

*San Francisco Estuary Regional Monitoring Program for Trace Substances*

# **A Simple Mass Balance Model for PAH Fate in the San Francisco Estuary**

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## ABSTRACT

In the San Francisco Estuary (California, USA), polycyclic aromatic hydrocarbons (PAHs) have been identified by local regulatory agencies as potential threats to water quality. Increasing urbanization in this densely populated region may increase PAH loading in the future, making it important to estimate loading and the long-term fate of PAHs. We present findings from a mass balance model that simulates the cycling of PAHs in the San Francisco Estuary. The model was previously developed for PCBs (Davis, 2003; Davis, 2004), and treats the Estuary as a single box with interacting water and sediment compartments. The model explicitly incorporates loading, volatilization, outflow to the ocean, degradation, and burial in deep sediment. Model results vary widely depending on the PAH compound modeled; this variation predominantly results from differences in degradation rates and octanol-water partition coefficients. In the absence of loading, the estimated time required for loss of one-half of the mass in the Estuary ranges from 21 days for naphthalene to five years for benzo(b)fluoranthene. Uncertainty analysis using Monte Carlo simulation indicates a high degree of influence and uncertainty for degradation rates, suggesting that improved estimates of degradation would significantly improve predictive ability of the model.

## ABBREVIATIONS USED

PAH = polycyclic aromatic hydrocarbon  
LPAH = Low molecular weight PAH (having 2 or 3 aromatic rings)  
HPAH = high molecular weight PAH (having 4, 5 or 6 aromatic rings)  
MTC = mass transfer coefficient  
HLC = Henry's law constant  
 $K_{ow}$  = octanol-water partitioning coefficient  
RMP = Regional Monitoring Program for Trace Substances  
BPTCP = Bay Protection and Toxic Cleanup Program  
SFEI = San Francisco Estuary Institute  
The Estuary = The San Francisco Estuary  
TMDL = Total Maximum Daily Load  
USGS = U.S. Geological Survey

## INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) constitute a potential environmental threat because they pose hazards to fish and wildlife at environmentally relevant concentrations (e.g., Long et al., 1995; Carls et al., 1999) and because they have elevated environmental concentrations in urbanized and industrial areas (e.g., Spies and Rice, 1988; Lun et al., 1998; Mackay and Hickie, 2000; McCain et al., 2000; Su et al., 2000). The actual threat posed by PAHs to an ecosystem depends on the sensitivity of resident organisms, present and future PAH loading rates, and long-term environmental

persistence. Environmental fate models can be useful for estimating loading and long-term fate of compounds such as PAHs, and identifying key data gaps in understanding these processes (e.g., Mackay et al., 1994; Lun et al., 1998; Davis, 2004).

In the San Francisco Estuary, PAH concentrations dramatically increased in the early 20th-century with the advent of industrialization. Historic sources (wood-burning, peat, and naturally occurring fossil fuels) have been augmented by sources associated with increased population density and industrial activity (coal burning and fossil-fuel combustion) (Pereira et al., 1999). At present, some locations in the Estuary have among the highest sediment PAH concentrations of all sites monitored on the U.S. Pacific Coast (McCain et al., 2000). Furthermore, Estuary sediment PAH contamination is correlated with adverse impacts on fish and invertebrates (Spies and Rice, 1988; Thompson et al., 1999). With the projected future increase in human population (ABAG, 2002) and automobile use in the region, the extent of local contamination may also increase. Due to the presence of PAHs at concentrations that may adversely impact aquatic animals, the San Francisco Bay Regional Water Quality Control Board placed PAHs on a 303d watch list of compounds that may be impairing San Francisco Bay, for which further study is needed (SFBRWQCB, 2001).

Contaminant environmental fate models can be very helpful for identifying which chemical properties are most influential for a contaminant's fate within an ecosystem. This is valuable for PAHs because there is a wide range of compounds, each having a range of available estimates for their chemical properties. Recent studies bring into question previous methods of estimating Henry's law constants (Bamford et al., 1999) and degradation rates (Talley et al., 2002), and there are wide ranges of published values. Other traits, such as mass transfer coefficient between air and water, have not been experimentally determined and must be estimated using theoretical methods (e.g., Tucker and Nelken, 1982). If models indicate that certain chemical properties are not influential on environmental fate, then estimation accuracy becomes less of a concern.

Since 1993, the Regional Monitoring Program for Trace Substances (RMP) has collected annual data on PAH concentrations in the Estuary in water, sediments, and bivalves. In recent years, the RMP has begun developing contaminant mass balance models in order to synthesize these and other data, identify and prioritize data gaps, and determine the long-term fate and ecological impact of priority contaminants. The first mass balance model achieves these objectives for PCBs (Davis, 2004) by simulating the Estuary in a single box long-term fate model. This report presents the application of the Davis (2004) mass balance model to the fate of PAHs in the San Francisco Estuary.

This modeling exercise has three major objectives. First, the report synthesizes relevant literature values and local data on PAH chemical properties, current concentrations, and recent time trends. Secondly, sensitivity and uncertainty analyses illustrate the influence of different PAH chemical properties, and provide an indication of which parameters must be more accurately characterized to improve confidence in the results. This provides the basis for recommendations on future research directions. Finally, the model predicts the loss rate of several representative PAHs from the Estuary,

which helps in understanding how quickly the ecosystem would be expected to respond to load reductions.

## **METHODS**

### ***Study Area Description***

San Francisco Bay is the largest estuary on the Pacific coast of both North and South America. The landward boundary of the Bay is at the confluence of the Sacramento and San Joaquin rivers. The seaward boundary is the Golden Gate, where the Bay empties into the Pacific Ocean. The watershed of the Bay encompasses 40 % of the land area of California, including the expansive agricultural land of the Central Valley lying between the Sierra Nevada mountains on the east and the Coast Range on the west. The Bay is a complex ecosystem, exhibiting considerable variability at multiple temporal scales due to tidal action, climatic variation, and strong seasonal and interannual variability in rainfall in a Mediterranean climate. The Bay is also heterogeneous spatially, with large differences in residence time and other hydrodynamic properties among the major subembayments (Smith, 1987). The Bay is surrounded by the fourth largest metropolitan area in the U.S. and the nation's historically most productive mercury mining region. Due to a combination of water diversion, introduction of nonnative species, habitat alteration, and contamination the Bay is considered perhaps the most highly altered coastal ecosystem in the U.S. In spite of this history of ecological damage, the Bay remains a highly productive ecosystem that sustains a diversity of wildlife and a food supply for Bay Area anglers.

Primary PAH sources to San Francisco Bay include combustion processes, associated with urbanization and industrialization (Oros and Ross, 2004). Dated sediment cores indicate significant increases in fossil fuel combustion since the 1950s (Pereira et al., 1999), likely associated with the substantial vehicle traffic in the San Francisco Bay area. PAHs are loaded to the Bay via direct atmospheric deposition (Tsai et al., 2002), runoff from small urban rivers and storm drains (Gunther et al., 1991; Maruya et al., 1996; Davis et al., 2000), and loading from large rivers draining the San Jose metropolitan area watersheds and Central Valley (Gunther et al., 1991; Davis et al., 1999).

The PAH profile of San Francisco Bay predominantly consists of high molecular weight PAHs. Fluoranthene, pyrene, benzo(b)fluoranthene, and benzo(g,h,i)perylene are relatively abundant in sediment and phenanthrene, fluoranthene, and pyrene are relatively abundant in water (Table 1). The high ratio of phenanthrene to methylphenanthrene, indicates predominantly pyrogenic sources, possibly including automotive and diesel fuel combustion and biomass burning (Table 1; Risebrough, 1994; Maruya et al., 1996; Pereira et al., 1999; Oros and Ross, 2004). Concentrations are generally below regulatory criteria promulgated by the California Toxics Rule (U. S. EPA, 2000), although some compounds occasionally exceed screening values (Table 1; SFBRWQCB, 2001).

## *The Model*

This model treats the Estuary as one box with a water and sediment compartment. It incorporates the major mechanisms of transport between the water and sediments and also determines loss rate from the Estuary. Loss processes include outflow, degradation, volatilization, and sediment burial (Table 2). Many of the model attributes, including water flow rate, sediment deposition and transport, active sediment depth, and burial (all presented in Davis, 2004), are independent of the contaminant modeled, making it possible to efficiently reapply the model to other contaminants monitored by the RMP.

This mass balance model was originally developed by Mackay et al. (1994) for Lake Ontario and applied to the San Francisco Estuary by Davis (2004). Both authors present detailed discussions of the equations, structure, and assumptions of this model. Davis develops model parameters for the physical properties of the San Francisco Estuary (summarized in Table 3). The reader is referred to these reports for detailed discussion of the model, including how environmental parameters were estimated and incorporated. Model spreadsheets may be obtained by contacting us.

A brief summary of the model follows. The model represents contaminant loss pathways, treating the San Francisco Estuary as two well-mixed compartments, the water column and the active sediment layer. Inputs and losses to the water column and the active sediment layer are represented by two mass balance equations:

$$\Delta M_w/\Delta t = L + k_{sw} * M_s - (k_v + k_o + k_{wr} + k_{ws}) * M_w$$

$$\Delta M_s/\Delta t = k_{ws} * M_w - (k_{sw} + k_b + k_{sr}) * M_s$$

The two equations represent the change in water column PAH mass ( $M_w$ ) and sediment PAH mass ( $M_s$ ) over time. Each "k" is a daily rate constant, indicating the daily proportion of present PAH mass transformed and moved by volatilization ( $k_v$ ), outflow ( $k_o$ ), degradation in water ( $k_{wr}$ ), water to sediment transport ( $k_{ws}$ ), sediment to water transport ( $k_{sw}$ ), sediment burial ( $k_b$ ), and degradation in sediment ( $k_{sr}$ ). Inputs to the water column include loading (L; includes all external sources) and transport from the sediment layer. Losses from the water column include volatilization, outflow, degradation, and transport to the sediment. PAH is input to the actively mixed sediments by deposition and diffusion from the water column. Losses from the sediment include transport to the water column, burial, and degradation.

In order to allow examination of model structure without referring to Davis (2004), we present equations for rate constant calculations in Table 2. The outflow rate constant ( $k_o$ ) is a function of rate of water outflow through the Golden Gate ( $F/X_w$ ). The rate constant is multiplied by a ratio of PAH concentration at seaward sites versus concentration throughout the Estuary ( $PAH_o/PAH_A$ ), which corrects for reduced PAH concentrations at the seaward end of the Estuary. The volatilization rate constant ( $k_v$ ) is directly proportional to the Estuary water surface area to volume ratio ( $S_{AW}/X_w$ ), the fraction of PAH that is freely dissolved and thus available for volatilization ( $\phi_{DW}$ ), and

the volatilization mass transfer coefficient ( $V_E$ ). PAH compound-specific air and water-side mass transfer coefficients ( $V_{EA}$ ,  $V_{EW}$ ) and Henry's law constant ( $H$ ) all influence the volatilization mass transfer coefficient. The degradation rate constants for water and sediment ( $k_{WR}$ ,  $k_{SR}$ ) are directly estimated from literature as described later. The water to sediment and sediment to water transport rates ( $k_{WS}$ ,  $k_{SW}$ ) are summations of both dissolved and particulate transfer. Finally, the burial rate constant ( $k_B$ ) is a function of the Estuary sediment surface area to volume ratio ( $S_{AS}/X_S$ ), the particle-bound fraction of PAH in the sediment ( $1 - \phi_{DS}$ ), and the sediment burial mass transfer coefficient ( $V_B$ ). We followed the assumption of Davis (2004) that the sediment burial mass transfer coefficient is zero, based on recent findings that net erosion is occurring in substantial parts of the Estuary, while net deposition occurs in others. Significant areas of San Pablo Bay, Suisun Bay, and South Bay all exhibit net erosion, resulting from reduced sediment supply from the upper watersheds (Jaffe et al., 1998; Cappiella et al., 1999). Other locations exhibit net burial, as evidenced by historical trends in sediment core contamination (Pereira et al. 1999). Loading from erosion of buried sediment is accounted for in the combined loading term  $L$ .

Davis (2004) provides an in-depth assessment of the relative importance of Estuary physical attributes on model results. Davis (2004) indicates that, when applied to PCBs, model results are particularly sensitive to depth of active sediment layer and rate of water outflow. Sediment burial mass transfer coefficient, concentration of solids in sediment, and organic carbon content of suspended solids are moderately influential on model results. Davis identifies the depth of actively mixing sediment as a significant information need because the depth determines the pool size of contaminants that must be lost for Estuary contaminant concentrations to decline.

Our report evaluates the chemical properties of PAHs and how they influence model results. We also use Monte Carlo simulation to evaluate the relative contribution of uncertainty in PAH chemical properties, and Bay chemical and physical properties, to overall model uncertainty. The remainder of this section details how each chemical property was determined for PAH model input parameters, and how the Monte Carlo simulation was conducted.

### ***PAH Selection For the RMP Ecosystem Model***

From among the 25 PAHs that are regularly analyzed by the RMP, seven were chosen for modeling (Table 1; Table 4). Selection criteria included incorporating a range of chemical properties, representing a high proportion of PAH mass found in the Estuary, and choosing PAHs that have exceeded water quality objectives (Table 1; SFBRWQCB 2001). By selecting PAHs with varying ring numbers, we cover a range of PAH chemical properties, because many chemical properties closely follow number of rings. The PAHs with 2 or 3 rings are referred to as low molecular weight PAHs (LPAHs). LPAHs are volatile, have relatively high water solubility, and biodegrade readily. Consequently, LPAHs are expected to have rapid ecosystem loss rates in the Estuary. PAHs with 4 or more rings are referred to as high molecular weight PAHs (HPAHs). As the number of rings increases, the hydrophobicity and chronic toxicity generally increase,



and the degradation and volatilization rates decrease significantly. For 4 and 5 ring PAHs, four compounds were modeled, to represent the range of different ring structures (and chemical properties) for these HPAHs. The PAHs with 4-6 rings are expected to have lower ecosystem loss rates than LPAHs.

Of the 7 PAHs modeled, benzo(b)fluoranthene was chosen for more detailed analysis. This detailed analysis included evaluation of sensitivity to individual chemical properties, uncertainty of model results resulting from lack of knowledge about parameter values, and an attempt to estimate loading rate and long-term fate. Benzo(b)fluoranthene is relatively persistent, and has a low water quality objective because it is carcinogenic. In RMP sampling it has exceeded water quality objectives more frequently than most other PAHs (a total of 5 exceedances in 393 water measurements between 1993 and 2001).

### ***Contaminant Concentrations in Water and Sediments***

To estimate present concentrations of PAHs in the Estuary, two averages were generated. One included only the RMP Status and Trends stations. The other included these in addition to the Southern Slough sites (San Jose and Sunnyvale), the Estuary Interface sites (Guadalupe River and Standish Dam), and the Bay Protection and Toxic Cleanup Program sites (BPTCP). In the BPTCP, sites were generally chosen for high toxic concentrations in the Estuary margins (Hunt et al., 1999). For sediments, the total number of sites for the larger and smaller data sets was 139 and 22 sites, respectively. RMP wetland monitoring sites in China Camp were not included. Samples with blank contamination, matrix interference, coelution, or samples that fell outside QA limits were removed from the analyses. Samples with PAH concentrations below detection limits were treated as zero. For sediments, site means were generated for all samples collected at a given site between 1993 and 1999. Then the overall median was calculated for all the sites sampled. Using this approach, the sum of PAH concentrations for the 25 measured PAHs (total PAHs) in sediment was calculated. For the 22 Estuary RMP sites, median total PAHs were 1524 ng/g (dry weight; N = 22; minimum = 131 ng/g; maximum = 4227 ng/g). When the RMP sites were combined with the Southern Slough, Estuary Interface, and BPTCP sites, median PAH concentrations were somewhat higher, at 1998 ng/g (N = 139; minimum = 30 ng/g; maximum = 227,900 ng/g). 1500 ng/g was chosen as the nominal value of total PAH concentrations in sediment for the model and 1500 to 2000 ng/g was chosen as the 95 % confidence interval range for Monte Carlo simulations (Table 3). Davis (2004) explores the influence of the contaminant average concentration input into the model and concludes that it has no impact on either the contaminant response time to changes in loading or the final steady state contaminant concentration.

For water, the BPTCP did not collect samples so only RMP sites were included. Using the averaging method described for sediment, the total (dissolved plus particulate) PAH concentration in water was 26.5 ng/L for all RMP sites including Southern Slough and Estuary Interface sites. The standard error of this mean (used for Monte Carlo simulations) was 0.6 ng/L. When the Southern Slough and Estuary Interface sites were excluded, the calculated concentration was 25.2 ng/L. 26 ng/L was chosen as the input

value for the total PAH concentrations in water in the Estuary (Table 3).

### ***Temporal Trends in Concentrations***

As part of the modeling exercise, we input best available parameters and used them to back-calculate total loading into the Estuary. This estimate of loading is highly uncertain but it can be compared to the limited data available on tributary loadings and storm drain runoff. One of the parameters required to estimate loading is the long-term trend in contaminant concentrations in the Estuary.

We evaluated 3 data sources to determine recent temporal trends in PAHs in the Estuary: 1) sediment concentration data from the RMP and Pilot RMP collected from 1991 through 2001; 2) concentration data from transplanted bivalves sampled by the RMP from 1994 through 2001; and 3) sediment core concentrations evaluated by USGS and collaborators (Pereira et al., 1999). For RMP sediment concentration evaluation, dry season annual total PAH means were determined for all RMP stations and corresponding Pilot RMP stations. The bivalve data represented the annual mean lipid weight concentrations from 6 Bay monitoring stations (Pinole Point, Red Rock, Yerba Buena Island, Alameda, and Dumbarton Bridge). For mussel concentration evaluation, Bay mussels (*Mytilus* spp.) were transplanted from a typically less contaminated reference location to the stations in early summer and collected after 90 days.

### ***Mass Transfer Coefficients***

Water-side and air-side evaporation mass transfer coefficients influence the rate of chemical transfer across the air-water interface. They therefore affect the rate of chemical volatilization into the atmosphere. The chemical property that controls the mass transfer coefficient is molecular diffusivity. Reviews of the literature did not provide experimentally determined molecular diffusivities for PAHs. Therefore, molecular diffusivities in water were calculated for each PAH using Hayduk and Laudie's method at 15° C (Tucker and Nelken, 1982). This was then converted to the unitless Schmidt number, which is the ratio of the kinematic viscosity of water to the molecular diffusivity of the compound in water (kinematic viscosity is viscosity/density). Schmidt number values were then used to calculate the water-side mass transfer coefficient using the method described in Zhang et al. (1999), which is also the method of Hornbuckle et al. (1994). For calculation of Schmidt number, we assumed constant wind speed and temperature, as described in Davis (2004).

Molecular diffusivities in air at 15° C were calculated using two methods, the method of Fuller, Schettler, and Giddings and the method of Wilke and Lee (Tucker and Nelken, 1982). These methods produced very similar results; the mean of the two methods was used as the molecular diffusivity in air.

### ***Degradation Rates***

The degradation loss process is potentially very important for PAHs.

Mechanisms of degradation may include biological, chemical, and photoinduced degradation. Because natural processes such as combustion and petroleum formation generate PAHs, PAHs are more susceptible to biological degradation than synthetic compounds such as PCBs. Although some laboratory studies have indicated that photodegradation may be significant for high molecular weight PAHs (e.g., Zepp and Schlotzhauer, 1979; Fasnacht and Blough, 2002), photodegradation is not generally believed to be a significant loss pathway in natural waters (Donald Mackay, Canadian Environmental Modeling Centre, personal communication; Dick Luthy, Stanford University, personal communication), and has not been explicitly incorporated into previous models of PAH fate in natural ecosystems (Ryan and Cohen, 1986; Lun et al., 1998; Mackay and Hickie, 2000). This is because light penetration is reduced by sediments and suspended particulate material, and also because high molecular weight PAHs tend to be tightly bound to organic particles, which themselves may cause shading (Talley et al., 2002). Therefore, we do not explicitly model photodegradation but instead include one degradation term representing combined losses of PAHs.

It is extremely difficult to accurately determine degradation rates of PAHs within a given ecosystem. Although there is substantial research on degradation rates in different systems, theoretical or empirical relationships are not available for extrapolation between ecosystems. For any given PAH, recorded values are widespread, sometimes spanning 3 - 4 orders of magnitude (Table 5; Appendix 1). In the absence of data for the Estuary and given this widespread variability, we estimated biodegradation rates from published literature values. For the PAHs of interest, values were assembled from studies on aquatic sediments and natural surface waters. Most studies were laboratory assays of samples collected from natural systems, although there were also a small number of in-situ field studies. All values were converted to per day rates. Where first-order relationships were described, rates were back calculated as:

Rates per day =  $-\log_e(\text{proportion remaining at time measured}) / (\text{time passage since experiment initiation})$

For half-lives, this is simply:

$$-\log_e(0.5) / t_{1/2}$$

When zero order relationships were reported (for example when transformation rate was reported as time required for complete degradation of PAH), rate per day was simply equal to the reciprocal of the number of days required for degradation.

Once values were compiled, box plots and histogram plots indicated that they were not normally distributed. Therefore, median values of all assembled degradation rates were chosen as representative values rather than mean values.

For some of the PAHs modeled, very little published literature exists on degradation rates of natural aquatic samples. Mackay and Hickie (2000) used identical degradation rates for each of several HPAHs for which few data were available. In our

study, it was necessary to compile degradation rates for these PAHs lacking data. Fluoranthene and benz(a)anthracene were set with the same degradation rate because of the lack of fluoranthene data. The five and six ring PAHs (benzo(b)fluoranthene, dibenz(a,h)anthracene, and benzo(ghi)perylene) were simulated using degradation rates for benzo(a)pyrene (for which there exists more extensive experimental and field data; Table 5). The use of benzo(a)pyrene for other HPAHs is supported by the fact that some laboratory studies have demonstrated that they exhibit similar degradation behavior (e.g., Juhasz et al., 1996; Wolter et al., 1997).

### ***K<sub>ow</sub> – the Octanol-Water Partition Coefficient***

K<sub>ow</sub> values (Table 4) were obtained as the median of all calculated or measured values for each compound, as compiled in Mackay et al. (2000). Values were also compiled from de Maagd et al. (1998) and Mackay and Hickie (2000).

### ***Henry's Law Constant***

Henry's law constants (Table 4) were obtained from published literature values. Depending on the PAH, between 1 and 13 published values were found. Published values and literature citations are presented in Appendix 2. Henry's law constants are temperature dependent and most values were not obtained at 15° C, the modeled temperature for the Estuary. To convert Henry's law constant to the 15° C value, the conversion equation presented in ten Hulscher et al. (1992) was used when original temperatures of 25° C were available or in de Maagd et al. (1998) when original temperatures of 20° C were available.

### ***Uncertainty Analysis***

Uncertainty analyses were conducted using Monte Carlo simulation, examples of which may be found in McKone and Bogen (1991), Ragas et al. (1999), and MacLeod et al. (2002). Monte Carlo simulation is a method of determining the range of expected model results given current uncertainty in input parameters. It presents a more realistic depiction of range of possible results than separately varying individual input parameters (McKone and Bogen, 1991). Monte Carlo simulation can also demonstrate the relative sensitivity of results to uncertainty in individual input parameters, which is important for prioritizing future research needs. In Monte Carlo simulation, the uncertainty range and distribution of model input parameters are estimated, and then model results are repeatedly calculated using input parameter values randomly selected from the estimated distributions. Monte Carlo analysis was conducted with the Crystal Ball<sup>®</sup> software package, using 10,000 iterations. Relative importance of individual input parameters was determined by calculating a rank correlation coefficient between results and each input parameter. This rank correlation coefficient is converted to the contribution to total variance explained, by squaring it and normalizing to 100 % (Werckman et al., 2001).

Parameter ranges for Monte Carlo simulation were based on Davis (2004). Parameter distributions, presented in Table 3, were estimated following the

recommendation by MacLeod et al. (2002) to focus on identifying variance structure for influential parameters. Parameters with an expected coefficient of variation (SD/mean) less than 25 % were modeled using a normal distribution with the 5 % and 95 % confidence intervals as the minimum and maximum values estimated by Davis (2004). Normally distributed parameters included water temperature, concentration of particles in water, concentration of solids in sediment, density of suspended solids, and Bay wide PAH concentrations in water. Parameters with available local data indicating lognormal distribution or with extremely high estimated value ranges were modeled using a lognormal distribution with the 5 % and 95 % confidence intervals as the minimum and maximum values estimated by Davis (2004). These included water outflow, solids settling rate, and Bay wide PAH concentrations in sediment. Parameters shown in preliminary simulations to have low impact on model output and parameters for which insufficient information was available to make distributional assumptions were modeled using uniform or triangular distributions with minimum, most likely, and maximum values following Davis (2004).

## RESULTS AND DISCUSSION

### *Properties of Selected PAHs*

The seven PAHs chosen comprise approximately 42 percent of the total mass in Estuary sediments, based on RMP data for all stations monitored between 1993 and 1999 (Table 4). Chemical properties range widely as a function of molecular weight, with low molecular weight PAHs (LPAHs) having relatively low  $K_{ow}$ 's and relatively high Henry's law constants and degradation rates (Table 4). Literature estimates of degradation rate for individual PAHs varied widely, sometimes spanning several orders of magnitude (Table 5; Appendix 1).

### *Fates of Different PAHs*

In order to evaluate differences among individual compounds in long-term fate, the model was run varying PAH chemical parameters according to PAH type and holding all other model parameters constant. In the absence of loading, percent of initial mass lost in five years varied widely among PAHs, mostly as a result of variation in degradation in sediment (Table 6, Table 7). The amount of time required for 1/2 of the initial mass to be lost (i.e., the PAH half-life) was shortest for the LPAHs naphthalene (20 days) and phenanthrene (63 days), just under one year for the four ring PAHs fluoranthene and benz(a)anthracene, and greater than five years for the HPAHs, benzo(b)fluoranthene, dibenz(a,h)anthracene, and benzo(ghi)perylene (Table 6). The much longer half-lives of the HPAHs suggests that long-term management of these compounds would be a greater concern than for the LPAHs, which will have very rapid loss rates.

Similar variations among PAH type were observed when simulations were run with an annual loading of 10,000 kg/year. The long-term steady-state mass given a constant external load of 10,000 kg/year varied considerably among the seven PAHs.

While steady-state concentrations of naphthalene and phenanthrene are less than 1 % and 2 % of the initial concentrations given this loading rate, concentrations of five and six ring PAHs would remain at two-thirds of current concentrations (Table 7, last cell).

For all PAHs, the predominant loss pathway was degradation in sediment, generally equaling 80 % to 90 % of total loss (Table 6, Figure 1). For the lower molecular weight PAHs, naphthalene, phenanthrene, and fluoranthene, volatilization was the second most important loss process, equaling about 10 percent of total loss (Table 6, Figure 1). In contrast, for the five and six ring HPAHs (benzo(b)fluoranthene, dibenz(a,h)anthracene, and benzo(ghi)perylene), outflow was the second most important loss process, equaling about 10 percent of total loss.

Comparison of these model findings to the results of other PAH modeling exercises provides an indication of the generality of patterns observed. Lun et al. (1998) use a similar mass balance modeling approach to determine the fate of naphthalene, phenanthrene, and benzo(a)pyrene in a 200 m deep fjord. Similar to our study, they observe that degradation is the major loss pathway for naphthalene, with volatilization playing a secondary role. Our results in combination with Lun et al. (1998) suggest the hypothesis that the rapid degradation rate of LPAHs is their predominant loss pathway from aquatic ecosystems.

Unlike our study, Lun et al. (1998) observe loss due to advection (outflow) to be relatively important for phenanthrene (a three ring PAH; 19 % of total loss) and benzo(a)pyrene (a five ring PAH; 57 % of total loss). Additionally, two other studies of benzo(a)pyrene and other HPAHs show outflow to be the most important loss pathway (Ryan and Cohen, 1986; Mackay and Hickie, 2000). These studies are of shallow riverine systems with high water flow. In such systems, accurate modeling of particle transport becomes very important for high molecular weight PAHs. Compared to these systems, the San Francisco Estuary has low hydrological flow relative to water body size. The model estimates that it would take 78 days for the total water volume in the Estuary to flow out of the Golden Gate, and literature values, though extremely variable, frequently report Estuary hydraulic residence time to be several months (reviewed in Smith, 1987). Thus, the relatively long water residence time in San Francisco Bay, compared to more lotic systems, may explain the relatively low outflow rates indicated in our model. However, part of the reason for the lower outflow loss may be limitations in the outflow modeling method. Our model calculated outflow as the total mass in the water column (dissolved and particulate) times calculated water outflow rate through the Golden Gate. Following the assumptions of Davis (2004), our study did not explicitly model bed sediment transport or particle advection due to tidal exchange, each of which could contribute to greater outflow.

### ***Relative Importance of Chemical Properties***

Independent manipulation of each PAH chemical attribute ( $K_{ow}$ , Henry's law constant, air and water mass transfer coefficients, and degradation rate in water and sediments) helped indicate which loss processes the attribute controlled. This

manipulation also served as a sensitivity analysis by indicating which properties the model was most sensitive to and must therefore be most carefully estimated.

When the six parameters were manipulated across the range that would be expected for the PAHs modeled, all had an effect on the model output with the exception of the air-side and water-side evaporation mass transfer coefficients (Table 7). The lack of importance of mass transfer coefficients stems from the fact that these parameters only exerted a moderate impact on a relatively minor loss process (volatilization). Mass transfer coefficients are also unimportant for modeled fate of PCBs in the Estuary (Davis, 2004).

For both response time and steady-state mass modeling exercise, sensitivity was greatest for sediment degradation rate and was also high for octanol-water partition coefficient. Results were moderately sensitive to water degradation rate and Henry's law constant (Table 7). Simultaneous variation in water and sediment degradation rate caused a massive difference in five-year losses, ranging from complete removal when the degradation rates of naphthalene or phenanthrene were used, to only 7 percent removal assuming no degradation (Table 8).

Variation in  $K_{ow}$  also caused significant differences in model output (Table 9). Using the  $K_{ow}$  of naphthalene, virtually all of the initial mass was lost within five years. When  $K_{ow}$ 's from the HPAHs were used (benzo(b)fluoranthene, dibenz(a,h)anthracene, benzo(ghi)perylene), slightly more than half of the initial mass remained after five years (Table 9).  $K_{ow}$  affected loss rates by affecting the abundance of PAH in the water column, where it became exposed to the volatilization and outflow loss pathways (Table 9). The dramatic increase in outflow rate with lower  $K_{ow}$ 's resulted from a reduced flux of PAH from the water column compartment to the sediment compartment. In contrast, Davis (2004) found that  $K_{ow}$  had little effect on modeled outflow rate for PCB 118 (only volatilization rate was affected). PCB 118 has a much higher Henry's law constant than benzo(b)fluoranthene, causing volatilization to have greater importance as a potential loss pathway.

Maruya et al. (1996) demonstrated that in a Richmond Harbor mudflat,  $K_{ow}$  accurately represents PAH sediment-water partitioning ( $K_{ow}$  = octanol/water,  $K_d$  = sediment/water partitioning) during the dry season but underestimates particle affinity in the wet season by an order of magnitude. The authors hypothesize that soot particles introduced during watershed runoff exhibit stronger binding affinity than predicted from equilibrium experiments, suggesting caution in use of literature derived  $K_{ow}$  values for the Estuary.

Variation in Henry's law constant caused modest differences among all PAHs (Table 10). Increased Henry's law constant caused more rapid volatilization, although volatilization was always a substantially smaller loss pathway than sediment degradation (Table 6). In the case of HPAHs, the very low Henry's law constants caused the volatilization loss to be negligible (Table 10). Other PAH modeling studies in different ecosystems also show volatilization to be a relatively unimportant loss pathway,

particularly for HPAHs (Ryan and Cohen, 1986; Lun et al., 1998; Mackay and Hickie, 2000).

The majority of the difference among the PAHs modeled resulted from differences in degradation rate. This is apparent from the observation that those compounds having identical estimated degradation rates (Table 4) exhibited similar environmental fates. For example, benzo(b)fluoranthene, dibenz(a,h)anthracene, and benzo(ghi)perylene all lost 46 percent of initial mass in five years (Table 6). Slight differences in overall loss rates among contaminants resulted from variation in other chemical properties. For example, in the absence of external load, 57 percent of fluoranthene was lost while only 53 percent of benz(a)anthracene was lost, despite having the same modeled degradation rates (Table 7, bottom row). As we have seen, overall model results appear to be more sensitive to  $K_{ow}$  than Henry's law constant, suggesting that  $K_{ow}$  caused most of the differences not related to degradation.

Model sensitivity to both  $K_{ow}$  and Henry's law constant was reduced with increasing molecular weight of PAHs. For example, when  $K_{ow}$  was shifted by an order of magnitude from the  $K_{ow}$  of naphthalene to that of phenanthrene, there was a 25 percent shift in the amount of mass lost in five years (Table 9). The same magnitude shift in  $K_{ow}$  from the  $K_{ow}$  of benzo(b)fluoranthene to that of benzo(ghi)perylene caused less than a 1 percent change in mass lost (Table 9). This difference is probably because at low  $K_{ow}$ , more loss resulted from volatilization and outflow rate, which were sensitive processes to  $K_{ow}$ . In contrast, at high  $K_{ow}$  almost all loss stemmed from degradation, which occurred in both water and sediments, and was therefore not sensitive to water/sediment partitioning. It is convenient that these parameters become less sensitive for PAHs with increased molecular weight because accurate estimates of high  $K_{ow}$  and low Henry's law constants are difficult to obtain, causing relatively high variation in estimated values (Mackay et al., 2000).

### *Uncertainty Analysis*

Monte Carlo simulations were conducted using data representative for benzo(b)fluoranthene to characterize the degree to which individual parameters affected model output. A response time simulation evaluated two factors: residence time for the modeled PAH in the Bay (initial total mass in the Bay (kg) / instantaneous annual losses (kg/yr)) and percent of original PAH mass lost after 5 years of simulation. A steady-state simulation evaluated the steady state mass of PAH with a fixed annual loading rate of 15,000 kg, after 100 simulation years.

Variation among the range of plausible values of sediment degradation rate strongly affected results of both the response time and steady-state simulations. Simulations conducted across the full range of degradation rates in Table 5 did not provide results within a meaningful range. When degradation rate was ranged between observed literature values of  $4 \times 10^{-5}$  to  $1 \times 10^{-2} \text{ d}^{-1}$ , loss in 5 years ranged from 0 to 100 % and predicted residence times ranged from weeks to over 100 years. Even when degradation rates were constrained to the order of magnitude range found more



commonly in the literature ( $4 \times 10^{-5}$  to  $4 \times 10^{-4} \text{ d}^{-1}$ ; Table 5), more than 97 percent of the variation in model outputs (steady state mass, residence time, and percent loss after 5 years) was attributable to sediment degradation rate variation, indicating that uncertainty in this parameter was dominating model results. Very high uncertainty was apparent for residence time (mean = 16.2 years; CV = 0.66; Figure 2a), percent decline after 5 years (mean = 37 %; CV = 0.33; Figure 2b), and steady state mass (mean =  $1.9 \times 10^5 \text{ kg}$ ; CV = 0.53; Figure 2c). Additionally, instantaneous annual losses (i.e., the initial sum of PAH lost due to burial, degradation, volatilization, and outflow) varied substantially (mean = 14,000 kg/y; CV = 0.60).

To explore uncertainty of model predictions if degradation rates were well characterized, the Monte Carlo simulations were then repeated with a fixed degradation rate representative of literature values ( $3 \times 10^{-4} \text{ d}^{-1}$ ; Table 5). This also enabled determination of other input parameters important for on model results. When the degradation rate was fixed, model uncertainty was relatively low for residence time (mean = 8.9 years; CV = 0.01; Figure 2a), percent decline after 5 years (mean = 46 %; CV = 0.04; Figure 2b), and steady state mass (mean =  $1.2 \times 10^5 \text{ kg}$ ; CV = 0.06; Figure 2c). In this scenario, instantaneous annual losses were estimated at a mean of 19,000 kg/y (CV = 0.35).

When degradation rate was fixed, the depth of the active sediment layer explained the most variation in the four response variables: response rate (as percent lost in 5 years with no external loading), steady state mass (after 100 years with  $15,000 \text{ kg yr}^{-1}$  loading), residence time, and instantaneous annual loss (Table 11). Concentration of solids in sediment was also an influential parameter for the four response variables. Residence time was also influenced by sediment burial mass transfer coefficient. Rate of water outflow had moderate influence on response rate, steady state mass, and residence time (Table 11). The relatively high impact of sediment properties (e.g., active sediment layer depth, solids concentration, and sediment burial mass transfer coefficient) was also apparent for PCB simulations, and reflects the fact that in San Francisco Bay, the vast majority of hydrophobic organic contaminants tends to be sequestered in bed and suspended sediments (Davis, 2004). In this modeling exercise, both the initial sediment contamination pool and the sediment burial rate influence PAH loss rates. The importance of water outflow reflects that PAH outflow through the Golden Gate may become a more significant uncertainty, once degradation rate is better characterized. Compared to Bay sediment properties and uncertainty regarding degradation rate, uncertainty for other chemical properties of high molecular weight PAHs such as benzo(b)fluoranthene have relatively low impact on model results.

Given the extremely wide range of model results using estimates of degradation rates, we concluded that our current understanding of degradation rates is not sufficiently accurate to confidently predict long-term PAH fate in the Estuary. If there is a future need to accurately predict long-term PAH fate in the Estuary, locally derived degradation rate estimates should probably be obtained.

### ***Calibration of Loading Rate Versus Degradation Rate***

A key unknown for many contaminants is the annual rate of loading from all sources to the Estuary (Davis et al., 1999). Obtaining better estimates of contaminant loads is an ongoing objective of both the RMP and the Clean Estuary Partnership. This is because loading rate estimates are needed to determine necessary source reduction for TMDL regulatory decisions associated with the TMDL process.

If all parameters in our mass balance model were relatively certain, it would be possible to use it to place useful bounds on plausible loading rates. Achieving this would require low uncertainty for estimates of chemical properties, current concentrations, and long-term trends (Davis, 2004). For PAHs, useful loading rate estimates could not be calculated because the most important loss process (degradation in sediment) was poorly characterized. For this reason, model predictions of loading rate were compared to loading rate estimates based on previous field and modeling studies. This may allow for bounds to be established for loading and degradation rates, with the understanding that improved parameter estimates and/or model calibration will be required to refine the loading estimates.

A key input for a comparison of loading versus degradation rates is the long-term trend in contaminant concentrations in the Estuary (Davis, 2004). Analysis of PAH trends also helps in evaluating potential future risk due to this contaminant (Oros and Ross, 2004). Graphical evaluation of annual average sediment total PAH concentrations provided no evidence for increasing or decreasing trend (Figure 3). The same lack of trend was apparent when wet season data were included (data not shown). This observation was consistent with linear regression analyses of 26 different monitoring stations, indicating a general absence of temporal trends throughout the Bay (Oros and Ross, 2004). Dry season concentrations of HPAHs in transplanted bivalves showed considerable interannual variability but also showed no apparent trend (Figure 4). As shown by Pereira et al. (1999), sediment cores do indicate significant increasing trends in several PAHs in the Estuary from the early 20th-century to the 1970s. However, samples from these cores representing the 1970s to the present do not show clear trends, with concentrations increasing in the 1970s and 1980s but decreasing in the most recent sediment layers (Figure 3 in Pereira et al., 1999). In general, there is not clear indication of trend in total PAHs within the last decade. Therefore, loading rates within the last decade were estimated assuming stable PAH concentrations over time. As annual data collection continue in the RMP, future modeling efforts may need to adjust this assumption of stable PAH concentrations over time.

Annual loading to the Estuary is not well characterized, and best available estimates range widely from 300 to about 10,000 kg/year (Table 12). Of particular concern is the estimate of river loading, which had great uncertainty due to frequent measured concentrations below the detection limit of the PAH concentration measurements (Gunther et al., 1991) Nevertheless, use of this wide range of loading estimates did provide bounds on likely degradation rates.

When the model was implemented using the best estimated properties for benzo(b)fluoranthene (including a degradation of 0.00035/day), a loading rate of 18,000 kg/year was needed to maintain stable PAH concentrations over time (Table 13). This is about two times the maximum expected loading rate based on previous estimates, which is plausible given the limitations of the studies. However, assuming degradation rates an order of magnitude greater than the nominal value (0.0035/day) would require an exceedingly high loading of 140,000 kg/year (Table 13). Given that this is more than an order of magnitude greater than the maximum value estimated by all of the loading studies (which, themselves, assumed very wide error margins to account for their methodological limitations), it becomes implausible that PAH degradation rates were an order of magnitude greater than the nominal value for HPAHs. This interpretation was based on parameter estimates for benzo(b)fluoranthene but the same result was found for other PAHs. As LPAHs have elevated loss rates due to other pathways, the amount of loading needed to maintain steady concentrations would be even greater. In short, assuming that other model parameters were correct, the degradation of PAHs in the Estuary is likely to be at or below the nominal value.

Our interpretation of relatively low degradation rates compared to the range of literature values presented in Appendix 1 is consistent with research on natural degradation of combustion product PAHs. Most PAHs in the Estuary are combustion derived rather than petrogenic (Risebrough, 1994; Pereira et al., 1999; Oros and Ross, 2004), and a portion of the PAH mass is likely bound to soot particles (Maruya et al., 1996). Because soot PAHs are tightly bound to particles, they are often less available for biodegradation, leading to relatively slow biodegradation rates (Talley et al., 2002).

When the model was implemented assuming a degradation rate of 0, the loading rate became 1700 kg/year. This provided a lower bound estimate of loading, assuming that the model was correct, because less loading would require a negative degradation rate. Assuming the range of degradation rates observed in most laboratory examinations of benzo(a)pyrene ( $4 \times 10^{-5}$  to  $4 \times 10^{-4} \text{ d}^{-1}$ ; Table 5), the rate of loading needed to achieve a steady state mass in the Bay would range from 4,000 kg/year to 21,000 kg/year. It should be noted that the degradation rates determined by Shiaris (1989) of  $1.2 \times 10^{-2}$  to  $1.9 \times 10^{-2}$  would require loadings orders of magnitude higher than the maximum literature value, suggesting that the study by Shiaris (1989) is a suspect value for determining PAH degradation rates in Bay sediments.

### ***Fate of PAHs Versus PCBs in the Estuary***

The lack of a precise loading estimate precludes prediction of long-term PAH time trends in the Estuary given present loading. However it was possible to estimate the overall loss rates of the PAH mass that is currently present in the Estuary. As discussed previously, the time required for half of the current PAH mass in the Estuary to be lost is about three weeks for naphthalene, two months for phenanthrene, one year for the four ring PAHs, and about 5 1/2 years for the 5 and 6 ring PAHs modeled (Table 6). Modeling studies of other aquatic ecosystems have also found PAH residence times of

less than a year for LPAHs and one to several years for HPAHs (Lun et al., 1998; Mackay and Hickie, 2000).

A comparison of PAH and PCB loss rates in the Estuary indicated that the PAH loss rate was considerably more rapid (Figure 5). The time required for half the original mass of PCB 118 to be lost is estimated at about 20 years (Davis, 2004), more than threefold slower than the slowest PAHs. From a management perspective, this finding indicates that PAH mass in the Estuary is likely to be more responsive to loading reductions than PCBs, particularly for the LPAHs.

Evaluation of rate constants for the loss and transfer pathways helps in understanding why loss rates are relatively rapid for LPAHs, moderate for HPAHs, and relatively slow for PCBs (Table 14). In the case of benzo(b)fluoranthene, parameter values were fairly similar to PCB 118 values with two exceptions. Benzo(b)fluoranthene has an order of magnitude higher expected degradation rate and PCB 118 has about a 25 fold greater volatilization rate (Table 14). The relatively low volatilization rate of benzo(b)fluoranthene stems from the fact that it has a much lower Henry's law constant ( $0.033 \text{ Pa m}^3/\text{mol}$ ) than PCB 118 ( $3.94 \text{ Pa m}^3/\text{mol}$ ). Interestingly, when the simulation was run for benzo(b)fluoranthene with only the degradation rate set for PCB 118, the loss rate was actually slower than when the simulation was run for PCB 118. This results from the lower volatilization of benzo(b)fluoranthene. Therefore, the more rapid loss of HPAHs than PCBs resulted almost entirely from a higher putative degradation rate. As the previous section indicated that the nominal degradation rate may have been higher than the actual rate, the actual long-term loss rate of benzo(b)fluoranthene may be much slower than predicted by the model.

Several loss rates are greater for the LPAH, phenanthrene, than for HPAHs or PCB 118 (Table 14). In particular, degradation rate is several orders of magnitude greater and volatilization rate is an order of magnitude greater than for PCB 118. The difference in volatilization rate did not stem from differences in Henry's law constant, which is similar for phenanthrene and PCB 118. Instead, the increased volatilization rate resulted from phenanthrene's lower  $K_{ow}$  ( $\log K_{ow} = 4.46$  versus  $6.7$ ). The lower  $K_{ow}$  put more phenanthrene in the freely dissolved fraction, where it becomes available for volatilization. This lower  $K_{ow}$  also reduced the solids settling rate compared to HPAHs or PCB 118, with the result that more phenanthrene remains in the water column where it is available for volatilization and outflow. Even though most of the phenanthrene is lost due to the very high putative degradation rate (Table 6), the higher amount of phenanthrene that remains in the water column and volatilizes would still cause more rapid loss assuming similar degradation rates.

### ***Conclusions and Future Directions***

A primary objective of preliminary models such as this one is to evaluate the extent and limitations of present knowledge and to indicate priorities for future research. The predictions of this modeling exercise are highly uncertain, but the model has provided useful information regarding the relative importance of different PAH chemical

properties. Our results indicated that given present understanding of the Estuary, degradation rate is a very important process governing long-term PAH fate, particularly for HPAHs. This is in contrast to ecosystems with rapid throughput of water and sediments, for which outflow of contaminant is much more important (e.g., Ryan and Cohen, 1986; Mackay and Hickie, 2000). Our literature review and uncertainty analysis also indicated that the degradation rate is poorly characterized. Therefore, locally derived degradation estimates would be valuable if accurate determination of HPAH long-term fate becomes a local management priority.

The model has also indicated that for the most recalcitrant PAHs (i.e., the HPAHs), loss due to volatilization is extremely low. Therefore, better estimates of volatilization-related parameters (i.e., Henry's law constant and mass transfer coefficients) are unnecessary. Consistent with the PCB model,  $K_{ow}$  variation strongly impacted model output (Table 9). Although the model sensitivity to  $K_{ow}$  estimation uncertainty was modest (Table 11), our literature-based  $K_{ow}$ 's may underestimate the particle binding affinity of soot-bound PAHs in the Estuary (Maruya et al., 1996). Therefore, better estimates of sediment-water partitioning may improve model calibration for the Estuary.

Future iterations of the model could explicitly incorporate the processing of a soot-bound fraction. This would be appropriate because PAH phase partitioning in urbanized estuaries often involves more sediment affinity than expected by equilibrium models, suggesting that soot-bound PAHs may be an important component (Maruya et al., 1996; Brunk et al., 1997). Furthermore, aquatic sediment PAH degradation behavior often indicates a soot-like fraction that is effectively not available for degradation (Talley et al., 2002). In a partitioning model, a soot-bound fraction would not be available for dissolution or degradation. It would only be subject to burial, suspended particle outflow, and bed-sediment advection loss processes. The absence of degradation would significantly slow the predicted loss of PAHs in the Estuary. An estimation of the proportion of soot-bound PAH in the Estuary would be required for modeling of this soot-bound fraction.

The model indicated that PAHs have fairly rapid residence times, with half-lives ranging from several weeks to several years. This finding was consistent with other modeling studies (e.g., Lun et al., 1998; Mackay and Hickie, 2000). The rapid residence times suggest that the Estuary would respond within several years or less to loading reductions such as source curtailment or measures to control runoff of particle-bound PAH. However, PAH concentrations are also high in deeply buried sediment, and this model does not account for erosive remobilization of this buried sediment. Sediment remobilization would expose more PAHs and delay Estuary response to loading reductions.

The San Francisco Estuary is a dynamic ecosystem that exhibits considerable spatial and temporal variability in attributes important to this model. This model presents the Estuary as a single box of well-mixed water and sediment; as such, the model may be used to identify parameter uncertainties and prioritize future research areas. Before the

model could be used to predict contaminant dynamics within and among different regions of the Estuary, or responses of specific regions to changes in loading, the model would need to incorporate spatial heterogeneity of this ecosystem. This includes heterogeneity among water and sediment transport rates for different portions of the Estuary (e.g., Smith, 1987), in addition to vertical stratification that occurs as a result of seasonal salinity gradients (e.g., Cloern, 1996). Volatilization might be more important than predicted by the model in shallow, well-mixed areas, such as the large shallow portions of San Pablo Bay. Portions of San Pablo Bay and the Central Bay exhibit sediment burial (Pereira et al., 1999), causing that to be a loss pathway in those locations.

RMP scientists at the USGS and SFEI are currently developing a more sophisticated multibox model, which explicitly simulates sediment advection and other sediment transport processes. This model also incorporates Estuary-wide spatial variation in contaminant concentrations, and better describes water transport in the Estuary. The parameters assembled in our report should be combined with improved degradation rate estimates in the multi-box model formulation. Future simulations would provide estimates of PAH flux within the Estuary and responses to management actions.

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## TABLES

Table 1. Abundance and properties of 25 PAHs in San Francisco Bay samples, collected from 1993 to 2001. Mean concentrations and percent of total concentrations are indicated for PAHs in sediments ( $\mu\text{g}/\text{kg}$ , dry weight), bivalves ( $\mu\text{g}/\text{kg}$ , dry weight), and dissolved PAHs in water ( $\text{ng}/\text{L}$ ). “Number of Exceedances” indicates the total number of individual samples collected from 1993 to 2001 that exceed the water quality criteria for human health established by the California Toxics Rule for total (dissolved + particulate) concentrations in water (U.S. EPA 2000). The total number of samples collected was 396, although not all samples were analyzed for all compounds. NA = criterion not established.

| PAH                          | Number of Rings | Mean Concentration and Percent of Total |              |                         |              |                      |              | Number Exceedances |
|------------------------------|-----------------|-----------------------------------------|--------------|-------------------------|--------------|----------------------|--------------|--------------------|
|                              |                 | Sediment                                |              | Bivalves                |              | Water                |              |                    |
|                              |                 | $\mu\text{g}/\text{kg}$                 | %            | $\mu\text{g}/\text{kg}$ | %            | $\text{ng}/\text{L}$ | %            |                    |
| Biphenyl                     | 2               | 6                                       | 0.4%         | 3                       | 0.9%         | 0.23                 | 2.6%         | NA                 |
| <b>Naphthalene</b>           | <b>2</b>        | <b>25</b>                               | <b>1.6%</b>  | <b>19</b>               | <b>5.2%</b>  | <b>0.27</b>          | <b>3.1%</b>  | <b>NA</b>          |
| 1-Methylnaphthalene          | 2               | 6                                       | 0.4%         | 6                       | 1.5%         | 0.23                 | 2.6%         | NA                 |
| 2-Methylnaphthalene          | 2               | 11                                      | 0.7%         | 10                      | 2.8%         | 0.36                 | 4.1%         | NA                 |
| 2,6-Dimethylnaphthalene      | 2               | 6                                       | 0.4%         | 2                       | 0.6%         | 0.28                 | 3.2%         | NA                 |
| 2,3,5-Trimethylnaphthalene   | 2               | 4                                       | 0.3%         | 1                       | 0.1%         | 0.31                 | 3.5%         | NA                 |
| Acenaphthene                 | 3               | 8                                       | 0.5%         | 1                       | 0.3%         | 0.72                 | 8.1%         | 0                  |
| Acenaphthylene               | 3               | 10                                      | 0.7%         | 3                       | 0.7%         | 0.09                 | 1.0%         | NA                 |
| Anthracene                   | 3               | 27                                      | 1.7%         | 13                      | 3.6%         | 0.04                 | 0.4%         | 0                  |
| Dibenzothiophene             | 3               | 6                                       | 0.4%         | 1                       | 0.3%         | 0.09                 | 1.0%         | NA                 |
| Fluorene                     | 3               | 11                                      | 0.7%         | 3                       | 0.9%         | 1.21                 | 13.7%        | 0                  |
| <b>Phenanthrene</b>          | <b>3</b>        | <b>85</b>                               | <b>5.4%</b>  | <b>22</b>               | <b>6.0%</b>  | <b>1.25</b>          | <b>14.2%</b> | <b>NA</b>          |
| 1-Methylphenanthrene         | 3               | 13                                      | 0.8%         | 2                       | 0.5%         | 0.32                 | 3.6%         | NA                 |
| <b>Benz(a)anthracene</b>     | <b>4</b>        | <b>79</b>                               | <b>5.0%</b>  | <b>19</b>               | <b>5.2%</b>  | <b>0.17</b>          | <b>1.9%</b>  | <b>3</b>           |
| Chrysene                     | 4               | 88                                      | 5.6%         | 27                      | 7.3%         | 0.12                 | 1.3%         | 0                  |
| <b>Fluoranthene</b>          | <b>4</b>        | <b>192</b>                              | <b>12.1%</b> | <b>61</b>               | <b>16.4%</b> | <b>1.58</b>          | <b>17.9%</b> | <b>0</b>           |
| Pyrene                       | 4               | 245                                     | 15.5%        | 72                      | 19.6%        | 1.24                 | 14.1%        | 0                  |
| Benzo(a)pyrene               | 5               | 134                                     | 8.5%         | 12                      | 3.4%         | 0.01                 | 0.1%         | 2                  |
| Benzo(e)pyrene               | 5               | 100                                     | 6.3%         | 26                      | 7.0%         | 0.09                 | 1.0%         | NA                 |
| <b>Benzo(b)fluoranthene</b>  | <b>5</b>        | <b>142</b>                              | <b>9.0%</b>  | <b>24</b>               | <b>6.5%</b>  | <b>0.13</b>          | <b>1.4%</b>  | <b>5</b>           |
| Benzo(k)fluoranthene         | 5               | 52                                      | 3.3%         | 12                      | 3.3%         | 0.03                 | 0.4%         | 1                  |
| <b>Dibenz(a,h)anthracene</b> | <b>5</b>        | <b>14</b>                               | <b>0.9%</b>  | <b>1</b>                | <b>0.2%</b>  | <b>0.01</b>          | <b>0.1%</b>  | <b>0</b>           |
| Perylene                     | 5               | 62                                      | 3.9%         | 10                      | 2.7%         | 0.00                 | 0.0%         | NA                 |
| <b>Benzo(ghi)perylene</b>    | <b>6</b>        | <b>137</b>                              | <b>8.6%</b>  | <b>12</b>               | <b>3.2%</b>  | <b>0.01</b>          | <b>0.1%</b>  | <b>NA</b>          |
| Indeno(1,2,3-cd)pyrene       | 6               | 119                                     | 7.5%         | 7                       | 1.8%         | 0.05                 | 0.6%         | 4                  |

Table 2. Equations for assessment of rate constants used in environmental fate model.

**Rate Constants:**

|                                                                |                                                        |
|----------------------------------------------------------------|--------------------------------------------------------|
| $k_O = [F/(1000X_W)] * PAH_O / PAH_A$                          | (outflow rate constant; $d^{-1}$ )                     |
| $k_V = S_{AW} \phi_{DW} V_E / X_W$                             | (volatilization rate constant ; $d^{-1}$ )             |
| $k_{WR} =$ obtained from literature                            | (degradation in water rate constant; $d^{-1}$ )        |
| $k_{SR} =$ obtained from literature                            | (degradation in sediment rate constant; $d^{-1}$ )     |
| $k_{WS} = k_{WS1} + k_{WS2}$                                   | (water to sediment transport rate constant; $d^{-1}$ ) |
| $k_{SW} = k_{SW1} + k_{SW2}$                                   | (sediment to water transport rate constant; $d^{-1}$ ) |
| $k_B = S_{AS} V_B (1 - \phi_{DS}) / X_S$                       | (burial rate constant; $d^{-1}$ )                      |
| $k_{WS1} = S_{AW} \nu_{SS} (1 - \phi_{DW}) / X_W$              | (solids settling rate; $d^{-1}$ )                      |
| $k_{WS2} = S_{AS} V_D \phi_{DW} / X_W$                         | (water to sediment diffusion rate; $d^{-1}$ )          |
| $k_{SW1} = 1000(\text{ResFlux} / C_{SS})(1 - \phi_{DS}) / X_S$ | (solids resuspension rate; $d^{-1}$ )                  |
| $k_{SW2} = S_{AS} V_D \phi_{DS} / X_S$                         | (sediment to water diffusion rate; $d^{-1}$ )          |

**Other Equations and Properties:**

|                                                                                             |
|---------------------------------------------------------------------------------------------|
| $F =$ outflow rate of water ( $L d^{-1}$ )                                                  |
| $X_W =$ Estuary water volume ( $m^3$ )                                                      |
| $X_S =$ Estuary active sediment layer volume ( $m^3$ )                                      |
| $PAH_A =$ average total water column PAH concentration Estuary-wide ( $pg/L$ )              |
| $PAH_O =$ PAH concentration at seaward locations (Yerba Buena Island and Red Rock; $pg/L$ ) |
| $S_{AW} =$ Estuary water surface area ( $m^2$ )                                             |
| $\phi_{DW} =$ freely dissolved PAH fraction in water (unitless)                             |
| $\phi_{DW} = 1 / (1 + (C_{PW} OC_{PW} K_{OW} / d_{PW}))$                                    |
| $C_{PW} =$ concentration of particles in water (TSS) ( $mg L^{-1}$ )                        |
| $OC_{PW} =$ organic carbon content of suspended solids (unitless)                           |
| $K_{OW} =$ octanol water partition coefficient (unitless)                                   |
| $d_{PW} =$ density of suspended solids ( $kg L^{-1}$ )                                      |
| $V_E =$ volatilization mass transfer coefficient ( $m d^{-1}$ )                             |
| $1/V_E = 1/V_{EW} + 1/(K_{AW} V_{EA})$                                                      |
| $V_{EW} =$ water-side evaporation mass transfer coefficient ( $m d^{-1}$ )                  |
| $V_{EA} =$ air-side evaporation mass transfer coefficient ( $m d^{-1}$ )                    |
| $K_{AW} =$ dimensionless Henry's Law constant (unitless)                                    |
| $K_{AW} = H / (8.314 * (T + 273))$                                                          |
| $H =$ Henry's Law constant ( $Pa m^3 mol^{-1}$ )                                            |
| $T =$ water temperature (deg C)                                                             |
| $\nu_{SS} =$ solids settling rate ( $m d^{-1}$ )                                            |
| $S_{AS} =$ Estuary sediment surface area ( $m^2$ )                                          |
| $V_D =$ water-to-sediment diffusion mass transfer coefficient ( $m d^{-1}$ )                |
| $\text{ResFlux} =$ resuspension flux of sediment solids ( $kg d^{-1}$ )                     |
| $\text{ResFlux} = 1000(C_{PW} \nu_{SS} S_{AW} - C_{SS} V_B S_{AS})$                         |
| $C_{SS} =$ concentration of solids in sediment ( $kg L^{-1}$ )                              |
| $V_B =$ sediment burial mass transfer coefficient ( $m d^{-1}$ )                            |
| $\phi_{DS} =$ fraction of freely dissolved PCB in sediments (unitless)                      |
| $\phi_{DS} = 1 / (1 + (C_{SS} OC_{SS} K_{OW} / d_{SS}))$                                    |
| $OC_{SS} =$ organic carbon content of bottom sediment (unitless)                            |
| $d_{SS} =$ density of sediment solids ( $kg L^{-1}$ )                                       |

Table 3. Input data for the model.

| PARAMETER                                                                  | SYMBOL           | BEST ESTIMATE         | MONTE CARLO DISTRIBUTION                                                         | SOURCE AND COMMENTS                                                                                                                                       |
|----------------------------------------------------------------------------|------------------|-----------------------|----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------|
| Water surface area (m <sup>2</sup> )                                       | S <sub>AW</sub>  | 1.1X10 <sup>9</sup>   | Not Varied                                                                       | Described in Davis (2003)                                                                                                                                 |
| Sediment surface area (m <sup>2</sup> )                                    | S <sub>AS</sub>  | 1.1X10 <sup>9</sup>   | Not Varied                                                                       | Described in Davis (2003)                                                                                                                                 |
| Depth of active sediment layer (m)                                         |                  | 0.15                  | Triangular (0.05, 0.15, 0.25)                                                    | Described in Davis (2003)                                                                                                                                 |
| Water volume (m <sup>3</sup> )                                             | X <sub>W</sub>   | 5.5X10 <sup>9</sup>   | Triangular (5.5X10 <sup>9</sup> , 5.5X10 <sup>9</sup> , 6.2X10 <sup>9</sup> )    | Described in Davis (2003)                                                                                                                                 |
| Sediment volume of Estuary (m <sup>3</sup> )                               | X <sub>S</sub>   | 1.6X10 <sup>8</sup>   | Not Varied                                                                       | Described in Davis (2003)                                                                                                                                 |
| Water temperature (deg C)                                                  | T                | 15                    | Normal (μ = 15.25, SD = 1.37)                                                    | Described in Davis (2003)                                                                                                                                 |
| Water outflow (L d <sup>-1</sup> )                                         | F                | 7.0X10 <sup>10</sup>  | Lognormal (5%CI = 5.3X10 <sup>10</sup> , 95%CI = 9.1X10 <sup>10</sup> )          | Described in Davis (2003)                                                                                                                                 |
| Concentration of particles in water (kg L <sup>-1</sup> )                  | C <sub>PW</sub>  | 8.5 X10 <sup>-5</sup> | Normal (μ = 8.5X10 <sup>-5</sup> , SD = 6.1X10 <sup>-6</sup> )                   | Described in Davis (2003)                                                                                                                                 |
| Concentration of solids in sediment (kg L <sup>-1</sup> )                  | C <sub>SS</sub>  | 0.5                   | Normal (μ = 0.6, SD = 0.12)                                                      | Described in Davis (2003)                                                                                                                                 |
| Density of suspended solids (kg L <sup>-1</sup> )                          | d <sub>PW</sub>  | 1.1                   | Normal (μ = 1.1, SD = 0.24)                                                      | Described in Davis (2003)                                                                                                                                 |
| Density of sediment solids (kg L <sup>-1</sup> )                           | d <sub>SS</sub>  | 2.7                   | Triangular (1.5, 2.7, 2.7)                                                       | Described in Davis (2003)                                                                                                                                 |
| Organic carbon content of suspended solids                                 | OC <sub>PW</sub> | 0.030                 | Triangular (0.01, 0.03, 0.05)                                                    | Described in Davis (2003)                                                                                                                                 |
| Organic carbon content of bottom sediment                                  | OC <sub>SS</sub> | 0.01                  | Triangular (0.005, 0.01, 0.02)                                                   | Described in Davis (2003)                                                                                                                                 |
| Water-side evaporation mass transfer coefficient (m d <sup>-1</sup> )      | V <sub>EW</sub>  | 0.77                  | Triangular (0.75, 0.77, 0.92)                                                    | Calculated for benzo(b)fluoranthene at wind speed of 10.6 mi/hr and water temperature of 15 deg C. After Hornbuckle et al. (1994) and Zhang et al. (1999) |
| Air-side evaporation mass transfer coefficient (m d <sup>-1</sup> )        | V <sub>EA</sub>  | 398                   | Triangular (390, 398, 495)                                                       | Calculated for benzo(b)fluoranthene at wind speed of 10.6 mi/hr and water temperature of 15 deg C. After Hornbuckle et al. (1994) and Zhang et al. (1999) |
| Sediment burial mass transfer coefficient (m d <sup>-1</sup> )             | V <sub>B</sub>   | 0                     | Triangular (0, 0, 1.1X10 <sup>-6</sup> )                                         | Described in Davis (2003)                                                                                                                                 |
| Solids settling rate (m d <sup>-1</sup> )                                  | v <sub>SS</sub>  | 1.0                   | Lognormal (5%CI = 0.4, 95%CI = 10)                                               | Described in Davis (2003)                                                                                                                                 |
| Water-to-sediment diffusion mass transfer coefficient (m d <sup>-1</sup> ) | V <sub>D</sub>   | 2.40X10 <sup>-3</sup> | Triangular (2.4X10 <sup>-4</sup> , 2.4X10 <sup>-3</sup> , 2.4X10 <sup>-2</sup> ) | Described in Davis (2003)                                                                                                                                 |
| Henry's law constant (Pa m <sup>3</sup> mol <sup>-1</sup> )                | H                | 0.033                 | Triangular (0.008, 0.033, 0.054)                                                 | Mean of 4 values for benzo(b)fluoranthene compiled in Appendix Table 2                                                                                    |

|                                                                                          |          |                    |                                                                             |                                                                                                               |
|------------------------------------------------------------------------------------------|----------|--------------------|-----------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------|
| Octanol-water partitioning coefficient                                                   | $K_{ow}$ | $2.51 \times 10^6$ | Triangular ( $5.01 \times 10^5$ , $2.51 \times 10^6$ , $3.98 \times 10^6$ ) | Median of 10 values for benzo(b)fluoranthene, obtained from Mackay et al. (2000) and Mackay and Hickie (2000) |
| Average concentration in water ( $\text{ng L}^{-1}$ )                                    |          | 26                 | Normal ( $\mu = 26$ , $SD = 0.6$ )                                          | Sum of 19 PAHs. RMP average for Estuary stations 1993-1999.                                                   |
| Typical concentration in water at Red Rock and Yerba Buena Island ( $\text{ng L}^{-1}$ ) |          | 11.5               | Normal ( $\mu = 11.5$ , $SD = 0.3$ )                                        | Sum of 19 PAHs. RMP average for Estuary stations 1993-1999.                                                   |
| Average concentration in sediment ( $\text{ng g}^{-1}$ dry)                              |          | 1500               | Lognormal (5%CI = 1500, 95%CI = 2000)                                       | Sum of 19 PAHs. RMP average for Estuary stations 1993-1999.                                                   |
| Average wind speed ( $\text{km hr}^{-1}$ )                                               |          | 17.1               | Triangular (12.9, 17.1, 20.9)                                               | Described in Davis (2003)                                                                                     |

Table 4. Properties of PAHs modeled. Percent of Total PAH = the average percentage of total PAHs in RMP sediment samples collected from 1993 through 1999.  $K_{ow}$  = the octanol-water partition coefficient, obtained as median of values presented in Mackay et al. (2000), de Maagd et al. (1998), and MacKay and Hickie (2000). HLC = Henry's law constant at 15°C, as determined in Appendix Table 2. MTC = mass transfer coefficient, calculated using methods presented in Hornbuckle et al. (1994) and in Zhang et al. (1999).

| PAH                   | Percent of Total PAH | Number of rings | Molecular Weight | Log $K_{ow}$ | HLC ( $\text{Pa m}^3 \text{mol}^{-1}$ ) | Degradation Rate ( $\text{d}^{-1}$ ) | Water-side MTC (m/d) | Air-side MTC (m/d) |
|-----------------------|----------------------|-----------------|------------------|--------------|-----------------------------------------|--------------------------------------|----------------------|--------------------|
| Naphthalene           | 1.3                  | 2               | 128              | 3.36         | 24.3                                    | 0.03                                 | 0.92                 | 495                |
| Phenanthrene          | 5.7                  | 3               | 178              | 4.46         | 2.04                                    | 0.01                                 | 0.85                 | 443                |
| Fluoranthene          | 12.1                 | 4               | 202              | 5.22         | 0.59                                    | 0.002                                | 0.82                 | 430                |
| Benz(a)anthracene     | 4.8                  | 4               | 228              | 5.86         | 0.33                                    | 0.002                                | 0.79                 | 408                |
| Benzo(b)fluoranthene  | 8.7                  | 5               | 252              | 6.40         | 0.033                                   | 0.0003                               | 0.77                 | 398                |
| Dibenz(a,h)anthracene | 0.9                  | 5               | 278              | 6.64         | 0.008                                   | 0.0003                               | 0.75                 | 382                |
| Benzo(ghi)perylene    | 8.7                  | 6               | 276              | 7.05         | 0.011                                   | 0.0003                               | 0.76                 | 390                |

Table 5. Representative literature values for rates of benzo(a)pyrene degradation in sediments.

| Rate (d <sup>-1</sup> )                              | Description                                     | Method          | Reference                   |
|------------------------------------------------------|-------------------------------------------------|-----------------|-----------------------------|
| None detected                                        | Combustion Generated PAH in Stream Sediments    | Sediment Core   | Su et al. 2000              |
| 4.2 x 10 <sup>-5</sup> to 2.8 x 10 <sup>-4</sup>     | Combustion Generated PAH in Estuarine Sediments | Lab Incubation  | Lun et al. 1998             |
| < 4.8 x 10 <sup>-5</sup> to < 8.0 x 10 <sup>-4</sup> | Petroleum PAH in Freshwater Stream Sediments    | Lab Incubation  | Herbes and Schwall 1978     |
| 3.0 x 10 <sup>-4</sup>                               | Combustion Generated PAH in Estuarine Sediments | Literature Est. | Mackay and Hickie 2000      |
| 3.3 x 10 <sup>-4</sup>                               | Moderately Contaminated Lake Sediments          | Lab Incubation  | Heitkamp and Cerniglia 1987 |
| 4.4 x 10 <sup>-4</sup>                               | General Estimate For Aquatic Sediments          | Literature Est. | Mackay et al. 2000          |
| 1.2 x 10 <sup>-2</sup> to 1.9 x 10 <sup>-2</sup>     | Combustion Generated PAH in Estuarine Sediments | Lab Incubation  | Shiaris 1989                |



Table 6. Predicted losses from the Estuary through different pathways over a 5 yr period for different PAHs. Assumes no external load and hypothetical identical starting mass of each PAH. All data in kg, except as noted.

| PAH                     | N      | P      | F      | B(a)a  | B(b)f  | Da     | Bp     |
|-------------------------|--------|--------|--------|--------|--------|--------|--------|
| Starting mass           | 120100 | 120100 | 120100 | 120100 | 120100 | 120100 | 120100 |
| Volatilization          | 11700  | 9900   | 10900  | 600    | 200    | 0      | 0      |
| Outflow                 | 400    | 1100   | 4500   | 2100   | 6100   | 5700   | 5400   |
| Burial                  | 0      | 0      | 0      | 0      | 0      | 0      | 0      |
| Degradation in water    | 2300   | 2000   | 1600   | 700    | 300    | 300    | 300    |
| Degradation in sediment | 105700 | 107100 | 101400 | 113900 | 48800  | 48900  | 49000  |
| Total losses            | 120100 | 120100 | 118400 | 117300 | 55400  | 54900  | 54700  |
| Mass in 5 yr            | 0      | 0      | 1700   | 2800   | 64700  | 65200  | 65400  |
| % of initial mass lost  | 100%   | 100%   | 99%    | 98%    | 46%    | 46%    | 46%    |
| Half Life               | 20 d   | 63 d   | 302 d  | 338 d  | 5.6 yr | 5.7 yr | 5.7 yr |

| PAH Name              | Abbreviation |
|-----------------------|--------------|
| Naphthalene           | N            |
| Phenanthrene          | P            |
| Fluoranthene          | F            |
| Benz(a)anthracene     | B(a)a        |
| Benzo(b)fluoranthene  | B(b)f        |
| Dibenz(a,h)anthracene | Da           |
| Benzo(ghi)perylene    | Bp           |

Table 7. Summary of sensitivity of the model to variation in PAH chemical properties and external loading rates. Each chemical property is varied across the range expected for the modeled PAHs (Table 4). Degradation rates of zero (i.e., no degradation) are also modeled. Other than the manipulated parameter, values are set for benzo(b)fluoranthene. In the second to last row, external loading rate is varied between 0 and 60,000 kg yr<sup>-1</sup>, holding PAH chemical properties constant. In the last row, all chemical properties are varied according to the seven modeled PAHs (following Table 4). Response time simulation = % of initial mass lost after 10 years with no external loading. Steady state mass simulation = % of initial mass lost after 100 years with 10,000 kg yr<sup>-1</sup> external load. PAH name abbreviations as in Table 6.

| PARAMETER                                                             | NOMINAL VALUE | MODEL INPUT                                            | EFFECT ON RESPONSE TIME: RANGE OF LOSSES IN 10 YR WITH NO EXTERNAL LOAD (% OF INITIAL MASS)    | EFFECT ON LONG-TERM STEADY STATE MASS: RANGE OF LOSSES AFTER 100 YR WITH EXTERNAL LOAD OF 10,000 KG YR <sup>-1</sup> (% OF INITIAL MASS) |
|-----------------------------------------------------------------------|---------------|--------------------------------------------------------|------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------|
| Water-side evaporation mass transfer coefficient (m d <sup>-1</sup> ) | 0.77          | 0.92,0.85,0.82,0.77,0.75<br>(N, P, F, B(b)f, Bp)       | No effect                                                                                      | No effect                                                                                                                                |
| Air-side evaporation mass transfer coefficient (m d <sup>-1</sup> )   | 398           | 495, 443, 430, 398, 390<br>(N, P, F, B(b)f, Bp)        | No effect                                                                                      | No effect                                                                                                                                |
| Degradation half-life in water (yr)                                   | 0.0003        | 0.03, 0.01, 0.002, 0.0003, 0<br>(N, P, F, B(b)f, Zero) | 84, 77, 72, 71, 71                                                                             | 62, 47, 37, 35, 34                                                                                                                       |
| Degradation half-life in sediment (yr)                                | 0.0003        | 0.03, 0.01, 0.002, 0.0003, 0<br>(N, P, F, B(b)f, Zero) | 100, 100, 100, 71, 14                                                                          | 99, 98, 89, 35, -345                                                                                                                     |
| K <sub>ow</sub> (log units)                                           | 6.4           | 3.4, 4.5, 5.2, 6.4, 7.1<br>(N, P, F, B(b)f, Bp)        | 100, 94, 79, 71, 71                                                                            | 96, 79, 51, 35, 34                                                                                                                       |
| Henry's law constant (Pa m <sup>3</sup> mol <sup>-1</sup> )           | 0.033         | 24.3, 2.04, 0.59, 0.033, 0.011<br>(N, P, F, B(b)f, Bp) | 80, 75, 72, 71, 71                                                                             | 55, 44, 38, 35, 35                                                                                                                       |
| External load (kg/yr)                                                 | 10000         | 0, 3000, 10000, 30000, 60000                           | 71, 57, 25, -68, -207                                                                          | 100, 80, 35, -96, -292                                                                                                                   |
| PARAMETER                                                             | NOMINAL VALUE | SENSITIVITY RANGE                                      | EFFECT ON RESPONSE TIME: RANGE OF LOSSES IN 365 DAYS WITH NO EXTERNAL LOAD (% OF INITIAL MASS) | EFFECT ON LONG-TERM STEADY STATE MASS: RANGE OF LOSSES AFTER 100 YR WITH EXTERNAL LOAD OF 10000 KG YR <sup>-1</sup> (% OF INITIAL MASS)  |
| PAH compound (all properties)                                         |               | N, P, F, B(a)a, B(b)f, Da, Bp                          | 100, 98, 57, 53, 12, 11, 11                                                                    | 100, 99, 93, 89, 35, 34, 33                                                                                                              |

Table 8. Predicted losses from the Estuary through different pathways over a 5 yr period with varying degradation rates. Assumes no external load and hypothetical identical starting mass of each PAH. Degradation rate is manipulated simultaneously for sediment and water. The final column lists results in the absence of degradation. All chemical parameters other than degradation rate are set for benzo(b)fluoranthene. All data in kg, except as noted.

| Degradation Rate (d <sup>-1</sup> ) | 0.03   | 0.01   | 0.002  | 0.0003 | No Deg. |
|-------------------------------------|--------|--------|--------|--------|---------|
| Starting mass                       | 120100 | 120100 | 120100 | 120100 | 120100  |
| Volatilization                      | 0      | 0      | 100    | 200    | 200     |
| Outflow                             | 100    | 400    | 2100   | 6100   | 7800    |
| Burial                              | 0      | 0      | 0      | 0      | 0       |
| Degradation in water                | 700    | 800    | 800    | 300    | 0       |
| Degradation in sediment             | 119300 | 119000 | 114300 | 48800  | 0       |
| Total losses                        | 120100 | 120100 | 117300 | 55400  | 8000    |
| Mass in 5 yr                        | 0      | 0      | 2800   | 64700  | 112100  |
| % of initial mass lost              | 100%   | 100%   | 98%    | 46%    | 7%      |

| <u>Degradation Rate (d<sup>-1</sup>)</u> | <u>PAH</u> | <u>Rate</u> |
|------------------------------------------|------------|-------------|
| Naphthalene                              | N          | 0.03        |
| Phenanthrene                             | P          | 0.01        |
| Fluoranthene                             | F          | 0.002       |
| Benz(a)anthracene                        | B(a)a      | 0.002       |
| Benzo(b)fluoranthene                     | B(b)f      | 0.0003      |
| Dibenz(a,h)anthracene                    | Da         | 0.0003      |
| Benzo(ghi)perylene                       | Bp         | 0.0003      |

Table 9. Predicted losses from the Estuary through different pathways over a 5 yr period with varying octanol-water partition coefficient ( $K_{ow}$ ). Assumes no external load and hypothetical identical starting mass of each compound. All chemical parameters other than  $K_{ow}$  are set for benzo(b)fluoranthene. All data in kg, except as noted.

| Octanol-water partition coefficient ( $K_{ow}$ ; log scale) | 3.36   | 4.46   | 5.22   | 5.86   | 6.40   | 6.64   | 7.05   |
|-------------------------------------------------------------|--------|--------|--------|--------|--------|--------|--------|
| Starting mass                                               | 120100 | 120100 | 120100 | 120100 | 120100 | 120100 | 120100 |
| Volatilization                                              | 17000  | 8300   | 2300   | 600    | 200    | 100    | 0      |
| Outflow                                                     | 88200  | 45500  | 16400  | 8100   | 6100   | 5700   | 5400   |
| Burial                                                      | 0      | 0      | 0      | 0      | 0      | 0      | 0      |
| Degradation in water                                        | 4700   | 2400   | 900    | 400    | 300    | 300    | 300    |
| Degradation in sediment                                     | 9800   | 33700  | 45000  | 48100  | 48800  | 48900  | 49000  |
| Total losses                                                | 119700 | 89900  | 64600  | 57200  | 55400  | 55000  | 54700  |
| Mass in 5 yr                                                | 400    | 30200  | 55500  | 62900  | 64700  | 65100  | 65400  |
| % of initial mass lost                                      | 100%   | 75%    | 54%    | 48%    | 46%    | 46%    | 46%    |

| <u><math>K_{ow}</math> for each PAH</u> | <u>PAH</u> | <u><math>K_{ow}</math></u> | <u>Log <math>K_{ow}</math></u> |
|-----------------------------------------|------------|----------------------------|--------------------------------|
| Naphthalene                             | N          | 2.3E+03                    | 3.36                           |
| Phenanthrene                            | P          | 2.9E+04                    | 4.46                           |
| Fluoranthene                            | F          | 1.7E+05                    | 5.22                           |
| Benz(a)anthracene                       | B(a)a      | 7.2E+05                    | 5.86                           |
| Benzo(b)fluoranthene                    | B(b)f      | 2.5E+06                    | 6.40                           |
| Dibenz(a,h)anthracene                   | Da         | 4.4E+06                    | 6.64                           |
| Benzo(ghi)perylene                      | Bp         | 1.1E+07                    | 7.05                           |

Table 10. Predicted losses from the Estuary through different pathways over a 5 yr period with varying Henry's law constant. Assumes no external load and hypothetical identical starting mass of each compound. All chemical parameters other than Henry's law constant are set for benzo(b)fluoranthene. All data in kg, except as noted.

| Henry's Law Constant (Pa m <sup>3</sup> mol <sup>-1</sup> ) | 24.3   | 2.04   | 0.59   | 0.33   | 0.033  | 0.008  | 0.011  |
|-------------------------------------------------------------|--------|--------|--------|--------|--------|--------|--------|
| Starting mass                                               | 120100 | 120100 | 120100 | 120100 | 120100 | 120100 | 120100 |
| Volatilization                                              | 16900  | 6900   | 2700   | 1600   | 200    | 0      | 100    |
| Outflow                                                     | 5000   | 5600   | 5900   | 6000   | 6100   | 6100   | 6100   |
| Burial                                                      | 0      | 0      | 0      | 0      | 0      | 0      | 0      |
| Degradation in water                                        | 300    | 300    | 300    | 300    | 300    | 300    | 300    |
| Degradation in sediment                                     | 44700  | 47200  | 48200  | 48400  | 48800  | 48800  | 48800  |
| Total losses                                                | 66900  | 60000  | 57100  | 56300  | 55400  | 55200  | 55300  |
| Mass in 5 yr                                                | 53200  | 60100  | 63000  | 63800  | 64700  | 64900  | 64800  |
| % of initial mass lost                                      | 56%    | 50%    | 48%    | 47%    | 46%    | 46%    | 46%    |

| <u>Henry's law constant (Pa m<sup>3</sup> mol<sup>-1</sup>)</u> | <u>PAH</u> | <u>HLC</u> |
|-----------------------------------------------------------------|------------|------------|
| Naphthalene                                                     | N          | 24.3       |
| Phenanthrene                                                    | P          | 2.04       |
| Fluoranthene                                                    | F          | 0.59       |
| Benz(a)anthracene                                               | B(a)a      | 0.33       |
| Benzo(b)fluoranthene                                            | B(b)f      | 0.033      |
| Dibenz(a,h)anthracene                                           | Da         | 0.008      |
| Benzo(ghi)perylene                                              | Bp         | 0.011      |

Table 11. Contribution to variance of model results in Monte Carlo simulations in which degradation rate was held fixed. Only parameters explaining at least 1 % of variation in one of the model scenarios are listed. Negative values indicate negative correlation between parameter values and model results. When degradation rate was allowed to vary, it explained between 69.3 % and 99.7 % of results variance.

| Parameter                                           | Percent (%) Contribution to Variance |               |                   |                           |
|-----------------------------------------------------|--------------------------------------|---------------|-------------------|---------------------------|
|                                                     | Residence Time                       | Response Rate | Steady State Mass | Instantaneous Annual Loss |
| Active sediment layer depth                         | 49.4                                 | -54.7         | 41.2              | 62.6                      |
| Concentration of solids in sediment                 | 12.0                                 | -24.5         | 16.5              | 31.4                      |
| Sediment burial mass transfer coefficient           | -29.3                                | 1.2           | -1.1              | 0.0                       |
| Water inflow and outflow                            | -6.4                                 | 11.1          | -15.8             | 0.1                       |
| Solids settling rate                                | 0.0                                  | 0.2           | 16.7              | 0.0                       |
| Average PAH concentration in sediments              | 2.6                                  | 0.0           | 0.0               | 5.8                       |
| Octanol water partitioning coefficient ( $K_{ow}$ ) | 0.1                                  | -2.9          | 2.5               | 0.0                       |
| Organic carbon content of suspended solids          | 0.0                                  | -2.1          | 3.0               | 0.0                       |
| Concentration of particles in water                 | 0.0                                  | 1.7           | -0.9              | 0.0                       |

Table 12. Best available literature estimates of annual PAH loading to San Francisco Bay via different pathways. All values are kilograms/year. Ranges are those presented by the individual study authors.

| Pathway                         | Minimum Value | Nominal Value | Maximum Value | Reference                              |
|---------------------------------|---------------|---------------|---------------|----------------------------------------|
| Point Source Effluent Discharge | 200           | 200           | 1100          | Davis et al. 2000                      |
| Atmospheric Deposition          | 0             | 270           | 890           | Tsai et al. 2002                       |
| Central Valley River Loading    | 0             | 300           | 3000          | Gunther et al. 1991; Davis et al. 2000 |
| Storm Drain Runoff              | 130           | 2800          | 5500          | Gunther et al. 1991                    |
| Total Loading                   | 330           | 3570          | 10490         |                                        |

Table 13. Model predicted estimates of degradation rates when loading rates are modified and all other parameters remain constant. The nominal literature values are presented in boldface. Chemical parameters are set for benzo(b)fluoranthene, a high molecular weight PAH. When parameters are set for fluoranthene (a 4 ring PAH), loadings must be about an order of magnitude higher at the corresponding degradation rates.

| Loading Rate (kg/y)     | Degradation Rate (d <sup>-1</sup> ) | Comments                                           |
|-------------------------|-------------------------------------|----------------------------------------------------|
| 330 <sub>a</sub>        | NA                                  | Minimum loading literature value                   |
| <b>3600<sub>a</sub></b> | 0.00004                             | Nominal loading literature value                   |
| 10,500 <sub>a</sub>     | 0.0002                              | Maximum loading literature value                   |
| 1700                    | 0                                   | Loading required for no degradation                |
| 3300                    | 0.000035 <sub>b</sub>               | Low-end degradation literature value               |
| 18,000                  | <b>0.00035<sub>b</sub></b>          | Nominal degradation literature value               |
| 140,000                 | 0.0035                              | Order of magnitude above nominal degradation value |
| 460,000                 | 0.01 <sub>b</sub>                   | High-end degradation literature value              |

a. From Table 12

b. Based on Table 4 and Appendix 1

NA. No positive degradation value fits with such a low loading rate.

Table 14. Rate constants ( $d^{-1}$ ) for LPAHs and HPAHs in the San Francisco Estuary based on best estimates of model input data and PAH parameters for phenanthrene (an LPAH) and benzo(b)fluoranthene (an HPAH). PCB 118 values (Davis, 2004) included for comparison.

| RATE CONSTANT               | Notation  | APPLIES TO MASS IN ... | Phenanthrene | Benzo(b)fluoranthene | PCB 118   |
|-----------------------------|-----------|------------------------|--------------|----------------------|-----------|
| Outflow                     | $k_O$     | WATER                  | 0.0056       | 0.0056               | 0.0054    |
| Volatilization              | $k_V$     | WATER                  | 0.049        | 0.00016              | 0.0044    |
| Solids settling             | $k_{WS1}$ | WATER                  | 0.013        | 0.17                 | 0.185     |
| Water-to-sediment diffusion | $k_{WS2}$ | WATER                  | 0.00045      | 0.00007              | 0.000035  |
| Degradation in water        | $k_{WR}$  | WATER                  | 0.01         | 0.0003               | 0.000034  |
| Solids resuspension         | $k_{SW1}$ | SEDIMENT               | 0.0011       | 0.0011               | 0.0011    |
| Sediment-to-water diffusion | $k_{SW2}$ | SEDIMENT               | 0.0003       | 0.0000035            | 0.0000012 |
| Burial                      | $k_B$     | SEDIMENT               | 0            | 0                    | 0         |
| Degradation in sediment     | $k_{SR}$  | SEDIMENT               | 0.01         | 0.0003               | 0.000034  |



## FIGURE CAPTIONS

Figure 1. Predicted losses from the Estuary through different pathways for different PAHs over a one year period. Assumes no external load and an initial starting mass of 120,000 kilograms.

Figure 2. Histogram plots of Monte Carlo simulation results for the long-term fate of HPAH in San Francisco Bay. Vertical axes represent number of results in 10,000 iterations. White bars (left axes) represent results given uniformly distributed degradation rates varying between  $4 \times 10^{-5}$  and  $4 \times 10^{-4} \text{ d}^{-1}$ . Black bars (right axes) represent results when degradation rate was held fixed at  $3 \times 10^{-4} \text{ d}^{-1}$ . Table 3 presents other parameter values and distributions used in simulations, and PAH chemical attributes were modeled using benzo(b)fluoranthene values. a) PAH residence time (initial total mass in the Bay (kg) / instantaneous annual losses (kg/yr)). b) Percent loss in 5 years, assuming no loading. c) Steady state PAH mass in Bay, assuming 15,000 kg/yr annual loading.

Figure 3. Annual Estuary-wide average sediment PAH concentrations. Data from 1993 through 2001 represents annual summer means of 26 RMP sediment monitoring stations. Data from 1991 and 1992 are Pilot RMP data collected from locations corresponding to RMP sediment sampling sites (N = 11 for 1991 and 1992). All data are summer data with the exception of 1992, which was sampled in March and April. Use of the spring sampling event for each year leads to qualitatively similar results.

Figure 4. Annual Estuary-wide average dry season total PAH and HPAH concentrations in Bay mussel (*Mytilus sp.*) from 6 RMP monitoring stations (1994 through 2001). Data are presented as lipid weight concentrations (ng/g lipid) and were assembled by Dane Hardin. HPAHs include 12 combustion product PAHs having four to six rings, in addition to phenanthrene.

Figure 5. Predicted losses from the Estuary for phenanthrene (a three ring PAH), fluoranthene (a four ring PAH), benzo(b)fluoranthene (a five ring PAH), and PCB118, presented as percent loss of the original starting mass.

Figure 1

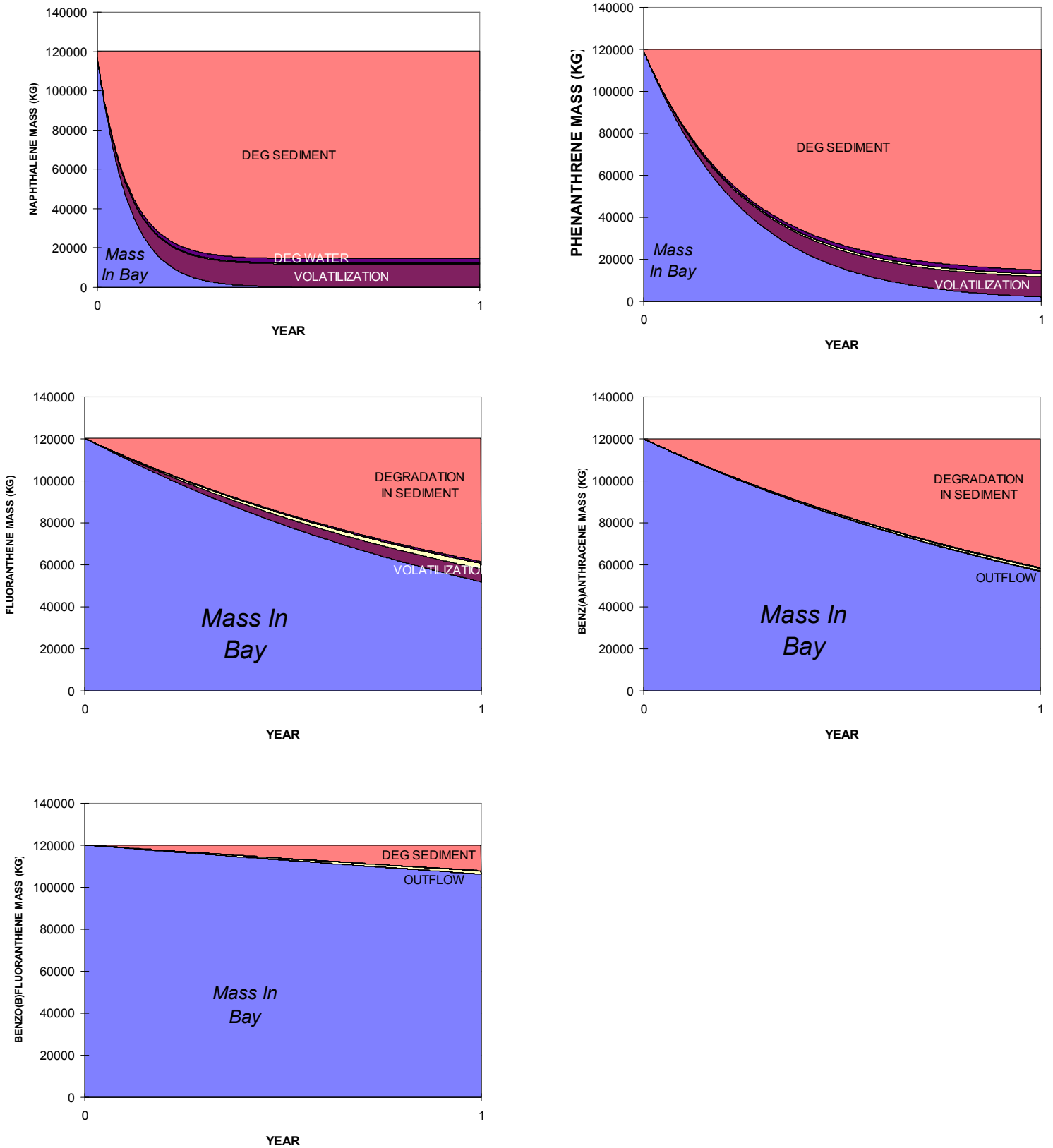


Figure 2

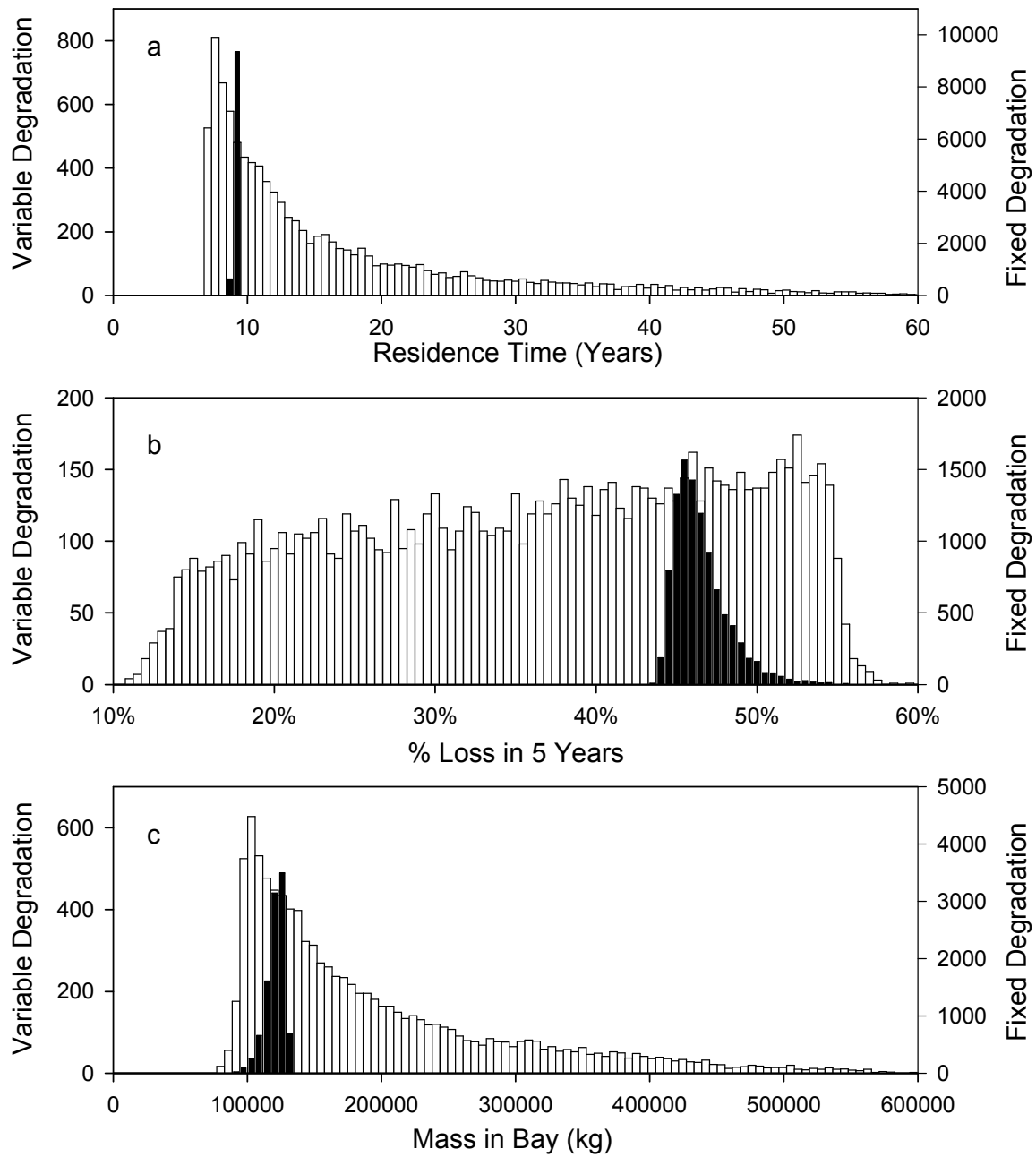


Figure 3

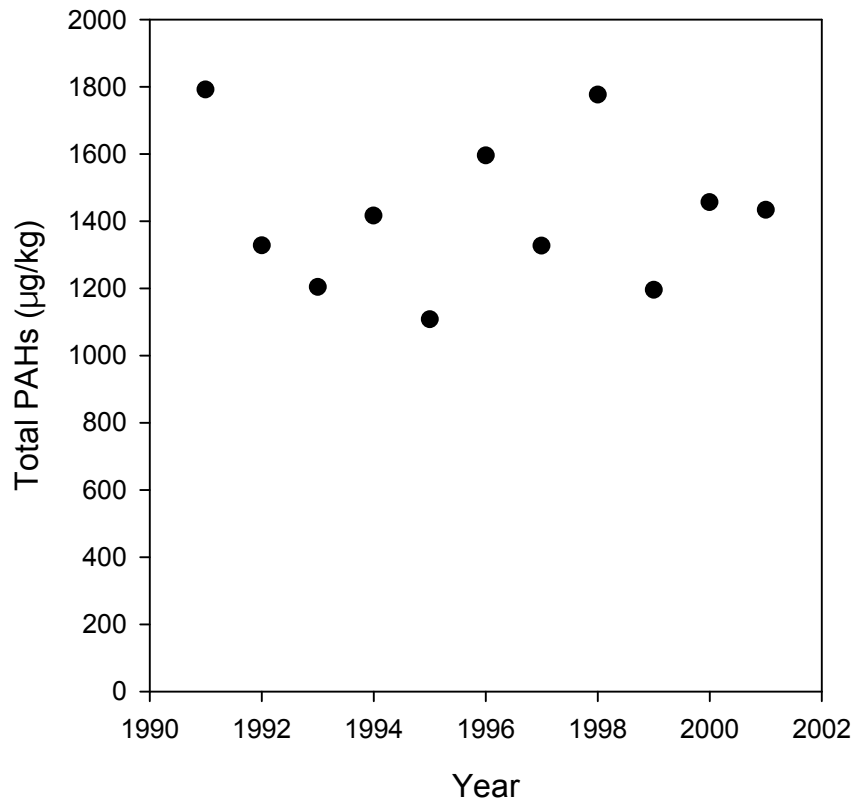


Figure 4

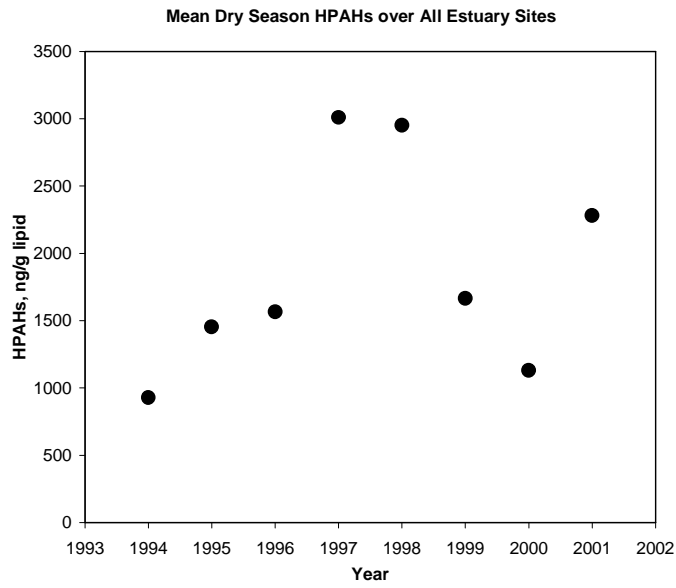
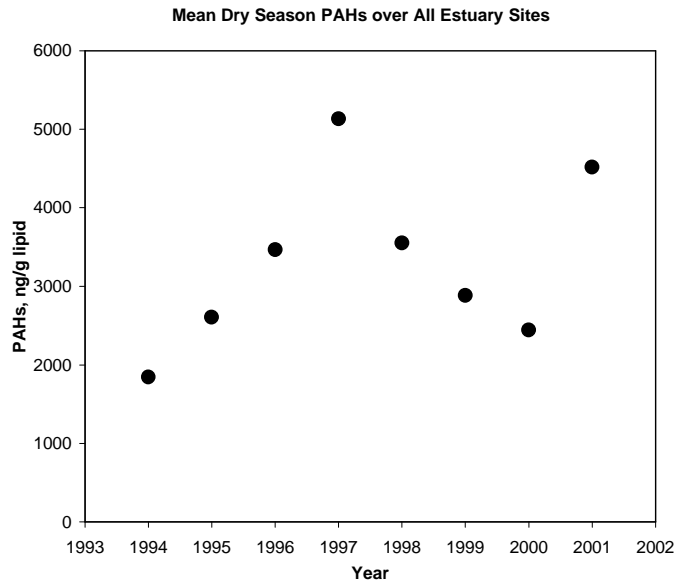
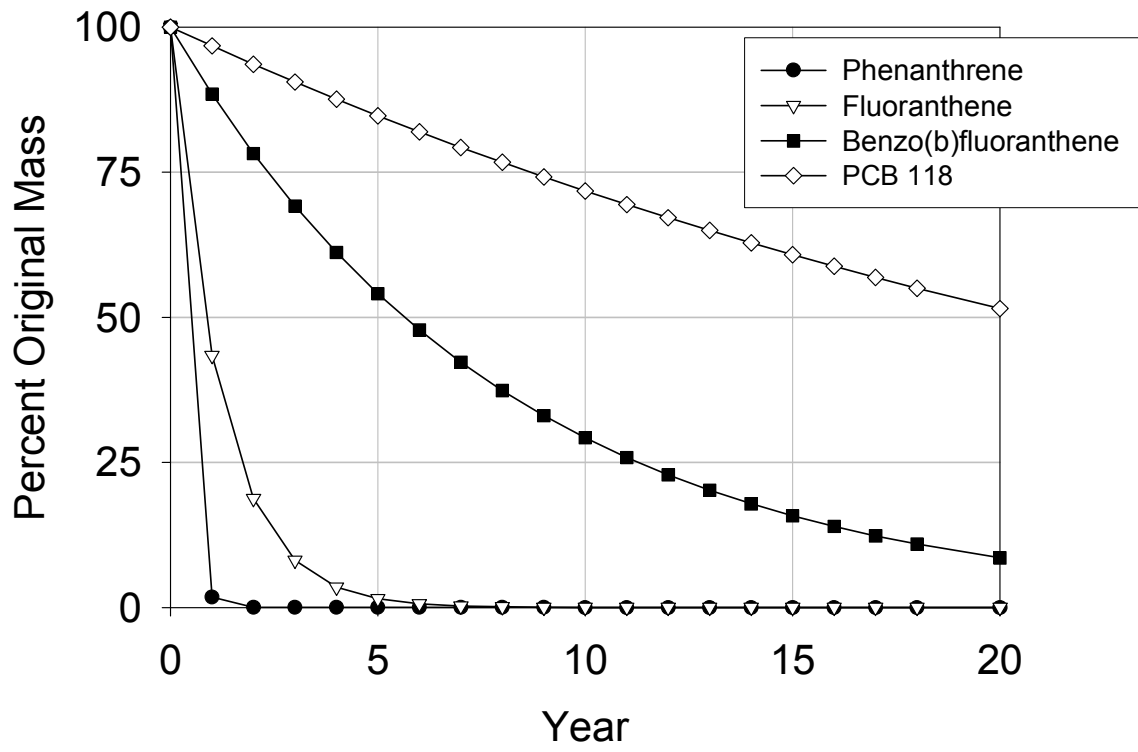


Figure 5



Notes on Appendix Table 1. Compilation of literature derived PAH degradation rates.

This table represents the results of a thorough but not exhaustive literature review compiling degradation rates of the PAHs we modeled. Because of the high availability of data, rates for benzo(a)pyrene are also reported. Only experiments using water and sediment samples were used (i.e., degradation in terrestrial soils, aerosols, and other non-aquatic materials were not used). Experiments involving nutrient addition were generally not included. When several independent results from separate sites were reported in a study, we present each as a separate data point.

Definitions of Appendix Table 1 headings and notations:

Matrix - the original material used in experiments. For laboratory experiments, this is sometimes combined with additional materials such as sand or water.

Method - the experimental method for determining rate. Note that most studies are laboratory incubations of sediment or water samples collected in the field.

Contaminated - indicates whether the study reports the matrix as coming from a contaminated site. When left blank, this indicates that the study or literature survey did not indicate.

Reaction order - indicates whether results were reported as first-order equations (1), such as half-lives, or as zero-order steady-state rate constants (0).

Type of degradation – B = biological; C = chemical; P = photodegradation  
Degradation rates are reported as rates per day.

Reference - when a reference is indicated as quoted from another reference, the original reference was not examined.

Appendix Table 1. Compilation of literature derived PAH degradation rates.

| Matrix                          | Method                     | Contaminated | Reaction Order | Type of Degradation | Temperature | Degradation Rate (1/Day) |              |              |                   |                      |                       |                    | Reference |                                                             |
|---------------------------------|----------------------------|--------------|----------------|---------------------|-------------|--------------------------|--------------|--------------|-------------------|----------------------|-----------------------|--------------------|-----------|-------------------------------------------------------------|
|                                 |                            |              |                |                     |             | Naphthalene              | Phenanthrene | Fluoranthene | Benz(a)anthracene | Benzo(b)fluoranthene | Dibenz(a,h)anthracene | Benzo(ghi)perylene |           | Benzo(a)pyrene                                              |
| Riverine Water                  | In Situ Field Measurements | 1            | BC             |                     |             | 1.19E-02                 | 8.32E-03     |              |                   |                      |                       |                    | 4.16E-04  | Lun et al., 1998                                            |
| Riverine Water                  | In Situ Field Measurements | 1            | BC             |                     |             | 1.19E-02                 | 6.93E-03     |              |                   |                      |                       |                    | 1.39E-03  | Lun et al., 1998                                            |
| Riverine Water                  | In Situ Field Measurements | 1            | BC             |                     |             | 4.38E-02                 | 9.79E-03     |              |                   |                      |                       |                    | 2.77E-03  | Lun et al., 1998                                            |
| Riverine Water                  | In Situ Field Measurements | 1            | BC             |                     |             | 4.62E-02                 | 5.55E-03     |              |                   |                      |                       |                    | 2.77E-04  | Lun et al., 1998                                            |
| Riverine Water                  | In Situ Field Measurements | 1            | BC             |                     |             | 1.04E-02                 | 8.32E-04     |              |                   |                      |                       |                    | 4.16E-04  | Lun et al., 1998                                            |
| Riverine Sediment               | In Situ Field Measurements | 1            | BC             |                     |             | 9.79E-03                 | 8.32E-03     |              |                   |                      |                       |                    | 4.16E-05  | Lun et al., 1998                                            |
| Riverine Sediment               | In Situ Field Measurements | 1            | BC             |                     |             | 9.79E-03                 | 4.16E-03     |              |                   |                      |                       |                    | 1.39E-04  | Lun et al., 1998                                            |
| Riverine Sediment               | In Situ Field Measurements | 1            | BC             |                     |             | 3.47E-02                 | 9.79E-03     |              |                   |                      |                       |                    | 2.77E-04  | Lun et al., 1998                                            |
| Riverine Sediment               | In Situ Field Measurements | 1            | BC             |                     |             | 3.78E-02                 | 2.87E-03     |              |                   |                      |                       |                    | 2.77E-04  | Lun et al., 1998                                            |
| Riverine Sediment               | In Situ Field Measurements | 1            | BC             |                     |             | 8.32E-03                 | 4.16E-04     |              |                   |                      |                       |                    | 4.16E-05  | Lun et al., 1998                                            |
| Clean Estuarine Stream          |                            | n            | 1              | B                   |             | 2.89E-02                 |              |              |                   |                      |                       |                    |           | Lee 1977, quoted MacKay et al. 1992                         |
| Coastal Waters                  |                            | 1            | B              |                     |             | 1.10E-02                 |              |              |                   |                      |                       |                    |           | Lee 1977, quoted MacKay et al. 1992                         |
| Estuarine River                 |                            | 1            | B              |                     |             | 3.47E-02                 |              |              |                   |                      |                       |                    |           | Lee and Ryan 1976, quoted Mackay et al. 1992                |
| River Waters                    |                            | 1            | B              |                     |             | 1.31E-02                 |              |              |                   |                      |                       |                    |           | Vaishnav and Babeau, 1987, quoted Mackay et al. 1992        |
| River Waters                    |                            | 1            | B              |                     |             | 1.78E-02                 |              |              |                   |                      |                       |                    |           | Vaishnav and Babeau, 1987, quoted Mackay et al. 1992        |
| Sandy Estuarine Sediment        | In Situ Field Measurements | n            | 1              | BC                  |             |                          | 2.31E-02     |              |                   |                      |                       |                    |           | Wilcock et al. 1996                                         |
| Contaminated Estuarine Sediment | Laboratory Incubation      | y            | 0              | B                   | 2-22        | 7.58E-02                 | 1.27E-01     |              |                   |                      |                       |                    | 1.86E-02  | Shiaris, M.P. 1989                                          |
| Contaminated Estuarine Sediment | Laboratory Incubation      | y            | 0              | B                   | 2-22        | 4.98E-02                 | 1.19E-01     |              |                   |                      |                       |                    | 1.22E-02  | Shiaris, M.P. 1989                                          |
| Contaminated Estuarine Sediment | Laboratory Incubation      | y            | 0              | B                   | 2-22        | 5.21E-02                 | 5.05E-02     |              |                   |                      |                       |                    | 1.25E-02  | Shiaris, M.P. 1989                                          |
| Groundwater                     | Multiple Methods           | 1            | B              |                     |             | 8.80E-01                 |              |              |                   |                      |                       |                    |           | Landmeyer et al., 1998                                      |
| Pristine Reservoir              | Laboratory Incubation      | n            | 1              | B                   | 22          | 2.25E-02                 | 5.50E-03     |              |                   |                      |                       |                    | 0.00E+00  | Heitkamp and Cerniglia, 1987                                |
| Lake Sediments                  | Laboratory Incubation      | y            | 1              | B                   | 22          | 3.09E-02                 | 1.24E-02     |              |                   |                      |                       |                    | 3.30E-04  | Heitkamp and Cerniglia, 1987                                |
| Coastal Sediments               | Laboratory Incubation      | y            | 1              | B                   | 22          | 4.13E-02                 | 2.48E-02     |              |                   |                      |                       |                    | 4.95E-04  | Heitkamp and Cerniglia, 1987                                |
| Estuarine Sediments             | Laboratory Incubation      | 0            | B              | 20                  |             | 4.76E-02                 |              |              |                   |                      |                       |                    |           | Bauer and Capone, 1985                                      |
| Estuarine Water                 | Laboratory Incubation      | 0            | B              |                     |             | 6.45E-02                 |              |              |                   |                      |                       |                    | 1.82E-04  | Readman et al. 1982                                         |
| Stream Sediments                | Laboratory Incubation      | y            | 0              | B                   | 12          | 3.33E+00                 |              | 2.40E-03     |                   |                      |                       |                    | 8.00E-04  | Herbes and Schwall 1978; quoted Cerniglia and Heitkamp 1989 |
| Stream Sediments                | Laboratory Incubation      | n            | 0              | B                   | 12          | 2.38E-02                 |              | 9.60E-05     |                   |                      |                       |                    | 4.81E-05  | Herbes and Schwall 1978; quoted Cerniglia and Heitkamp 1989 |
| Stream Sediments                | Laboratory Incubation      | y            | 0              | B                   |             | 1.85E+00                 |              | 8.00E-02     |                   |                      |                       |                    |           | Herbes 1981; quoted Cerniglia and Heitkamp 1989             |
| Stream Sediments                | Laboratory Incubation      | y            | 0              | B                   |             | 7.68E-02                 |              |              |                   |                      |                       |                    |           | Herbes 1981; quoted Cerniglia and Heitkamp 1989             |
| Georga Estuary Water            | Laboratory Incubation      | n            | 1              | B                   | 8           | 3.85E-03                 | 3.30E-03     |              |                   |                      |                       |                    |           | Lee and Ryan 1983                                           |
| Georga Estuary Water            | Laboratory Incubation      | n            | 1              | B                   | 15          | 9.90E-02                 |              |              |                   |                      |                       |                    |           | Lee and Ryan 1983                                           |
| Georga Estuary Water            | Laboratory Incubation      | n            | 1              | B                   | 26          | 3.47E-01                 |              |              |                   |                      |                       |                    |           | Lee and Ryan 1983                                           |
| South Carolina Estuary Water    | Laboratory Incubation      | y            | 1              | B                   | 22          | 4.95E-02                 |              |              |                   |                      |                       |                    |           | Lee and Ryan 1983                                           |
| Georga Estuary Water            | Laboratory Incubation      | n            | 1              | B                   | 27          |                          | 3.65E-02     |              |                   |                      |                       |                    |           | Lee and Ryan 1983                                           |
| Georga Estuary Sediment         | Laboratory Incubation      | n            | 1              | B                   | 28          |                          |              | 5.78E-03     |                   |                      |                       |                    |           | Lee and Ryan 1983                                           |
| Georga Estuary Water            | Laboratory Incubation      | n            | 1              | B                   | 28          |                          | 2.89E-02     |              |                   |                      |                       |                    |           | Lee and Ryan 1983                                           |
| South Carolina Estuary Water    | Laboratory Incubation      | y            | 1              | B                   | 27          |                          | 1.22E-02     |              |                   |                      |                       |                    |           | Lee and Ryan 1983                                           |
| Georga Estuary Sediment         | Laboratory Incubation      | n            | 1              | B                   | 18          |                          |              |              |                   |                      |                       |                    |           | Lee and Ryan 1983                                           |
| Georga Estuary Sediment         | Laboratory Incubation      | n            | 1              | B                   | 8           |                          |              | 1.47E-03     |                   |                      |                       |                    |           | Lee and Ryan 1983                                           |
| Georga Estuary Sediment         | Laboratory Incubation      | n            | 1              | B                   | 15          |                          |              | 2.04E-03     |                   |                      |                       |                    |           | Lee and Ryan 1983                                           |
| South Carolina Estuary Sediment | Laboratory Incubation      | y            | 1              | B                   | 27          |                          |              | 4.33E-02     |                   |                      |                       |                    |           | Lee and Ryan 1983                                           |
| Rhode Island Estuary Sediment   | Laboratory Incubation      | n            | 1              | B                   | 10          |                          |              |              |                   |                      |                       |                    |           | Lee and Ryan 1983                                           |
| Rhode Island Estuary Water      | Laboratory Incubation      | n            | 1              | B                   | 10          | 5.55E-03                 |              |              |                   |                      |                       |                    |           | Lee and Ryan 1983                                           |
| Rhode Island Estuary Water      | Laboratory Incubation      | n            | 1              | B                   | 2           |                          | 6.30E-05     |              |                   |                      |                       |                    |           | Lee and Ryan 1983                                           |
| Rhode Island Estuary Water      | Laboratory Incubation      | n            | 1              | B                   | 8           |                          | 3.85E-03     |              |                   |                      |                       |                    |           | Lee and Ryan 1983                                           |



Appendix Table 1. Compilation of literature derived PAH degradation rates (Continued).

| Matrix                         | Method                | Contaminated | Reaction Order | Type of Degradation | Temperature | Degradation Rate (1/Day) |              |              |                   |                      |                       |                    | Reference |                |                                                                     |
|--------------------------------|-----------------------|--------------|----------------|---------------------|-------------|--------------------------|--------------|--------------|-------------------|----------------------|-----------------------|--------------------|-----------|----------------|---------------------------------------------------------------------|
|                                |                       |              |                |                     |             | Naphthalene              | Phenanthrene | Fluoranthene | Benz(a)anthracene | Benzo(b)fluoranthene | Dibenz(a,h)anthracene | Benzo(ghi)perylene |           | Benzo(a)pyrene |                                                                     |
| Rhode Island Estuary Water     | Laboratory Incubation | n            | 1              | B                   | 18          |                          | 8.77E-03     |              |                   |                      |                       |                    |           |                | Lee and Ryan 1983                                                   |
| Rhode Island Estuary Sediment  | Laboratory Incubation | n            | 1              | B                   | 18          |                          |              |              |                   |                      |                       |                    |           |                | Lee and Ryan 1983                                                   |
| Rhode Island Estuary Sediment  | Laboratory Incubation | n            | 1              | B                   | 4           |                          |              |              | 3.30E-05          |                      |                       |                    |           |                | Lee and Ryan 1983                                                   |
| Rhode Island Estuary Sediment  | Laboratory Incubation | n            | 1              | B                   | 8           |                          |              |              | 2.89E-04          |                      |                       |                    |           |                | Lee and Ryan 1983                                                   |
| Rhode Island Estuary Sediment  | Laboratory Incubation | n            | 1              | B                   | 15          |                          |              |              | 6.30E-04          |                      |                       |                    |           |                | Lee and Ryan 1983                                                   |
| Rhode Island Estuary Water     | Laboratory Incubation | n            | 1              | B                   | 7           |                          |              |              |                   |                      |                       |                    |           |                | Lee and Ryan 1983                                                   |
| Rhode Island Estuary Water     | Laboratory Incubation | n            | 1              | B                   | 23          |                          |              |              |                   |                      |                       |                    |           |                | Lee and Ryan 1983                                                   |
| Rhode Island Estuary Sediment  | Laboratory Incubation | n            | 1              | B                   | 23          |                          |              |              |                   |                      |                       |                    |           |                | Lee and Ryan 1983                                                   |
| Sediment                       | Estimate              |              | 1              | BCP                 |             |                          |              |              |                   |                      |                       | 3.02E-04           |           |                | Beyer et al. 2000                                                   |
| Water and Suspended Sediment   | Estimate              |              | 1              | BCP                 |             |                          |              |              |                   |                      |                       | 9.79E-03           |           |                | Beyer et al. 2000                                                   |
| Sediment                       | Estimate              |              | 1              | BCP                 |             |                          | 1.39E-05     |              |                   |                      |                       | 1.39E-05           |           |                | F.A.P.C. Gobas, Unpublished                                         |
| Water                          | Estimate              |              | 1              | BCP                 |             |                          | 3.85E-04     |              |                   |                      |                       | 3.47E-04           |           |                | F.A.P.C. Gobas, Unpublished                                         |
| Water                          | Literature Value      |              | 1              | BCP                 | 10          |                          | 9.79E-03     |              |                   | 3.02E-02             |                       | 9.79E-03           |           |                | Mackay and Hickie 2000                                              |
| Sediment                       | Literature Value      |              | 1              | BCP                 | 10          |                          | 3.02E-04     | 3.02E-04     |                   | 9.79E-04             |                       | 3.02E-04           |           |                | Mackay and Hickie 2000                                              |
| Sediment                       | Sediment Core Model   |              | 1              | BCP                 |             |                          | 3.85E-03     |              | 0.00E+00          |                      |                       | 0.00E+00           |           |                | Su et al. 2000                                                      |
| Riverine Water                 | Literature Estimate   |              |                | B                   |             |                          |              |              |                   |                      |                       |                    |           |                | 3.50E-05 Ryan and Cohen 1986                                        |
| Estuarine Water                |                       |              | 0              |                     | 13          | 2.00E-03                 |              |              |                   |                      |                       |                    |           |                | Bauer et al. 1988; quoted MacGillivray and Shiaris 1994             |
| Seawater                       |                       |              | 0              |                     | 12          | 2.45E-03                 |              |              |                   |                      |                       |                    |           |                | Bauer et al. 1988; quoted MacGillivray and Shiaris 1994             |
| Estuarine Sediment             |                       |              | 0              |                     |             | 3.48E-03                 |              |              |                   |                      |                       |                    |           |                | Pruell and Quinn 1985; quoted MacGillivray and Shiaris 1994         |
| Estuarine Sediment             |                       | y            | 0              |                     | 22          | 2.94E-02                 | 1.79E-02     |              |                   |                      |                       |                    |           |                | 3.57E-04 Heitkamp et al. 1987; quoted MacGillivray and Shiaris 1994 |
| Reservoir Sediment             |                       |              | 0              |                     | 22          | 1.61E-02                 | 3.97E-03     |              |                   |                      |                       |                    |           |                | 2.38E-04 Heitkamp et al. 1987; quoted MacGillivray and Shiaris 1994 |
| Reservoir Sediment             |                       |              | 0              |                     | 22          | 2.22E-02                 | 8.93E-03     |              |                   |                      |                       |                    |           |                | Heitkamp et al. 1987; quoted MacGillivray and Shiaris 1994          |
| Estuarine Sediment             | Laboratory Incubation | y            | 0              |                     | 30          | 5.71E-02                 |              |              |                   |                      |                       |                    |           |                | Hambrick et al. 1980; quoted MacGillivray and Shiaris 1994          |
| Water                          | Laboratory Incubation |              | 1              |                     | 20          |                          |              |              | 1.16E-02          |                      |                       |                    |           |                | Herbes et al. 1980; quoted Howard 2002                              |
| Sediment, High PAH Conc.       | Laboratory Incubation | y            | 1              |                     | 20          |                          |              |              | 1.73E-01          |                      |                       |                    |           |                | Herbes et al. 1980; quoted Howard 2002                              |
| Sediment, Moderate PAH Conc.   | Laboratory Incubation | y            | 1              |                     | 20          |                          |              |              | 2.39E-03          |                      |                       |                    |           |                | Herbes et al. 1980; quoted Howard 2002                              |
| Sediment, Low PAH Conc.        | Laboratory Incubation | n            | 1              |                     | 20          |                          |              |              | 8.35E-04          |                      |                       |                    |           |                | Herbes et al. 1980; quoted Howard 2002                              |
| Estuarine Sediment             | Aquatic Microcosm     |              | 0              |                     | 4-25        |                          |              |              | 1.37E-03          |                      |                       |                    |           |                | Hinga et al. 1980; quoted MacGillivray and Shiaris 1994             |
| Sediment                       | Laboratory Incubation |              | 0              |                     | 15          | 8.88E-03                 |              |              |                   |                      |                       |                    |           |                | Sayler and Sherrill 1981; quoted Howard 2002                        |
| Water                          | Mesocosm Experiment   |              | 1              |                     |             | 8.63E-02                 |              |              |                   |                      |                       |                    |           |                | Wakeham et al 1983; quoted Howard 2002                              |
| Sediment                       | Enclosure Experiment  |              | 1              |                     |             | 6.93E-01                 |              |              |                   |                      |                       |                    |           |                | Lee and Anderson 1977; quoted Howard 2002                           |
| Sediment                       | Laboratory Incubation | y            | 0              |                     | 25          |                          | 1.40E-02     | 1.20E-02     | 9.60E-03          | 2.80E-03             | 5.10E-03              | 3.20E-03           |           |                | Johnson and Ghosh 1998                                              |
| Estuarine Saltmarsh Sediment   | Laboratory Incubation | n            | 1              | B                   | 20          | 1.60E-01                 | 1.00E-01     |              |                   |                      |                       |                    |           |                | Jackson and Pardue 1999                                             |
| Sediment, Moderate PAH Conc.   | Laboratory Incubation | y            | 0              |                     | 20          | 2.41E-04                 | 6.94E-04     |              |                   |                      |                       |                    |           |                | Hayes et al. 1999                                                   |
| Sediment, High PAH Conc.       | Laboratory Incubation | y            | 0              |                     | 20          | 3.07E-03                 | 5.69E-03     |              |                   |                      |                       |                    |           |                | Hayes et al. 1999                                                   |
| Sediment, High PAH Conc.       | Laboratory Incubation | y            | 0              |                     | 20          | 5.18E-03                 | 4.17E-03     |              |                   |                      |                       |                    |           |                | Hayes et al. 1999                                                   |
| Sediment, High PAH Conc.       | Laboratory Incubation | y            | 0              |                     | 20          | 4.14E-03                 | 8.86E-03     |              |                   |                      |                       |                    |           |                | Hayes et al. 1999                                                   |
| Sediment, Low PAH Conc.        | Laboratory Incubation | n            | 0              |                     | 20          | 1.14E-03                 | 2.14E-04     |              |                   |                      |                       |                    |           |                | Hayes et al. 1999                                                   |
| Marine Sediment                | Laboratory Incubation | n            | 1              | BCP                 | 13          | 1.24E-02                 | 3.00E-03     |              |                   |                      |                       | 1.09E-03           |           |                | Apitz et al. 1999                                                   |
| Marine Sediment                | Laboratory Incubation | n            | 0              |                     | 18          |                          |              | 1.30E-02     |                   |                      |                       |                    |           |                | Kure and Forbes 1997                                                |
| Estuarine Sediment             | Laboratory Incubation | n            | 0              |                     |             | 1.08E-02                 |              |              |                   |                      |                       |                    |           |                | Guerin and Jones 1989                                               |
| Estuarine Sediment             | Laboratory Incubation | y            | 0              |                     |             | 3.50E-02                 |              |              |                   |                      |                       |                    |           |                | Guerin and Jones 1989                                               |
| Estuarine Sediment (Aerobic)   | Laboratory Incubation |              | 0              | B                   | 20          | 3.00E-01                 |              |              |                   |                      |                       |                    |           |                | Yamane et al. 1997                                                  |
| Estuarine Sediment (Anaerobic) | Laboratory Incubation |              | 0              | B                   | 20          | 0.00E+00                 |              |              |                   |                      |                       |                    |           |                | Yamane et al. 1997                                                  |

|                     |        |      |        |       |       |    |       |         |
|---------------------|--------|------|--------|-------|-------|----|-------|---------|
| <b>Median Rate</b>  | 0.03   | 0.01 | 0.01   | 0.002 | 0.003 | NA | 0.005 | 0.00033 |
| <b>Maximum Rate</b> | 3.3    | 0.3  | 0.01   | 0.2   | 0.03  | NA | 0.005 | 0.02    |
| <b>Minimum Rate</b> | 0.0002 | 0    | 0.0003 | 0     | 0.001 | 0  | 0.005 | 0       |
| <b>Sample Size</b>  | 49     | 44   | 5      | 17    | 3     | 0  | 1     | 31      |

Appendix Table 2. Compilation of literature derived Henry's Law Constants.

| Method            | Original Temperature | Published Henry's Law Constant (H) |              |              |                   |                      |                       | H at 15 C *        |             |              |              |                   |                      | Reference |                           |
|-------------------|----------------------|------------------------------------|--------------|--------------|-------------------|----------------------|-----------------------|--------------------|-------------|--------------|--------------|-------------------|----------------------|-----------|---------------------------|
|                   |                      | Naphthalene                        | Phenanthrene | Fluoranthene | Benz(a)anthracene | Benzo(b)fluoranthene | Dibenz(a,h)anthracene | Benzo(ghi)perylene | Naphthalene | Phenanthrene | Fluoranthene | Benz(a)anthracene | Benzo(b)fluoranthene |           | Dibenz(a,h)anthracene     |
| Experimental      | 25                   | 48.8                               | 9.4          |              |                   |                      |                       | 24.1               | 4.64        |              |              |                   |                      |           | Schwarzenbach et al. 1993 |
| Experimental      | 25                   | 49.6                               | 3.6          |              |                   |                      |                       | 24.5               | 1.78        |              |              |                   |                      |           | Schwarzenbach et al. 1993 |
| Calculated        | 25                   | 42.1                               | 2.5          |              |                   |                      |                       | 20.8               | 1.22        |              |              |                   |                      |           | Schwarzenbach et al. 1993 |
| Calculated        | 25                   |                                    | 2.6          | 1.06         | 0.58              |                      |                       |                    | 1.29        | 0.52         | 0.29         |                   |                      |           | Schwarzenbach et al. 1993 |
| Gas Stripping     | 25                   |                                    | 4.3          | 1.96         | 1.22              |                      |                       |                    | 2.12        | 0.97         | 0.60         |                   |                      |           | Bamford et al. 1999       |
| Literature Review | 25                   |                                    | 3.9          |              |                   |                      |                       |                    | 1.93        |              |              |                   |                      |           | Hoff et al. 1996          |
| Literature Review | 25                   |                                    | 3.2          | 1.04         |                   | 0.016                |                       |                    | 1.58        | 0.51         |              | 0.008             |                      |           | Mackay and Hickie 2000    |
| Gas Purge Method  | 20                   | 45.0                               | 2.9          | 1.1          |                   | 0.051                | 0.027                 | 23.9               | 1.92        | 0.49         |              | 0.038             |                      | 0.020     | de Maagd et al. 1998      |
| Calculated        | 15                   |                                    |              |              | 0.09              | 0.054                | 0.008                 |                    |             |              | 0.09         | 0.054             | 0.008                | 0.001     | Mackay et al. 1992        |
| Gas Stripping     | 25                   | 44.6                               | 3.6          |              |                   |                      |                       | 22.0               | 1.78        |              |              |                   |                      |           | Shiu and Mackay 1997      |
| Gas Stripping     | 25                   | 48.9                               | 4            |              |                   |                      |                       | 24.2               | 1.98        |              |              |                   |                      |           | Shiu and Mackay 1997      |
| Gas Stripping     | 20                   |                                    |              | 0.65         |                   | 0.051                | 0.027                 |                    |             | 0.43         |              | 0.038             |                      | 0.020     | Shiu and Mackay 1997      |
| Gas Stripping     | 25                   | 56.0                               | 5.6          |              |                   |                      |                       | 27.7               | 2.77        |              |              |                   |                      |           | Shiu and Mackay 1997      |
| Gas Stripping     | 25                   | 36.6                               | 2.4          |              |                   |                      |                       | 18.1               | 1.19        |              |              |                   |                      |           | Shiu and Mackay 1997      |
| Gas Stripping     | 25                   | 74.4                               | 4.7          |              |                   |                      |                       | 36.8               | 2.32        |              |              |                   |                      |           | Shiu and Mackay 1997      |
| Gas Stripping     | 25                   | 42.5                               |              |              |                   |                      |                       | 21.0               |             |              |              |                   |                      |           | Shiu and Mackay 1997      |
|                   |                      |                                    |              |              |                   |                      | <b>Mean</b>           | 24.3               | 2.04        | 0.59         | 0.33         | 0.034             | 0.008                | 0.014     |                           |
|                   |                      |                                    |              |              |                   |                      | <b>Maximum</b>        | 36.8               | 4.64        | 0.97         | 0.60         | 0.054             | 0.008                | 0.020     |                           |
|                   |                      |                                    |              |              |                   |                      | <b>Minimum</b>        | 18.1               | 1.19        | 0.43         | 0.09         | 0.008             | 0.008                | 0.001     |                           |
|                   |                      |                                    |              |              |                   |                      | <b>Sample Size</b>    | 10                 | 13          | 5            | 3            | 4                 | 1                    | 3         |                           |

\* Temperature conversion calculated using the equations presented in Ten Hulscher et al. 1992 or in de Maagd et al. 1998