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A PAH Fate Model For San Francisco Bay

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2 **ABSTRACT**

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4 A mass balance model was applied to simulate the long-term fate of PAHs in San
5 Francisco Bay. The model treats the Bay as a single box with interacting water and
6 sediment compartments, and includes loading, volatilization, outflow to the ocean,
7 degradation, and burial in deep sediment. The estimated time required for loss of one-
8 half of the mass in the Bay in the absence of loading ranged from 20 days for naphthalene
9 to five years for benzo(b)fluoranthene. Uncertainty analysis using Monte Carlo
10 simulation indicated a high degree of influence and uncertainty for degradation rates,
11 suggesting that improved estimates of degradation would significantly improve the
12 predictive ability of the model. A comparison of model calculations to literature values
13 suggested that external PAH loading to San Francisco Bay was at or above previous
14 estimates of 3600 kg yr⁻¹, and that degradation in the Bay was within the range of
15 commonly published estimates for high molecular weight PAHs ($4.0 \times 10^{-5} \text{ d}^{-1}$ to $4.0 \times$
16 10^{-4} d^{-1}).

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18 Keywords: polycyclic aromatic hydrocarbon, mass balance, degradation,
19 benzo(b)fluoranthene, response time, uncertainty analysis

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1 INTRODUCTION

2

3 Polycyclic aromatic hydrocarbons (PAHs) constitute a potential environmental
4 threat because they pose hazards to fish and wildlife at environmentally relevant
5 concentrations and because they have elevated environmental concentrations in urbanized
6 and industrial areas (e.g., Spies and Rice, 1988; Lun et al., 1998; Mackay and Hickie,
7 2000; McCain et al., 2000; Su et al., 2000; Wang et al., 2002). The actual threat posed by
8 PAHs to an ecosystem depends on PAH loading rates and long-term environmental
9 persistence (e.g., Mackay et al., 1994; Lun et al., 1998). In San Francisco Bay (the Bay),
10 PAH concentrations increased in the early 20th-century as historic sources were
11 augmented by coal burning and fossil-fuel combustion (Pereira et al., 1999). At present,
12 some locations in the Bay have among the highest sediment PAH concentrations of all
13 sites monitored on the U.S. Pacific Coast (McCain et al., 2000). Bay sediment PAH
14 contamination has been correlated with adverse impacts on fish and invertebrates (Spies
15 and Rice, 1988; Thompson et al., 1999). With the projected future increase in human
16 population (ABAG, 2002) and automobile use in the region, the extent of local
17 contamination may also increase. Due to the presence of PAHs at concentrations that may
18 adversely impact aquatic animals, the San Francisco Bay Regional Water Quality Control
19 Board placed PAHs on a regulatory watch list of compounds that may be impairing San
20 Francisco Bay (SFBRWQCB, 2001).

21 Contaminant environmental fate models can help estimate loading and long-term
22 fate of compounds such as PAHs, and identify key data gaps in understanding these
23 processes (e.g., Mackay et al., 1994; Lun et al., 1998; Davis, 2004). Contaminant

1 environmental fate models can also help identify which chemical properties strongly
2 influence long-term fate. Chemical properties, such as Henry's law constant and
3 degradation rate, can be difficult to measure accurately (e.g., Bamford et al., 1999; Talley
4 et al., 2002). Uncertainty analyses can evaluate variability in model output associated
5 with estimated parameters, and thereby prioritize future research needs.

6 In San Francisco Bay, the information gained by fate models has aided in
7 management of persistent organic pollutants. For example, the results of a long-term fate
8 model for PCBs (Davis, 2004) have helped to provide an initial conceptual framework for
9 the regulation of PCB loading into the Bay (SFBRWQCB, 2004). Because PAHs have
10 been identified by local regulators as a pollutant of concern for which more information
11 is needed (SFBRWQCB, 2001), models are needed to evaluate the loading and long-term
12 fate of these compounds.

13 The goal of the paper is to develop and evaluate a model that can be used to
14 assess the loading, removal, and long-term fate of PAHs in the San Francisco Bay. This
15 type of model may be used to support management decisions about how past and current
16 loadings of PAHs will impact the health of the Bay. The application of this PAH fate
17 model involves three important steps, each presented in this paper: 1.) synthesis of
18 relevant data on PAH chemical properties, current concentrations, and recent temporal
19 trends in the Bay; 2.) sensitivity and uncertainty analyses to identify model parameters
20 that should be more accurately characterized to improve confidence in the results; and 3.)
21 use of the models to estimate loss rate of several representative PAHs from the Bay. The
22 estimation of loss rates should aid in understanding how quickly the ecosystem would be
23 expected to respond to load reductions.

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2 **METHODS**

3

4 *Study Area Description*

5 San Francisco Bay is the largest estuary on the Pacific coast of both North and
6 South America. The landward boundary of San Francisco Bay is at the confluence of the
7 Sacramento and San Joaquin rivers. The seaward boundary is the Golden Gate, where
8 the Bay empties into the Pacific Ocean. The watershed of the Bay encompasses 40 % of
9 the land area of California, including the expansive agricultural land of the Central
10 Valley. The Bay is a complex ecosystem, exhibiting variability at multiple temporal
11 scales due to tidal action, climatic variation, and seasonal and interannual variability in
12 rainfall. The Bay is also spatially heterogeneous, with large hydrodynamic differences
13 among the major subembayments (Smith, 1987). The Bay is surrounded by the fourth
14 largest metropolitan area in the U.S. and the nation's historically most productive
15 mercury mining region. Due to a combination of water diversion, introduction of
16 nonnative species, habitat alteration, and contamination, the Bay is considered perhaps
17 the most highly altered coastal ecosystem in the U.S.

18 Primary PAH sources to San Francisco Bay are combustion processes, associated
19 with urbanization and industrialization (Oros and Ross, 2004). Dated sediment cores
20 indicate significant increases in fossil fuel combustion and PAH loading since the 1950s
21 (Pereira et al., 1999), likely associated with vehicle traffic in the San Francisco Bay area.
22 PAHs are transported to the Bay via direct atmospheric deposition (Tsai et al., 2002),
23 runoff from small urban rivers and storm drains (Gunther et al., 1991; Maruya et al.,

1 1996; Davis et al., 2000), and flows from rivers draining the San Jose metropolitan area
2 watersheds and Central Valley (Gunther et al., 1991).

3 The Regional Monitoring Program for Trace Substances, a comprehensive
4 contaminant and water quality monitoring program (SFEI, 2002; Hoenicke et al., 2003;
5 SFEI, 2003) has collected annual data on PAH concentrations in San Francisco Bay
6 water, sediments, and bivalves since 1993. Fluoranthene, pyrene, benzo(b)fluoranthene,
7 and benzo(g,h,i)perylene are relatively abundant in Bay sediment and phenanthrene,
8 fluoranthene, and pyrene are relatively abundant in water (Table 1). PAH fingerprints in
9 water and sediment indicate pyrogenic sources, possibly including automotive and diesel
10 fuel combustion and biomass burning (Table 1; Maruya et al., 1996; Pereira et al., 1999;
11 Oros and Ross, 2004). Concentrations are generally below regional regulatory criteria (U.
12 S. EPA, 2000), although some compounds occasionally exceed human health screening
13 values (Table 1; SFBRWQCB, 2001).

14

15 ***The Model***

16 This mass balance model (Table 2) was originally developed by Mackay et al.
17 (1994) for Lake Ontario and applied for PCB fate in San Francisco Bay by Davis (2004).
18 Both authors detail the equations, structure, and assumptions of this model, and Davis
19 develops model parameters for the physical properties of the Bay (summarized in Table
20 3). Model spreadsheets may be obtained by contacting the authors of this study. The
21 model represents contaminant loss pathways, treating San Francisco Bay as two well-
22 mixed compartments, the water column and the active sediment layer. Inputs and losses

1 to the water column and the active sediment layer are represented by two mass balance
2 equations:

$$3 \quad \Delta M_W / \Delta t = L + k_{SW} * M_S - (k_V + k_O + k_{WR} + k_{WS}) * M_W$$

$$4 \quad \Delta M_S / \Delta t = k_{WS} * M_W - (k_{SW} + k_B + k_{SR}) * M_S$$

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6
7 The two equations represent the change in water column PAH mass (M_W) and
8 sediment PAH mass (M_S) over time. Each "k" is a daily rate constant, indicating the
9 proportion of present PAH mass transformed and moved by volatilization (k_V), outflow
10 (k_O), degradation in water (k_{WR}), water to sediment transport (k_{WS}), sediment to water
11 transport (k_{SW}), sediment burial (k_B), and degradation in sediment (k_{SR}). Inputs to the
12 water column include loading (L ; includes all external sources) and transport from the
13 sediment layer (Table 2). Losses from the water column include volatilization, outflow,
14 degradation, and transport to the sediment. Inputs to the actively mixed sediments
15 include deposition and diffusion from the water column. Losses from the sediment
16 include transport to the water column, burial, and degradation.

17 The outflow rate constant (k_O) is a function of rate of water outflow through the
18 Golden Gate (F/X_W) (Table 2). The rate constant is multiplied by a ratio of PAH
19 concentration at seaward sites versus concentration throughout the Bay (PAH_O/PAH_A), to
20 account for reduced PAH concentrations at the seaward end of the Bay. The
21 volatilization rate constant (k_V) is directly proportional to the Bay water surface area to
22 volume ratio (S_{AW}/X_W), the fraction of PAH that is freely dissolved and thus available for
23 volatilization (ϕ_{DW}), and the volatilization mass transfer coefficient (V_E). PAH

1 compound-specific air and water-side mass transfer coefficients (V_{EA} , V_{EW}) and Henry's
2 law constant (H) all influence the volatilization mass transfer coefficient. The
3 degradation rate constants for water and sediment (k_{WR} , k_{SR}) are estimated from literature
4 values. The water to sediment and sediment to water transport rates (k_{WS} , k_{SW}) include
5 both dissolved and particulate transfer. Finally, the burial rate constant (k_B) is a function
6 of the Bay sediment surface area to volume ratio (S_{AS}/X_S), the particle-bound fraction of
7 PAH in the sediment ($1 - \phi_{DS}$), and the sediment burial mass transfer coefficient (V_B).
8 Following Davis (2004), the sediment burial mass transfer coefficient is set at zero, based
9 on recent findings that net erosion is occurring in substantial parts of the Bay (Cappiella
10 et al., 1999; Foxgrover et al., 2003). Loading from erosion of buried sediment is
11 accounted for in the combined loading term L . Uncertainty analyses test the sensitivity of
12 this assumption of zero net sediment burial.

13

14 ***PAH Selection***

15 From among the 25 PAHs analyzed by the Regional Monitoring Program for
16 Trace Substances (RMP), seven were chosen for modeling (Table 1; Table 4). Selected
17 PAHs spanned a range of chemical properties, represented a high proportion of Bay PAH
18 mass, and exceeded water quality objectives (Table 1; SFBRWQCB 2001). The seven
19 PAHs chosen comprise approximately 42 percent of the total mass in Bay sediments
20 (Table 4). The PAHs with 2 or 3 rings (low molecular weight PAHs; LPAHs) have
21 relatively rapid ecosystem loss rates due to their volatility, water solubility, and
22 biodegradability. PAHs with 4 or more rings (high molecular weight PAHs; HPAHs)
23 have increased hydrophobicity and chronic toxicity. HPAHs have relatively slow

1 degradation and volatilization rates, resulting in lower ecosystem loss rates than LPAHs
2 (Heitkamp and Cerniglia, 1987; de Maagd et al., 1998; Mackay et al., 2000).

3 Of the 7 PAHs modeled, benzo(b)fluoranthene was chosen for more detailed
4 analysis. This included evaluation of sensitivity to individual chemical properties, Monte
5 Carlo uncertainty analysis, and an attempt to estimate loading rate and long-term fate.

6 Benzo(b)fluoranthene is relatively persistent, has a low water quality objective because it
7 is carcinogenic, and exceeds water quality objectives more frequently than most other
8 PAHs (Table 1).

9

10 *PAH Concentrations in Water and Sediments*

11 Two estimates were generated of PAH concentrations in Bay sediments. One
12 included only the stations of the Regional Monitoring Program (RMP) within San
13 Francisco Bay (i.e., all stations north of and including the Coyote Creek station; SFEI,
14 2002; SFEI, 2003). The other included these in addition to four stations from rivers
15 draining into south San Francisco Bay and 115 stations from the Bay Protection and
16 Toxic Cleanup Program (BPTCP), which sampled sediments in the Bay margins (Hunt et
17 al., 1999). Mean sediment concentrations were compiled by site and then the overall
18 median was calculated for all sites. For the RMP sites, the median total PAHs was 1524
19 ng g^{-1} (dry weight; $N = 22$; minimum = 131 ng g^{-1} ; maximum = 4227 ng g^{-1}). For the
20 RMP and BPTCP sites, the median concentration was 1998 ng g^{-1} ($N = 139$; minimum =
21 30 ng g^{-1} maximum = 227,900 ng g^{-1}). 1500 ng g^{-1} was chosen as the nominal value of
22 total PAH concentrations in sediment for the model and 1500 to 2000 ng g^{-1} was chosen
23 as the 95 % confidence interval range for Monte Carlo simulations (Table 3). For water,

1 using the averaging method described for sediment, the total (dissolved plus particulate)
2 PAH concentration in water was 26.5 ng L^{-1} for all RMP sites including the four river
3 stations below south San Francisco Bay. The standard error of this mean (used for Monte
4 Carlo simulations) was 0.6 ng L^{-1} . When the stations south of South San Francisco Bay
5 were excluded, the calculated concentration was 25.2 ng L^{-1} . 26 ng L^{-1} was chosen as the
6 input value for the total PAH concentrations in water in the Bay (Table 3).

7

8 ***Temporal Trends in Concentrations***

9 The modeling simulations included a back-calculation of the total PAH loading
10 rate into the Bay. To back-calculate loading, the long-term trend in contaminant
11 concentrations in the Bay was estimated and fit to model results. Three data sources were
12 evaluated to determine long-term trends in PAHs in the Bay: 1) surface sediment
13 concentration data from the RMP and Pilot RMP collected from 1991 through 2001; 2)
14 concentration data from transplanted bivalves sampled by the RMP from 1994 through
15 2001; and 3) sediment core concentrations evaluated by USGS and collaborators (Pereira
16 et al., 1999). For surface sediments, dry season annual total PAH means were determined
17 for the 26 RMP stations and corresponding Pilot RMP stations (SFEI, 2002). The bivalve
18 data represented the annual mean lipid weight concentrations from 6 Bay monitoring
19 stations (Pinole Point, Red Rock, Yerba Buena Island, Alameda, Redwood Creek, and
20 Dumbarton Bridge), using transplanted *Mytilus spp.* mussels (SFEI, 2002).

21

22 ***PAH Chemical Properties***

23 PAH chemical properties required for model input include water-side and air-side

1 evaporation mass transfer coefficients, octanol-water partition coefficient (K_{ow}), Henry's
2 law constant, and PAH degradation rate (Table 4). Water-side and air-side mass transfer
3 coefficients influence the rate of chemical transfer across the air-water interface, and
4 subsequent volatilization into the atmosphere. To calculate the water-side mass transfer
5 coefficients, molecular diffusivities in water were calculated for each PAH using Hayduk
6 and Laudie's method at 15° C (Tucker and Nelken, 1982), and converted to the unitless
7 Schmidt number, assuming constant wind speed and temperature (following Davis,
8 2004). The Schmidt number was used to calculate the water-side mass transfer following
9 Hornbuckle et al. (1994) and Zhang et al. (1999). Molecular diffusivity in air at 15° C was
10 calculated following Tucker and Nelken (1982).

11 K_{ow} (Table 4) was obtained as the median of all calculated or measured values for
12 each compound, compiled in Mackay et al. (2000), de Maagd et al. (1998), and Mackay
13 and Hickie (2000).

14 Henry's law constant (Table 4) was compiled as the mean of values from
15 literature sources (Shiu and Mackay, 1997; de Maagd et al., 1998; Bamford et al., 1999;
16 Mackay et al., 2000). Henry's law constant was calculated at 15° C, following ten
17 Hulscher et al. (1992) and de Maagd et al. (1998).

18 Some PAHs are more susceptible to biological degradation than synthetic
19 compounds such as PCBs. PAH degradation rates were estimated from published
20 literature values from studies on surface waters and sediments. For any given PAH,
21 literature degradation rates are widespread, sometimes spanning 3 - 4 orders of
22 magnitude (Table 4; Greenfield and Davis, 2004). Given limited published data on
23 degradation rates for many HPAHs, four ring PAH degradation rates were estimated

1 using published values for benz(a)anthracene, and five and six ring PAH degradation
2 rates were estimated using degradation rates for benzo(a)pyrene. Previous fate modeling
3 studies have also used identical degradation rates for multiple HPAHs (e.g., Mackay and
4 Hickie, 2000), and laboratory studies indicate similar degradation behavior for similar
5 HPAHs (e.g., Juhasz et al., 1996; Wolter et al., 1997). Once values were compiled,
6 median values of assembled degradation rates were chosen as representative values.
7 Further information on chemical parameter estimation, including listings of literature
8 values compiled for degradation rates and Henry's law constants, are available in the
9 technical report upon which this publication is based (Greenfield and Davis, 2004). For
10 Monte Carlo simulation uncertainty analyses, ranges of published values for degradation
11 of benzo(a)pyrene were used (Table 5).

12 Based on the literature-derived values for the seven PAHs modeled, chemical
13 properties ranged widely as a function of molecular weight, with low molecular weight
14 PAHs (LPAHs) having relatively low K_{ow} s and relatively high Henry's law constants and
15 degradation rates (Table 4).

16

17 ***Model Simulations***

18 Simulations included evaluation of the response time of the PAH; i.e., the time
19 required for the current mass to undergo loss assuming no external loading. The response
20 time simulation provided an indication of the expected rate at which the compound would
21 respond to management activities, such as substantial increases or reductions in loading.
22 These response time simulations included evaluation of two factors: percent of original
23 PAH mass lost after 5 years of simulation and residence time for the modeled PAH in the

1 Bay (initial total mass in the Bay (kg) / instantaneous annual losses (kg yr⁻¹)). In addition
2 to response time simulations, the steady state mass of PAH was determined, using a fixed
3 annual loading rate and a time scale sufficient to achieve steady state (100 simulation
4 years).

6 ***Uncertainty Analysis***

7 Uncertainty analysis was conducted using Monte Carlo simulations, which
8 present a more realistic depiction of range and probability of results than separately
9 varying each input parameter (McKone and Bogen, 1991). Monte Carlo simulations can
10 also demonstrate the relative sensitivity of results to uncertainty in individual input
11 parameters, thereby prioritizing future research needs (MacLeod et al., 2002). In Monte
12 Carlo simulation, the uncertainty range and distribution of model input parameters are
13 estimated, and then model results are repeatedly calculated using input parameter values
14 randomly selected from the estimated distributions. Monte Carlo analysis was conducted
15 with the Crystal Ball[®] software package, using 10,000 iterations. The relative importance
16 of individual input parameters was determined by calculating a rank correlation
17 coefficient between results and each input parameter. This rank correlation coefficient is
18 converted to the contribution to total variance explained, by squaring it and normalizing
19 to 100 % (Werckman et al., 2001).

20 Parameter ranges for Monte Carlo simulation were based on Davis (2004).
21 Parameter distributions, presented in Table 3, were estimated following the
22 recommendation by MacLeod et al. (2002) to focus on identifying variance structure for
23 influential parameters. Parameters with an expected coefficient of variation (SD/mean)

1 less than 25 % were modeled using a normal distribution with the 5 % and 95 %
2 confidence intervals as the minimum and maximum values estimated by Davis (2004).
3 Normally distributed parameters included water temperature, concentration of particles in
4 water, concentration of solids in sediment, density of suspended solids, and Bay wide
5 PAH concentrations in water. Parameters with available local data indicating lognormal
6 distribution or with extremely high estimated value ranges were modeled using a
7 lognormal distribution with the 5 % and 95 % confidence intervals as the minimum and
8 maximum values estimated by Davis (2004). These included water outflow, solids
9 settling rate, and Bay wide PAH concentrations in sediment. Parameters shown in
10 preliminary simulations to have low impact on model output and parameters for which
11 insufficient information was available to make distributional assumptions were modeled
12 using uniform or triangular distributions with minimum, most likely, and maximum
13 values following Davis (2004). Monte Carlo simulations were conducted using data
14 representative of benzo(b)fluoranthene to characterize the degree to which individual
15 parameters affected model output. In Monte Carlo analysis, steady state mass
16 simulations assumed a fixed loading rate of 15,000 kg yr⁻¹.

17

18 **RESULTS AND DISCUSSION**

19

20 *Relative Importance of Chemical Properties*

21 We varied PAH chemical properties across the range expected among compounds
22 (Table 4), to determine which property most strongly influences fate in the Bay. Each
23 PAH chemical attribute (K_{ow} , Henry's law constant, air and water mass transfer

1 coefficients, and degradation rates in water and sediments) was separately manipulated
2 across the range of values for the seven selected PAHs (Table 4).

3 When values for six PAH chemical properties were varied across the range that
4 would be expected for the PAHs modeled, all had an effect on the model output with the
5 exception of the air-side and water-side evaporation mass transfer coefficients (Table 6).
6 For both the response time and steady-state mass modeling exercises, sensitivity was
7 greatest for sediment degradation rate and was also high for octanol-water partition
8 coefficient (K_{ow}), suggesting that refined estimates of these parameters may improve
9 PAH fate predictions. Given the model sensitivity to K_{ow} , and the fact that PAH particle
10 affinity exhibits seasonal variation in San Francisco Bay (Maruya et al., 1996), careful
11 estimates of sediment-water partitioning may be needed for accurate PAH fate
12 determination. Results were moderately sensitive to water degradation rate and Henry's
13 law constant (Table 6). The limited impact of Henry's law constant (Table 6) suggests
14 that volatilization was a relatively small loss pathway for HPAHs in the present study,
15 consistent with other PAH fate modeling exercises (Ryan and Cohen, 1986; Lun et al.,
16 1998; Mackay and Hickie, 2000; Wang et al., 2002). The mass transfer coefficients had
17 no impact on model results (Table 6) because they only moderately affected the
18 volatilization loss pathway (see Table 2).

19

20 *Uncertainty Analysis*

21 Variation in sediment degradation rate strongly affected results of both the
22 response time and steady-state Monte Carlo simulations, suggesting that PAH fate in San
23 Francisco Bay may be very sensitive to degradation rate. When degradation rate was

1 varied between observed literature values for benzo(a)pyrene of 4×10^{-5} to $1 \times 10^{-2} \text{ d}^{-1}$
2 (Table 5), the model did not produce useful bounds on HPAH fate; loss in 5 years ranged
3 from 0 to 100 % and predicted residence times ranged from weeks to over 100 years.
4 Even when degradation rates were constrained to the order of magnitude range found
5 more commonly in the literature (4×10^{-5} to $4 \times 10^{-4} \text{ d}^{-1}$; Table 5), more than 97 percent
6 of the variation in model outputs (steady state mass, residence time, and percent loss after
7 5 years) was attributable to sediment degradation rate variation, indicating that
8 uncertainty in this parameter was dominating model results. High uncertainty was
9 apparent for residence time (mean = 16.2 years; coefficient of variation, CV = 0.66;
10 Figure 1a), percent decline after 5 years (mean = 37 %; CV = 0.33; Figure 1b), and
11 steady state mass (mean = $1.9 \times 10^5 \text{ kg}$; CV = 0.53; Figure 1c). Additionally,
12 instantaneous annual losses (i.e., the initial sum of PAH lost due to burial, degradation,
13 volatilization, and outflow) varied substantially (mean = 14,000 kg y^{-1} ; CV = 0.60). The
14 wide range of model results and strong impact of degradation rate suggest that current
15 understanding of degradation rates is not sufficiently accurate to confidently predict long-
16 term PAH fate in the Bay.

17 To explore uncertainty of model predictions if degradation rate were well
18 characterized, the Monte Carlo simulations were then repeated with a fixed degradation
19 rate representative of literature values ($3 \times 10^{-4} \text{ d}^{-1}$; Table 5). This also enabled
20 determination of the relative importance of other input parameters for model results.
21 When degradation rate was fixed, model uncertainty was relatively low for residence
22 time (mean = 8.9 years; CV = 0.01; Figure 1a), percent decline after 5 years (mean = 46
23 %; CV = 0.04; Figure 1b), and steady state mass (mean = $1.2 \times 10^5 \text{ kg}$; CV = 0.06; Figure

1 1c). In this scenario, instantaneous annual loss averaged $19,000 \text{ kg yr}^{-1}$ ($\text{CV} = 0.35$). The
2 general reduction in uncertainty when degradation rate was fixed suggests that better
3 characterization of degradation rate would improve PAH fate estimates for San Francisco
4 Bay.

5 When degradation rate was fixed, the depth of the active sediment layer explained
6 the most variation in the four response variables: response rate (as percent lost in 5 years
7 with no external loading), steady state mass (after 100 years with $15,000 \text{ kg yr}^{-1}$ loading),
8 residence time, and instantaneous annual loss (Table 7). Davis (2004) previously
9 identified the depth of actively mixing sediment as a significant data requirement because
10 this depth determines the mass of contaminants that must be lost for Bay contaminant
11 concentrations to decline.

12 Concentration of solids in sediment was also an influential parameter for the four
13 response variables. Residence time was influenced by sediment burial mass transfer
14 coefficient. Rate of water outflow had moderate influence on response rate, steady state
15 mass, and residence time (Table 7). The relatively high impact of sediment properties
16 (e.g., active sediment layer depth, solids concentration, and sediment burial mass transfer
17 coefficient) is also apparent for PCB simulations, and reflects the fact that in San
18 Francisco Bay, the vast majority of hydrophobic organic contaminants tends to be
19 sequestered in bed and suspended sediments (Davis, 2004). The importance of water
20 outflow indicates that PAH outflow through the Golden Gate may become a more
21 significant uncertainty, once degradation rate is better characterized. Compared to Bay
22 sediment properties and uncertainty regarding degradation rate, uncertainty for other

1 chemical properties of high molecular weight PAHs such as benzo(b)fluoranthene have
2 relatively low impact on model results.

3

4 ***Calibration of Loading Rate Versus Degradation Rate***

5 A key unknown for many contaminants is the annual rate of loading from all
6 sources to the Bay. Loading rate estimates are needed to determine source reductions
7 needed to attain water quality goals (e.g., SFBRWQCB, 2004). Although mass balance
8 models may be used to back-calculate loading rates (Mackay et al., 1994; Davis, 2004),
9 this requires low uncertainty for estimates of chemical loss processes, current
10 concentrations, and long-term trends. For PAH fate in San Francisco Bay, the high
11 uncertainty in degradation rate dominates model results (Figure 1), making it difficult to
12 accurately back-calculate loading. However, modeled loading rates may be compared to
13 loading rate estimates based on previous studies, to establish bounds for loading and
14 degradation rates. To achieve this comparison, loading and degradation rates were
15 applied to the model and then model results were fitted to actual trends in San Francisco
16 Bay.

17 In general, there was not a clear upward or downward trend in total PAHs within
18 the last decade. Graphical evaluation of annual average sediment total PAH
19 concentrations provided no evidence for increasing or decreasing trend (Figure 2). This
20 observation was consistent with linear regression analyses of 26 different monitoring
21 stations, indicating a general absence of temporal trends throughout the Bay (Oros and
22 Ross, 2004). Dry season concentrations of HPAHs and total PAHs in transplanted
23 bivalves showed considerable interannual variability but also showed no apparent trend

1 (Figure 3). Sediment cores do not show clear trends after the 1970s, with concentrations
2 increasing in the 1970s and 1980s but decreasing in the most recent sediment layers
3 (Figure 3 in Pereira et al., 1999). Given the lack of evidence for trends in the past
4 decade, loading rates in the model were estimated assuming stable PAH concentrations
5 over time.

6 Annual loading to the Bay is not well characterized, and best available estimates
7 range widely from 300 to about 10,000 kg yr⁻¹ (Table 8). When the model was
8 implemented using the best estimated properties for benzo(b)fluoranthene (including a
9 degradation of 0.00035 d⁻¹), a loading rate of 18,000 kg yr⁻¹ was needed to maintain
10 stable PAH concentrations over time. If degradation rates were set an order of magnitude
11 greater than the nominal value (0.0035 d⁻¹), modeled total loading became 140,000 kg
12 yr⁻¹, which was inconsistent with the findings of other studies (Table 8). This result
13 would be robust using properties of other PAHs, as LPAHs have elevated loss rates, and
14 the amount of loading needed to maintain steady concentrations would be even greater.
15 Most PAHs in the Bay are combustion derived rather than petrogenic (Pereira et al.,
16 1999; Oros and Ross, 2004), and a portion of the PAH mass is likely bound to soot
17 particles (Maruya et al., 1996), where they would not be readily bioavailable for
18 degradation (Talley et al., 2002). This supports the model result that the degradation of
19 PAHs in the Bay appears to be at or below nominal literature values.

20 Assuming the range of degradation rates observed in most laboratory
21 examinations of benzo(a)pyrene (4×10^{-5} to 4×10^{-4} d⁻¹; Table 5), the rate of loading
22 needed to achieve a steady state mass in the Bay would range from 4,000 kg yr⁻¹ to
23 21,000 kg yr⁻¹. This suggests that the nominal literature loading estimate of 3,570 kg yr⁻¹

1 is likely to be at or below the actual external loading rate to the Bay. When the model
2 was run assuming a degradation rate of 0, the loading rate became 1700 kg yr⁻¹, providing
3 a lower bound estimate of loading. The degradation rates determined by Shiaris (1989) of
4 1.2×10^{-2} to 1.9×10^{-2} d⁻¹ would require loading rates orders of magnitude higher than the
5 maximum literature value, and are therefore not appropriate for application to the Bay.

6

7 *Fates of Different PAHs*

8 As indicated in the previous sections, there is substantial uncertainty in model
9 results, due to limitations in the current state of knowledge on PAH chemical properties
10 and Bay physical attributes. Nevertheless, there is value in obtaining preliminary
11 assessments of expected PAH persistence and response to management perturbations. In
12 order to evaluate differences in long-term fate among individual compounds, the model
13 was run varying chemical parameters according to PAH compound and holding all other
14 model parameters constant. These simulations were conducted both in the absence of
15 external loading and assuming an external loading rate of 10,000 kg yr⁻¹, selected based
16 on the range of probable loading rates obtained in the previous section (4,000 kg yr⁻¹ to
17 21,000 kg yr⁻¹).

18 In the absence of external loading, percent of initial mass lost in five years varied
19 widely among PAHs, mostly as a result of variation in degradation in sediment (Table 6,
20 Table 9). The amount of time required for half of the initial mass to be lost was shortest
21 for the LPAHs naphthalene (20 days) and phenanthrene (63 days), just under one year for
22 the four ring PAHs fluoranthene and benz(a)anthracene, and greater than five years for
23 the HPAHs, benzo(b)fluoranthene, dibenz(a,h)anthracene, and benzo(g,h,i)perylene

1 (Table 9). Modeling studies of other aquatic ecosystems have also found PAH residence
2 times of less than a year for LPAHs and one to several years for HPAHs (Lun et al.,
3 1998; Mackay and Hickie, 2000).

4 For all PAHs, the predominant loss pathway was degradation in sediment,
5 generally equaling 80 to 90 % of total loss (Table 9, Figure 4). For the lower molecular
6 weight PAHs naphthalene, phenanthrene, and fluoranthene, volatilization equaled about
7 10 percent of total loss. For the five and six ring HPAHs (benzo(b)fluoranthene,
8 dibenz(a,h)anthracene, and benzo(g,h,i)perylene), outflow equaled about 10 percent of
9 total loss (Table 9, Figure 4). HPAHs showed almost no volatilization loss, consistent
10 with their tendency to partition in the solid phase (e.g., Yaffe et al., 2001; Wang et al.,
11 2002), where they are not available for volatilization. In a mass balance of the Saguenay
12 Fjord, Canada, Lun et al. (1998) also observed that degradation is the major loss pathway
13 for naphthalene, with volatilization playing a secondary role.

14 When external loading was set at a rate of $10,000 \text{ kg yr}^{-1}$, the long-term steady-
15 state mass increased with PAH size. The total mass lost was greater than 99 % of initial
16 mass for naphthalene but only 34 % of initial mass for 5 and 6 ring PAHs (Table 6, last
17 row). Both the no loading and $10,000 \text{ kg yr}^{-1}$ loading scenarios indicated relatively rapid
18 loss of LPAHs, as compared to HPAHs. This finding suggests that LPAHs would
19 respond more rapidly to management actions such as the loading reductions prescribed in
20 the Total Maximum Daily Load regulatory process (SFBRWQCB, 2004). However,
21 because model results were very sensitive to two uncertain parameters (degradation and
22 active sediment layer depth), better estimation of these parameters is required before
23 actual response times in San Francisco Bay can be quantitatively predicted.

1 In contrast to our study, several studies found outflow to be the predominant loss
2 pathway for benzo(a)pyrene and other HPAHs (Ryan and Cohen, 1986; Lun et al., 1998;
3 Mackay and Hickie, 2000; Wang et al., 2002). Many of these studies evaluate shallow
4 riverine systems with lower water residence times than San Francisco Bay. San Francisco
5 Bay, having a hydraulic residence time estimated at several months or more (Smith,
6 1987), appears to exhibit a relatively low outflow loss rate compared to potential rates of
7 PAH degradation. However, the present study did not include bed sediment transport or
8 particle advection due to tidal exchange, which should be incorporated into future
9 contaminant fate models for San Francisco Bay (Davis, 2004).

10

11 *Fate of PAHs Versus PCBs in the Bay*

12 According to the model, PAH loss rates would be more rapid than PCB loss rates
13 in San Francisco Bay (Figure 5). The time required for half the original mass of PCB 118
14 to be lost is estimated at about 20 years (Davis, 2004), more than threefold slower than
15 the slowest PAHs. This finding suggests that in comparison to PCBs, PAHs would
16 respond more rapidly to loading reductions.

17 Evaluation of rate constants for the loss and transfer pathways helps in
18 understanding why loss rates were relatively rapid for LPAHs, moderate for HPAHs, and
19 relatively slow for PCBs (Table 10). In the case of benzo(b)fluoranthene, the degradation
20 rate was an order of magnitude higher than for PCB 118, resulting in more rapid loss of
21 HPAHs than PCBs. For the LPAH, phenanthrene, degradation and volatilization rates
22 were both substantially greater than for PCB 118 (Table 10). Although Henry's law
23 constant was similar for phenanthrene ($2.0 \text{ Pa m}^3 \text{ mol}^{-1}$) and PCB 118 ($3.9 \text{ Pa m}^3 \text{ mol}^{-1}$),

1 phenanthrene's lower K_{ow} ($\log K_{ow} = 4.5$ versus 6.7) caused more phenanthrene to enter
2 the freely dissolved fraction, where it was lost due to volatilization.

3

4 ***Conclusions and Future Directions***

5 A primary objective of preliminary models such as this one is to evaluate the
6 extent and limitations of present knowledge and to indicate priorities for future research.
7 Our results indicated that given present understanding of the Bay, degradation rate is a
8 potentially important process governing long-term PAH fate, particularly for HPAHs.
9 Uncertainty in degradation rates resulted in high model uncertainty, indicating that this
10 parameter should be better characterized before more complex models are developed for
11 PAH fate in San Francisco Bay. The model also indicated that for the most recalcitrant
12 PAHs (i.e., the HPAHs), loss due to volatilization was low. Therefore, literature or
13 calculated estimates of volatilization-related parameters should be adequate for PAH fate
14 modeling in this ecosystem.

15 San Francisco Bay is a dynamic ecosystem that exhibits considerable spatial and
16 temporal variability in attributes important to this model. This model presents the Bay as
17 a single box of well-mixed water and sediment and was used to identify parameter
18 uncertainties and prioritize future research areas. Once parameters are better
19 characterized, a number of refinements to the model could be undertaken to better predict
20 contaminant dynamics. PAH phase partitioning in urbanized estuaries often involves a
21 fraction tightly bound to soot particles, that is effectively not bioavailable for degradation
22 (Maruya et al., 1996; Talley et al., 2002). Future models could explicitly incorporate a
23 soot-bound fraction. PAH concentrations can be high in buried sediment (Pereira et al.,

1 1999), and future models could quantify erosive remobilization of this buried sediment as
2 a loading term. Remobilization of buried sediment would expose more PAHs and delay
3 Bay response to loading reductions. Finally, models that incorporate spatial heterogeneity
4 of the ecosystem could be used to predict contaminant dynamics within and among
5 different regions of the Bay, as well as localized responses to changes in loading. RMP
6 scientists at the USGS and SFEI are currently developing a more sophisticated multi-box
7 model, which better describes water transport in the Bay, explicitly simulates sediment
8 advection, and incorporates Bay-wide spatial variation in contaminant concentrations and
9 fluxes.

10

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12

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22

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12

1 **FIGURE CAPTIONS**

2

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

12

13 Figure 2. Annual Bay-wide average sediment PAH concentrations. Data from 1993
14 through 2001 represents annual summer means of 26 RMP sediment monitoring stations
15 (ng g^{-1} dry weight). Data from 1991 and 1992 are Pilot RMP data collected from
16 locations corresponding to RMP sediment sampling sites ($N = 11$ for 1991 and 1992). All
17 data are summer data with the exception of 1992, which was sampled in March and
18 April. Use of the spring sampling event for each year leads to qualitatively similar results.

19

20 Figure 3. Annual Bay-wide average dry season total PAH and HPAH concentrations in
21 Bay mussel (*Mytilus spp.*) from 6 RMP monitoring stations. Data are presented as lipid
22 weight concentrations (ng g^{-1} lipid weight). HPAHs include 12 combustion product PAHs
23 having four to six rings, in addition to phenanthrene.

1

2 Figure 4. Predicted losses from the Bay through different pathways for different PAHs
3 over a one year period. Assumes no external load and an initial starting mass of 120,000
4 kilograms.

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6 Figure 5. Predicted losses from the Bay for phenanthrene (a three ring PAH),
7 fluoranthene (a four ring PAH), benzo(b)fluoranthene (a five ring PAH), and PCB 118,
8 presented as percent lost from the original starting mass.

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1 **TABLES**

2

3 Table 1. Abundance of 25 PAHs in San Francisco Bay samples, collected from 1993 to
 4 2001. Compounds presented in boldface were selected for use in the environmental fate
 5 model. Mean concentrations and percent of total concentrations are indicated for PAHs in
 6 sediments ($\mu\text{g kg}^{-1}$, dry weight), bivalves ($\mu\text{g kg}^{-1}$, dry weight), and water (dissolved
 7 fraction; ng L^{-1}). “Number of Exceedances” indicates the total number of individual
 8 samples collected from 1993 to 2001 that exceed the water quality criteria for human
 9 health established by the California Toxics Rule for total (dissolved + particulate)
 10 concentrations in water (U.S. EPA 2000). The total number of samples collected was
 11 396, although not all samples were analyzed for all compounds. NA = criterion not
 12 established.

13

<u>PAH</u>	Number of Rings	Mean Concentration and Percent of Total						<u>Number Exceedances</u>
		<u>Sediment</u>		<u>Bivalves</u>		<u>Water</u>		
		$\mu\text{g/kg}$	%	$\mu\text{g/kg}$	%	ng/L	%	
Biphenyl	2	6	0.4%	3	0.9%	0.23	2.6%	NA
Naphthalene	2	25	1.6%	19	5.2%	0.27	3.1%	NA
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
Phenanthrene	3	85	5.4%	22	6.0%	1.25	14.2%	NA
1-Methylphenanthrene	3	13	0.8%	2	0.5%	0.32	3.6%	NA
Benz(a)anthracene	4	79	5.0%	19	5.2%	0.17	1.9%	3
Chrysene	4	88	5.6%	27	7.3%	0.12	1.3%	0
Fluoranthene	4	192	12.1%	61	16.4%	1.58	17.9%	0
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
Benzo(b)fluoranthene	5	142	9.0%	24	6.5%	0.13	1.4%	5
Benzo(k)fluoranthene	5	52	3.3%	12	3.3%	0.03	0.4%	1
Dibenz(a,h)anthracene	5	14	0.9%	1	0.2%	0.01	0.1%	0
Perylene	5	62	3.9%	10	2.7%	0.00	0.0%	NA
Benzo(g,h,i)perylene	6	137	8.6%	12	3.2%	0.01	0.1%	NA
Indeno(1,2,3-cd)pyrene	6	119	7.5%	7	1.8%	0.05	0.6%	4

1

1 Table 2. Equations for rate constants used in the environmental fate model.

2 **Rate Constants:**

3

4 $k_O = [F/(1000X_W)] * PAH_O/PAH_A$ (outflow rate constant; d^{-1})

5 $k_V = S_{AW}\phi_{DW}V_E/X_W$ (volatilization rate constant ; d^{-1})

6 $k_{WR} =$ obtained from literature (degradation in water rate constant; d^{-1})

7 $k_{SR} =$ obtained from literature (degradation in sediment rate constant; d^{-1})

8 $k_{WS} = k_{WS1} + k_{WS2}$ (water to sediment transport rate constant; d^{-1})

9 $k_{SW} = k_{SW1} + k_{SW2}$ (sediment to water transport rate constant; d^{-1})

10 $k_B = S_{AS}V_B(1 - \phi_{DS})/X_S$ (burial rate constant; d^{-1})

11 $k_{WS1} = S_{AW}V_{SS}(1 - \phi_{DW})/X_W$ (solids settling rate; d^{-1})

12 $k_{WS2} = S_{AS}V_D\phi_{DW}/X_W$ (water to sediment diffusion rate; d^{-1})

13 $k_{SW1} = 1000(\text{ResFlux}/C_{SS})(1 - \phi_{DS})/X_S$ (solids resuspension rate; d^{-1})

14 $k_{SW2} = S_{AS}V_D\phi_{DS}/X_S$ (sediment to water diffusion rate; d^{-1})

15

16 **Other Equations and Properties:**

17

18 $F =$ outflow rate of water ($L d^{-1}$)

19 $X_W =$ Bay water volume (m^3)

20 $X_S =$ Bay active sediment layer volume (m^3)

21 $PAH_A =$ average total water column PAH concentration Bay-wide ($pg L^{-1}$)

22 $PAH_O =$ PAH concentration at seaward locations (Yerba Buena Island and Red Rock; $pg L^{-1}$)

23 $S_{AW} =$ Bay water surface area (m^2)

24 $\phi_{DW} =$ freely dissolved PAH fraction in water (unitless)

25 $\phi_{DW} = 1/(1 + (C_{PW}OC_{PW}K_{OW}/d_{PW}))$

26 $C_{PW} =$ concentration of particles in water (TSS) ($mg L^{-1}$)

- 1 OC_{PW} = organic carbon content of suspended solids (unitless)
- 2 K_{OW} = octanol water partition coefficient (unitless)
- 3 d_{PW} = density of suspended solids ($kg L^{-1}$)
- 4 V_E = volatilization mass transfer coefficient ($m d^{-1}$)
- 5 $1/V_E = 1/V_{EW} + 1/(K_{AW}V_{EA})$
- 6 V_{EW} = water-side evaporation mass transfer coefficient ($m d^{-1}$)
- 7 V_{EA} = air-side evaporation mass transfer coefficient ($m d^{-1}$)
- 8 K_{AW} = dimensionless Henry's Law constant (unitless)
- 9 $K_{AW} = H/(8.314 * (T + 273))$
- 10 H = Henry's Law constant ($Pa m^3 mol^{-1}$)
- 11 T = water temperature (deg C)
- 12 v'_{SS} = solids settling rate ($m d^{-1}$)
- 13 S_{AS} = Bay sediment surface area (m^2)
- 14 V_D = water-to-sediment diffusion mass transfer coefficient ($m d^{-1}$)
- 15 ResFlux = resuspension flux of sediment solids ($kg d^{-1}$)
- 16 $ResFlux = 1000(C_{PW} v'_{SS} S_{AW} - C_{SS} V_B S_{AS})$
- 17 C_{SS} = concentration of solids in sediment ($kg L^{-1}$)
- 18 V_B = sediment burial mass transfer coefficient ($m d^{-1}$)
- 19 ϕ_{DS} = fraction of freely dissolved PCB in sediments (unitless)
- 20 $\phi_{DS} = 1/(1 + (C_{SS} OC_{SS} K_{OW}/d_{SS}))$
- 21 OC_{SS} = organic carbon content of bottom sediment (unitless)
- 22 d_{SS} = density of sediment solids ($kg L^{-1}$)

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2 Table 3. Input data for the model.

Parameter	Best Estimate	Monte Carlo Distribution
Water surface area (m ²)	1.1x10 ⁹	Not Varied
Sediment surface area (m ²)	1.1x10 ⁹	Not Varied
Depth of active sediment layer (m)	0.15	Triangular (0.05, 0.15, 0.25)
Water volume (m ³)	5.5x10 ⁹	Triangular (5.5x10 ⁹ , 5.5x10 ⁹ , 6.2x10 ⁹)
Sediment volume of Bay (m ³)	1.6x10 ⁸	Not Varied
Water temperature (deg C)	15	Normal ($\mu = 15.25$, SD = 1.37)
Water outflow (L d ⁻¹)	7.0x10 ¹⁰	Lognormal (5% CI = 5.3x10 ¹⁰ , 95% CI = 9.1x10 ¹⁰)
Concentration of particles in water (kg L ⁻¹)	8.5x10 ⁻⁵	Normal ($\mu = 8.5 \times 10^{-5}$, SD = 6.1x10 ⁻⁶)
Concentration of solids in sediment (kg L ⁻¹)	0.5	Normal ($\mu = 0.6$, SD = 0.12)
Density of suspended solids (kg L ⁻¹)	1.1	Normal ($\mu = 1.1$, SD = 0.24)
Density of sediment solids (kg L ⁻¹)	2.7	Triangular (1.5, 2.7, 2.7)
Organic carbon content of suspended solids	0.030	Triangular (0.01, 0.03, 0.05)
Organic carbon content of bottom sediment	0.01	Triangular (0.005, 0.01, 0.02)
Water-side evaporation mass transfer coefficient (m d ⁻¹)	0.77	Triangular (0.75, 0.77, 0.92)
Air-side evaporation mass transfer coefficient (m d ⁻¹)	398	Triangular (390, 398, 495)
Sediment burial mass transfer coefficient (m d ⁻¹)	0	Triangular (0, 0, 1.1x10 ⁻⁶)
Solids settling rate (m d ⁻¹)	1.0	Lognormal (5% CI = 0.4, 95% CI = 10)
Water-to-sediment diffusion mass transfer coefficient (m d ⁻¹)	2.40x10 ⁻³	Triangular (2.4x10 ⁻⁴ , 2.4x10 ⁻³ , 2.4x10 ²)
Henry's law constant (Pa m ³ mol ⁻¹)	0.033	Triangular (0.008, 0.033, 0.054)
Octanol-water partitioning coefficient	2.51x10 ⁶	Triangular (5.01x10 ⁵ , 2.51x10 ⁶ , 3.98x10 ⁶)
Average concentration in water (ng L ⁻¹)	26	Normal ($\mu = 26$, SD = 0.6)
Typical concentration in water at Red Rock and Yerba Buena	11.5	Normal ($\mu = 11.5$, SD = 0.3)
Island (ng L ⁻¹)		
Average concentration in sediment (ng g ⁻¹ dry)	1500	Lognormal (5% CI = 1500, 95% CI = 2000)
Average wind speed (km hr ⁻¹)	17.1	Triangular (12.9, 17.1, 20.9)

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1 Table 4. Properties of PAHs modeled. Percent Total PAH = the average percentage of
 2 total PAHs in RMP sediment samples collected from 1993 through 1999. K_{ow} = the
 3 octanol-water partition coefficient. HLC = Henry's law constant at 15°C. MTC = mass
 4 transfer coefficient.

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

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2 Table 5. Literature values for rates of benzo(a)pyrene degradation in sediments.

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

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

Parameter	Nominal value	Model input value	Response time simulation (% lost)	Steady state mass simulation (% lost)
Water-side evaporation mass transfer coefficient (m d ⁻¹)	0.77	0.92,0.85,0.82,0.77,0.75	No effect	No effect
Air-side evaporation mass transfer coefficient (m d ⁻¹)	398	495, 443, 430, 398, 390	No effect	No effect
Degradation loss rate in water (d ⁻¹)	0.0003	0.03, 0.01, 0.002, 0.0003, 0	84, 77, 72, 71, 71	62, 47, 37, 35, 34
Degradation loss rate in sediment (d ⁻¹)	0.0003	0.03, 0.01, 0.002, 0.0003, 0	100, 100, 100, 71, 14	99, 98, 89, 35, -345
K _{ow} (log units)	6.4	3.4, 4.5, 5.2, 6.4, 7.1	100, 94, 79, 71, 71	96, 79, 51, 35, 34

Henry's law constant (Pa m ³ mol ⁻¹)	0.033	24.3, 2.04, 0.59, 0.033, 0.011	80, 75, 72, 71, 71	55, 44, 38, 35, 35
External load (kg yr ⁻¹)	10000	0, 3000, 10000, 30000, 60000	71, 57, 25, -68, -207	100, 80, 35, -96, -292
PAH compound (all properties) ^a		N, P, F, B(a)a, B(b)f, Da, Bp	100, 98, 57, 53, 12, 11, 11 ^a	100, 99, 93, 89, 35, 34, 33

1 a. For PAH compound, response time simulation results are presented after 1 year simulation.

Table 7. Contribution to variance of model results in Monte Carlo simulations. Residence time = initial total mass in the Bay (kg) / instantaneous annual losses (kg yr⁻¹). Response rate = % of initial mass lost after 5 years with no external loading. Steady state mass = % of initial mass lost after 100 years with 15,000 kg yr⁻¹ external loading. Instantaneous annual loss = initial mass lost due to all loss pathways. Only parameters explaining > 1 % of variation in a scenario are listed (Table 3 lists all varied *parameters*). Negative values indicate negative correlation between parameter values and model results. In these simulations, degradation rate was held fixed. When degradation rate was allowed to vary, it explained between 69.3 % and 99.7 % of 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	0.1	-2.9	2.5	0.0

coefficient (K_{ow})				
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
Density of suspended solids	0.0	0.8	-1.5	0.0

Table 8. Best available literature estimates of annual PAH loading to San Francisco Bay via different pathways. All values are kg yr^{-1} . 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)
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 9. Predicted losses from the Bay through different pathways over a five yr period for seven PAHs. Assumes no external load and hypothetical identical starting mass of each PAH. All data in kg, except as noted. PAH name abbreviations as in Table 4.

PAH	N	P	F	B(a)a	B(b)f	Da	Bp
Starting mass	120,100	120,100	120,100	120,100	120,100	120,100	120,100
Volatilization	11,700	9,900	10,900	600	200	0	0
Outflow	400	1,100	4,500	2,100	6,100	5,700	5,400
Degradation in water	2,300	2,000	1,600	700	300	300	300
Degradation in sediment	105,700	107,100	101,400	113,900	48,800	48,900	49,000
Total losses	120,100	120,100	118,400	117,300	55,400	54,900	54,700
Mass in 5 yr	0	0	1,700	2,800	64,700	65,200	65,400
% of initial mass lost	100 %	100 %	99 %	98 %	46 %	46 %	46 %
Time at 50 % of initial mass	20 d	63 d	302 d	338 d	5.6 yr	5.7 yr	5.7 yr

Table 10. Rate constants (d^{-1}) for representative PAHs in San Francisco Bay 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	Phenanthrene	Benzo(b)fluoranthene	PCB 118
Outflow	k_O	0.0056	0.0056	0.0054
Volatilization	k_V	0.049	0.00016	0.0044
Solids settling	k_{WS1}	0.013	0.17	0.185
Water-to-sediment diffusion	k_{WS2}	0.00045	0.00007	0.000035
Degradation in water	k_{WR}	0.01	0.0003	0.000034
Solids resuspension	k_{SW1}	0.0011	0.0011	0.0011
Sediment-to-water diffusion	k_{SW2}	0.0003	0.0000035	0.0000012
Burial	k_B	0	0	0
Degradation in sediment	k_{SR}	0.01	0.0003	0.000034

Figure 1.

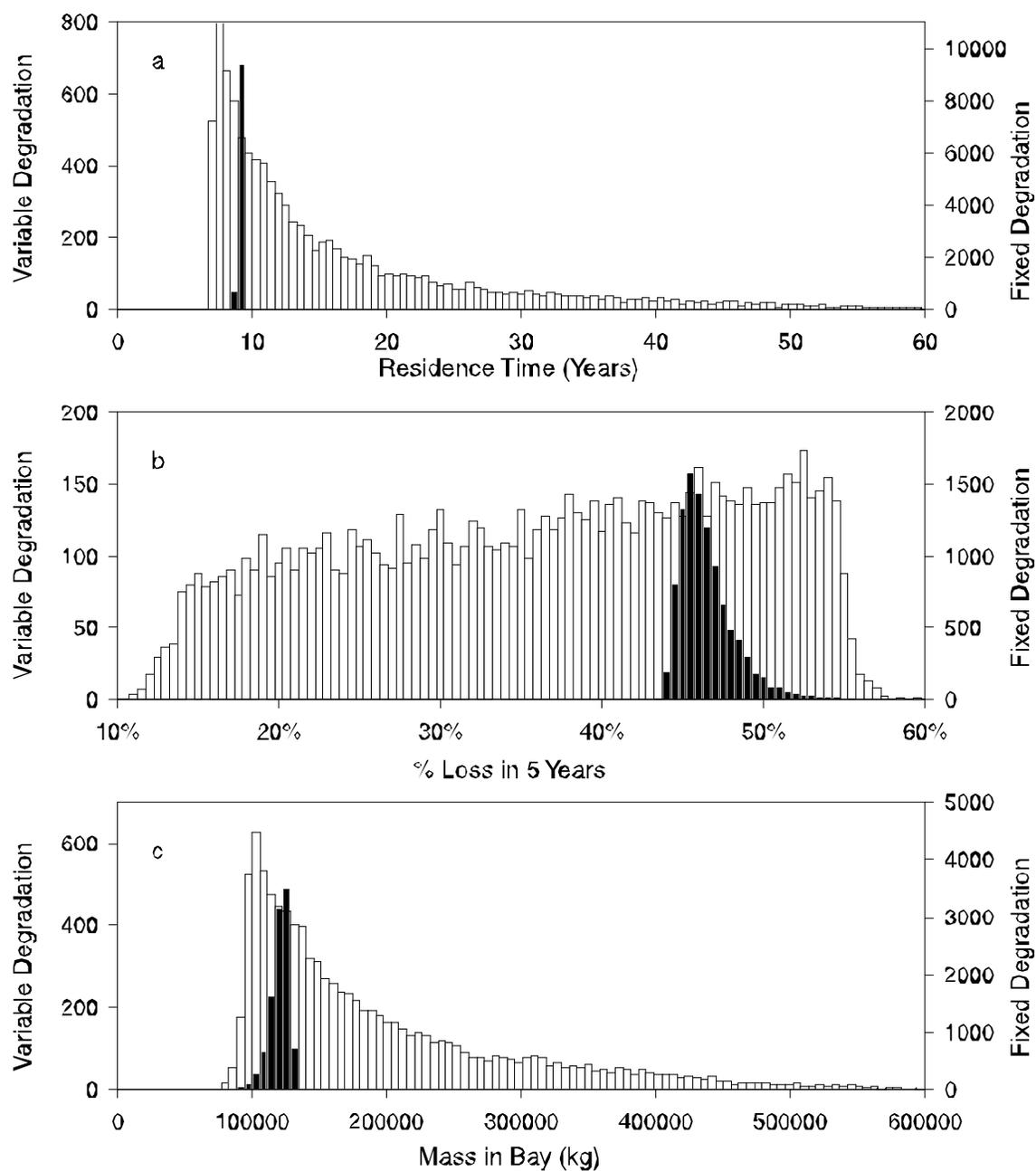


Figure 2.

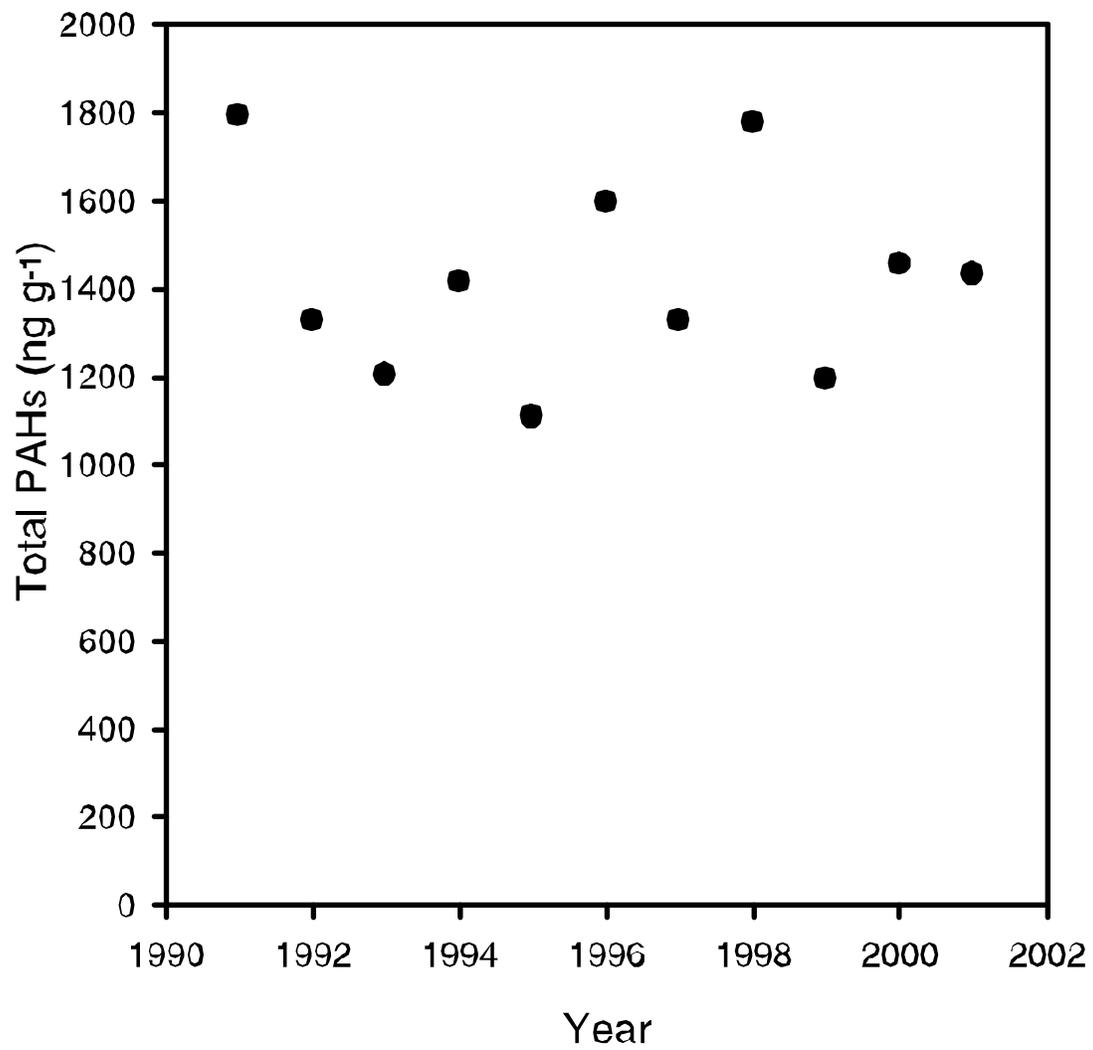


Figure 3.

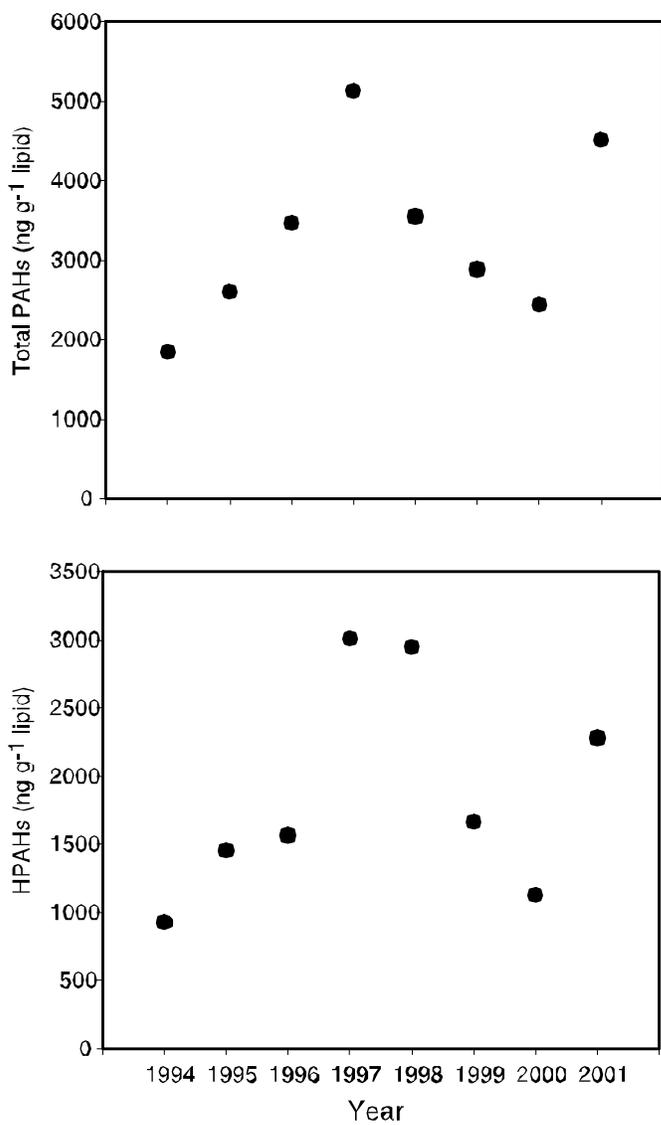


Figure 4.

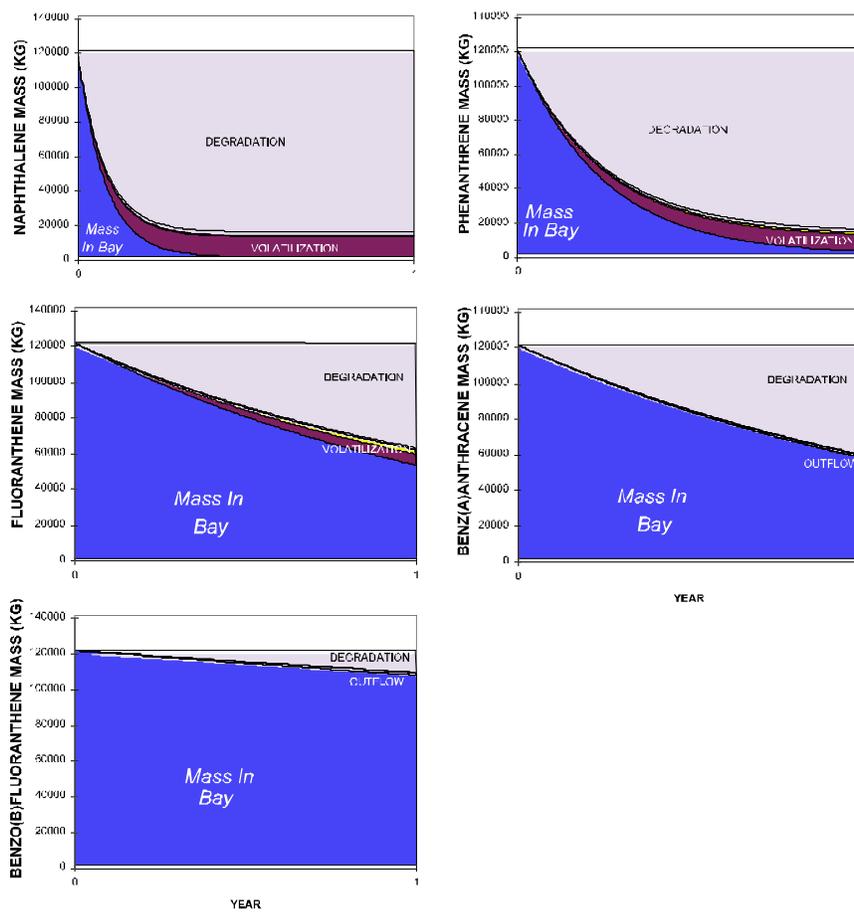


Figure 5.

