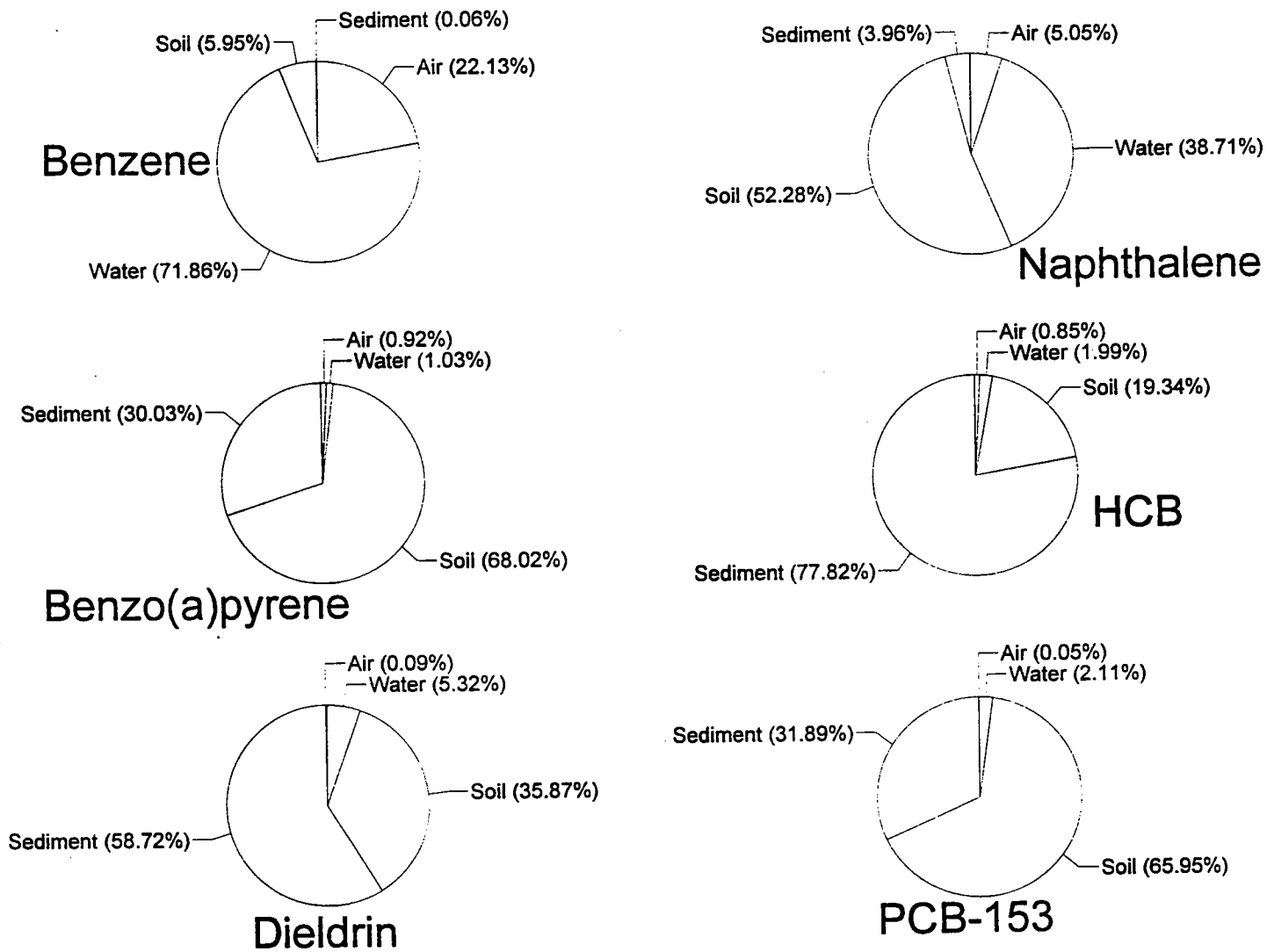


Figure 3. Contaminant mass distributions for the Massachusetts Bays Region.

The calculated concentrations (Table 4) and the general fate and mass distribution profiles (Figures 2 and 3) follow our intuitive understanding of these contaminants. The fate of the more water-soluble and volatile contaminants (benzene and naphthalene) are controlled by water and air processes. The more hydrophobic contaminants (benzo(a)pyrene, hexachlorobenzene, dieldrin, and PCB-153) are mostly bound to solid phases. Differences among the more hydrophobic contaminants are related to differences in their physical-chemical properties (Table 2) and to differences in the estimated emissions to the bulk compartments (air, water, and soil). These differences are somewhat speculative because of the large uncertainty in these emission estimates.

It is important to keep the unknown (or poorly characterized) uncertainty of our model parameters in perspective when viewing the model results. Poor agreement between the model and the measurements indicates that model refinement is necessary. The converse is not necessarily true; a good fit could be a fortuitous result of multiple errors in source loads and model parameters. Consequently, we suggest that the reader focus primarily on the concepts behind the model and the general fate profiles, and regard the predicted concentrations as more illustrative and speculative than definitive.

The primary purpose of this study was to determine whether a simple multimedia fate model could reasonably describe the fate of contaminants in Massachusetts Bay. We believe that our model not only provides a reasonable evaluation of the relative importance of various fate processes, but that it also provides a reasonable approximation of concentrations in environmental media. However, we also believe that more work is necessary before we would place much confidence in the absolute model calculations. Below, we suggest areas where additional work is necessary to either refine the multimedia fate model or to modify the model for different environmental scenarios and contaminants.

Sensitivity analysis would provide insight into which parameters have the greatest effect on the model results, and thus would allow for a more critical review of the model itself. Given the modest effort required for sensitivity analysis, we recommend that this be performed next. In addition, the accuracy of the source loadings could be improved when additional source terms are better quantified. In particular, new source loadings for atmospheric deposition, the Merrimack River, other tributaries and coastal dischargers, and the MWRA effluent will be available in the near future (M. Liebman and C. Hunt, pers. comm., 1995). The model should be rerun when these new source loadings are available.

We modeled only one scenario in this report: the present conditions and the entire Massachusetts Bays region. Modifications to our model could be used to answer the following questions about future environmental conditions in Massachusetts Bay and future recovery of Boston Harbor.

- (1) What will happen after the new MWRA outfall is online, both within the nearfield sampling region and in the entire Massachusetts Bay region?
- (2) What is the contaminant mass balance within Boston Harbor, where we have greater certainty in the emission rates and other model parameters?
- (3) What is the mass balance for other contaminants of concern? This could include other organic contaminants measured in the MWRA effluent and in Massachusetts Bay sediment and biota and/or contaminants that presently are not measured, but could have significant ecological importance (e.g., the environmental estrogen - nonylphenol). Trace metals also could be included, but the intermedia transport parameters used here for organic contaminants are not applicable to trace metals.
- (4) What about unsteady-state conditions? We could modify this model to incorporate unsteady-state conditions by solving numerically for the differential equations that correspond to the steady-state fugacity equations used in this report. This would provide the ability to determine how long it will take to reach steady-state conditions after the new outfall is online or how long it will take for Boston Harbor to recover to acceptable conditions. In theory, this would also allow the fate model to be linked to the USGS hydrodynamic model or to a geographic information system (GIS) so that unsteady-state modeling could be performed along the spatial grids of the USGS model or the GIS, rather than as a homogeneously mixed box. This would also allow the modeling to be performed under a single interface by incorporating model algorithms in the USGS model or the GIS.

Given the general success that we have had with this model and the relative ease with which the model can be modified, we are cautiously optimistic that the modifications listed above will lead to a significant improvement in our ability to predict environmental consequences of the new MWRA outfall and to evaluate other environmental scenarios. This would provide a valuable tool to help to manage the Massachusetts Bay ecosystem.

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