Organochlorine Pesticide Fate in San Francisco Bay

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EXECUTIVE SUMMARY

In this study, a single region, two-compartment mass balance model was applied to San Francisco Bay to improve our understanding of the long-term fate of the organochlorine (OC) pesticides, DDT, chlordane, and dieldrin. This study summarized the current state of knowledge of OC pesticides in San Francisco Bay, estimated overall residence times and long-term fate of pesticides in response to varying magnitudes of loading, and identified important characteristics, processes, and pathways of removal that require further investigation and evaluation for improving modeling capability. Although there are considerable uncertainties associated with applying the current model to the Bay, it is a valuable tool for environmental scientists and managers to use in understanding major processes affecting the fate of pesticides and the time scales of recovery in the Bay.

Model results indicate that the overall persistence, measured as overall residence times at steady state, of OC pesticides decreases in the following order: ΣDDT > Σchlordane > dieldrin. The overall residence times at steady state (T_{OV}) ranged from 3.1 to 6.5 years for DDT compounds and 0.07 to 1.8 years for chlordane compounds. The overall residence time for dieldrin was approximately 0.4 years. Long-term model forecasts of total pesticide mass in the Bay showed that with no future pesticide loading, DDT has greater mean lifetimes within the Bay system compared to other pesticides. Compared to the modeled pesticides, however, the model indicates that the mean chemical lifetime in the combined water and sediment system is longer for a high-molecular-weight PAH (benzo[b]fluoranthene) and a moderately high-molecular-weight PCB (PCB 118). Since OC pesticides are no longer produced, unlike PAHs, and less persistent than PCBs, the model suggests that the benefits of improving water quality and reducing concentrations in fish would be more readily apparent for pesticides than for PCBs or PAHs in response to management actions that reduced loading from internal and external sources.

Forecast recovery curves indicate that prevention of future pesticide loading would eliminate these pesticides from the Bay within a matter of decades. Approximately 95% of the current mass of DDTs, chlordanes, and dieldrin would be removed from the Bay within 25, eight, and six years, respectively. Model forecasts indicate that degradation in sediment is an important pathway of removal of all pesticides, while outflow through the Golden Gate and volatilization to the atmosphere are also important mechanisms of removal. In terms of management of the Bay, model results suggest that efforts that successfully reduce pesticide loading from external pathways, as well as from internal sources of remobilized deposits, may achieve large-scale reductions in pesticide contamination in relatively short time scales.

Long-term model forecasts of total pesticide mass in the Bay also showed that with continued loading of a constant magnitude, a steady-state condition would be reached in which pesticide mass in the Bay would remain constant. According to model forecasts, constant loading of approximately 30 kg yr^{-1} of ΣDDT, 15 kg yr^{-1} of Σchlordane, and 15 kg yr^{-1} of dieldrin would never allow greater than a 50% reduction in

the initial mass of pesticides. In addition, model forecasts provided estimates of the approximate magnitude of constant loading required to maintain the current mass of pesticides in the Bay: 60-70 kg yr^{-1} of ΣDDT, 20-40 kg yr^{-1} of Σchlordane, and 30 kg yr^{-1} of dieldrin. In this context, the model provides upper bounds of pesticide loading to the Bay if it is assumed that pesticide loading is decreasing or at worst remaining constant.

When compared to estimates of actual pesticide loading to the Bay, the upper bound modeled loads of ΣDDT and Σchlordane are of similar magnitude. With respect to dieldrin, the best estimate loads are approximately one-third of the upper bound modeled load. This general agreement between estimated loads and the range of forecasted model loads suggests that the model presents plausible scenarios of how the Bay responds to continued inputs of OC pesticides; however, the use of loading estimates to accurately predict whether pesticide mass in the Bay is changing (*i.e.*, decreasing or increasing) or staying constant would require a much greater degree of accuracy in the model and estimated loads than is currently available.

Given that the pesticides included in this study are sparingly soluble in the water column and have high affinity for organic material associated with sediment, their removal relies heavily on characteristics of the sediment. Several key parameters were associated with both high influence on model sensitivity and high variability in estimated values. The influence of initial concentrations of pesticide in sediment reflects an important limitation of using single average concentrations to represent the truly heterogeneous concentrations measured in water and sediment throughout the Bay. Similarly, treatment of the active sediment layer as a compartment of uniform depth presents another limitation that requires further investigation. Accordingly, future modeling efforts aimed at improving our understanding of pesticide fate require more accurate estimation of input parameters describing processes and properties of the bottom sediment of the Bay.

Monitoring data suggest that past decreases in pesticide loading led to subsequent declines in concentrations in biota; however, more recent trends are less apparent. Therefore, questions remain as to whether reductions in loading and contamination are still occurring and what effect does internal cycling of pesticides have on dampened trends in recent years. In particular, significant uncertainties in the magnitude of continued loading from tributaries that drain the local watersheds and Central Valley cause substantial variation in projected recovery rates of the Bay. Accordingly, answering these questions is especially important with respect to using a multimedia model to accurately predict the long-term fate of pesticides based on recent trends in contamination. Furthermore, a more spatially and temporally explicit modeling approach is needed to make proper management decisions between source reduction efforts aimed at internal and/or external sources and allowing for natural attenuation of pesticide contamination in the Bay.

I. INTRODUCTION

Organochlorine (OC) pesticides are persistent organic chemicals of current environmental concern in San Francisco Bay due to their persistence in the ecosystem and their potential deleterious effects on wildlife and human health. The OC pesticides of specific concern for regulation and management in the Bay are the DDT compounds (including the o,p'- and p,p'-isomers of DDT, DDE, and DDD), the chlordanes (including alpha-chlordane, gamma-chlordane, cis-nonachlor, trans-nonachlor, oxychlordane, heptachlor, and heptachlor epoxide), and dieldrin. All of these pesticides are neurotoxicants that also affect reproductive development and are classified by the U.S. EPA as probable carcinogens (USEPA, 2000). These pesticides have also been implicated as endocrine disruptors (Arnold *et al.*, 1996; Soto *et al.* 1995).

Beginning in the 1940s, OC pesticides were used primarily as insecticides for agricultural applications and were also used for pest control and mosquito abatement in urban areas. OC pesticides have been widely distributed throughout the state and the San Francisco Bay watershed due to extensive agricultural activity and the rapid growth of urban areas in the period in which they were used (Mischke *et al.*, 1985; Law and Goerlitz, 1974). In the 1980s, the San Joaquin River and its tributaries had some of the highest concentrations of DDT measured in any major river system in the United States (Gilliom and Clifton, 1990). Potential health effects and ecological concerns led to reductions in use of DDT in California beginning in 1963 (Mischke *et al.*, 1985) and a federal ban on DDT use a decade later in 1972 (USEPA, 2000). Similar restrictions were placed on production and use of chlordane and dieldrin in 1975 and 1974, respectively. The EPA canceled all uses of dieldrin in 1989 (USEPA, 1990), while the commercial sale of chlordane continued through 1988 (USEPA, 1988).

Decades after the implementation of restrictions or bans on use of these pesticides, concentrations measured in water and fish collected from the Bay continue to exceed guidelines established to protect human health. In 1994, concentrations of DDT, chlordane, and dieldrin in sport fish collected from the Bay were higher than fish screening values (Fairey *et al.*, 1997). High concentrations of these pesticides, and other bioaccumulative contaminants, such as mercury, PCBs, and dioxins, led the California Office of Environmental Health Hazard Assessment (OEHHA) to issue an interim sport fish consumption advisory for fish caught in San Francisco Bay (OEHHA, 1994). This health advisory remains in place and has led to the listing of all segments of San Francisco Bay on the Clean Water Act Section 303(d) list of impaired water bodies for impairment by DDT, chlordane, and dieldrin. At the time of the most recent revision to the 303(d) list in 2002, OC pesticides were listed as "low priority" and were not currently scheduled for TMDL development (SWRCB, 2003).

Since the time of restrictions, there have been significant declines in concentrations measured in sediment cores (Venkatesan *et al.*, 1999), bivalves (Gunther *et al.*, 1999), and sport fish (Greenfield *et al.*, 2002) in San Francisco Bay. Despite such declines in Bay sediment and biota, studies have found continued inputs of OC pesticides to the Bay via Central Valley runoff (Bergamaschi *et al.*, 2001), runoff from creeks and

storm drains in the local watersheds (Leatherbarrow *et al.*, 2002; McKee et al., 2004; KLI, 2002), and wastewater effluent (Yee *et al.*, 2001). There is also evidence of continued cycling of contaminated sediment from historic deposits (*e.g.*, a former pesticide packaging plant on the Lauritzen Canal in the Richmond Harbor: Pereira *et al.*, 1996; Anderson *et al.*, 2000).

To understand the long-term impacts of persistent contaminants in the Bay, a five-year review of the RMP conducted in 1997 recommended that the RMP begin developing mass budget models (Bernstein and O'Connor, 1997). Modeling efforts were initiated in a study that predicted the long-term fate of PCBs in the Bay (Davis, 2004) and continued in a study on the fate of PAHs by Greenfield and Davis (2005). This report presents the third application of the mass budget model to understand the fate of OC pesticides in San Francisco Bay. The objectives of this study are to apply the regional model to the Bay using input data for specific chemical properties of DDT, chlordane, and dieldrin to: (1) synthesize existing information and data on OC pesticides in the Bay; (2) estimate residence times and removal rates of OC pesticides in the Bay under varying magnitudes of loading; (3) identify the dominant processes of removal for each pesticide; and (4) compare model results with existing data on trends and loading.

II.   THE MODEL

OVERVIEW

The model used in this study and previous studies for San Francisco Bay was based on a model developed by Mackay *et al.* (1994) and Gobas *et al.* (1995) to predict the fate of PCBs in Lake Ontario. The model was modified and applied to San Francisco Bay by Davis (2004) to understand the long-term fate of PCBs in the Bay and then applied in a second RMP modeling study to understand the fate of PAHs (Greenfield and Davis, 2005).

The model treats San Francisco Bay as a single region with two major components: the water column and sediment (Figure 1). The sediment compartment is designated as the active sediment layer that interacts with the overlying water column and rests above a mass of buried sediment that serves as a sink for contaminants. The regional mass balance approach assumes that exchange of pesticide mass between compartments is more important than spatial variations in concentration, which are neglected in the model. As a result, the model assumes that each compartment is represented by a single average concentration.

The model accounts for five major pathways of addition or removal of pesticides to the Bay: pesticide loading to the Bay, outflow to the Pacific Ocean through the Golden Gate, volatilization to the atmosphere, permanent burial in sediment, and degradation via biotic or abiotic mechanisms. The loading term in the model encompasses all inputs from various external pathways, which may include runoff from the Central Valley and the local watersheds, wastewater effluent, and atmospheric deposition, as well as internal inputs of historic in-Bay deposits through erosion or dredging of buried sediment.
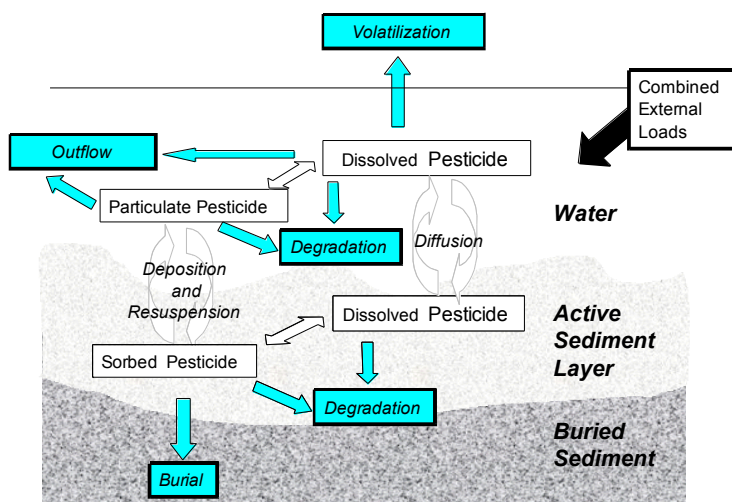
Figure 1.   Diagram of OC pesticide fate in San Francisco Bay showing processes included in the model.

In addition to movement of OC pesticides into and out of the Bay, there are several processes that account for transfer between water and sediment. These processes include diffusion between sediment and porewater and the settling or resuspension of particle-associated pesticides.

The model uses two governing equations to calculate the change in contaminant mass in both the water column and sediment:

$$\Delta M_W / \Delta t = L + (k_{SW1} + k_{SW2}) * M_S - (k_V + k_O + k_{WR} + k_{WS1} + k_{WS2}) * M_W \quad (1)$$

$$\Delta M_S / \Delta t = (k_{WS1} + k_{WS2}) * M_W - (k_{SW1} + k_{SW2} + k_B + k_{SR}) * M_S \qquad (2)$$

where:

M_W	= mass of pesticides in water (kg)
M_S	= mass of pesticides in sediment (kg)
t	= time (d)
L	= rate of pesticide loading to the water column (kg d^{-1})
k_{SW1}	= rate of solids resuspension (d^{-1})
k_{SW2}	= rate of sediment-to-water diffusion (d^{-1})
k_V	= rate of volatilization (d^{-1})
k_O	= rate of outflow to the Pacific Ocean (d^{-1})
k_{WR}	= rate of degradation in water (d^{-1})
k_{WS1}	= rate of solids settling (d^{-1})
k_{WS2}	= rate of water-to-sediment diffusion (d^{-1})
k_B	= rate of burial in sediment (d^{-1})
k_{SR}	= rate of degradation in sediment (d^{-1})

The equations describe the change in mass per unit time of pesticides in the water column ($\Delta M_W / \Delta t$) and sediment ($\Delta M_S / \Delta t$) on a daily time step with respect to rate constants (k) of important processes and external loading (L). The OC pesticide mass in the water column increases by addition of mass through loading (L) and inputs from the active sediment layer (k_{SW1} and k_{SW2}) and decreases by removal of mass through volatilization (k_V), outflow (k_O), degradation (k_{WR}), and loss to the active sediment layer (k_{WS1} and k_{WS2}). Similarly, the OC pesticide mass in the active sediment layer increases by addition of mass from inputs from the water column (k_{WS1} and k_{WS2}) and decreases by removal of mass through degradation (k_{SR}), burial (k_B), and loss to the water column (k_{SW1} and k_{SW2}).

The model was used to compare the overall persistence of individual pesticides, including components of DDT and chlordane, within the Bay and evaluate their long-term fate under various loading scenarios. In this study, overall persistence was evaluated in terms of overall residence times at steady state as described in previous studies on multimedia models (*e.g.*, MacLeod and McKone, 2004; Bennett et al., 1999). The overall residence time (T_{OV}) is the residence time of a contaminant being removed from a modeled system through chemical transformation and degradation, and physical advection. It is defined as the reciprocal of the overall loss rate (k_{OV}) of pesticide removal from the system. These parameters are derived for a two-compartment system using the following equations:

$$T_{OV} = 1/k_{OV} \tag{3}$$

$$k_{OV} = (M_W k_W + M_S k_S)/(M_W + M_S) \tag{4}$$

where:

      k_W = rate of pesticide removal from Bay via water compartment
      k_S = rate of pesticide removal from Bay via sediment compartment

Based on the above equations, k_{OV} and T_{OV} represent overall loss rates and residence times, respectively, that are weighted in proportion to the mass fraction in each compartment. For example, a pesticide with its greatest proportion of total mass residing in the active sediment layer, as is expected for all modeled pesticides in this study, will have its loss rate from sediment (k_S) more heavily weighted in determining the overall loss rate (k_{OV}). This approach provides a more realistic measure of overall persistence of chemical contaminants in multimedia environments than a single media (or compartment) approach (Webster et al., 1998).

In this model, k_W is the overall rate of pesticide removal from the water column via degradation in water (k_{WR}), volatilization (k_V), and outflow through the Golden Gate (k_O). Similarly, k_S is the overall rate of pesticide removal from the active sediment layer via degradation in sediment (k_{WS}) and burial (k_B). Rates of inter-media transfer of pesticides between water and sediment (*i.e.*, diffusion, settling, and resuspension) are not included in calculations of overall residence times because no net removal of pesticides from the system occurs; however, these parameters are important in distributing

pesticides between the two compartments, which in turn, influences the overall persistence of pesticides in the Bay.

INPUT DATA

Input data for the model were selected based on a review of available literature to obtain best estimates of physical and chemical characteristics of San Francisco Bay and pesticides. Rate constants (k) describing important processes that control the fate of pesticides were calculated in the model using best estimates of individual model parameters. Equations used in this model to calculate rate constants for San Francisco Bay are described in detail in Davis (2004) and are listed in Table 1. The simplicity of the model and uncertainties associated with past and current loadings and concentrations preclude validation of the model. Moreover, the application of robust uncertainty analyses is beyond the scope of this initial effort. However, sensitivity analyses were conducted for modeled parameters to determine the extent to which model results vary in response to variation in the input parameters.

Selection of OC pesticides

DDT and chlordane were originally produced and sold as technical mixtures of several individual chemicals (Dearth and Hites, 1991; WHO, 1989). The mass of ΣDDT in San Francisco Bay is significantly weathered and comprised mostly of DDD and DDE compared to the original DDT mixtures that were primarily comprised of o,p'- and p,p'-DDT (Table 2). This is primarily due to transformation of DDT to DDE under aerobic conditions and to DDD under anaerobic conditions. There are also direct inputs of DDD as result of its previous use as a pesticide. As discussed later, the transformation of DDT compounds to DDE or DDD compounds was not explicitly included in model formulations, but implicitly included in overall degradation rates in water and sediment.

Predominant chlordane compounds found in Bay water and sediment include alpha-chlordane, gamma-chlordane, and trans-nonachlor. Input values based on the abundant compounds of DDT and chlordane were chosen to reflect the change in total mass per time in the Bay in the modeling scenarios for which pesticide loading varied over 20-year time periods. Modeling was conducted using input data for p,p'-DDE and p,p'-DDD to represent ΣDDT and alpha-chlordane, gamma-chlordane, and trans-nonachlor to represent Σchlordane. In addition to comprising large fractions of ΣDDT and Σchlordane in Bay water and sediment, these compounds are also highly resistant to degradation or transformation compared to other compounds, and thus, are more likely to persist in the Bay over the long term.

Table 1. Equations used for calculation of rate constants in the model.

Rate Constants:

$k_O = [F/(1000 X_W)] * PEST_O/PEST_A$ (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})

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

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

$k_{SW1} = 1000(ResFlux/C_{SS})(1 - \phi_{DS}) / X_S$ (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)

$PEST_A = $ average total water column PEST concentration Estuary-wide (pg/L)

$PEST_O = $ PEST concentration at seaward locations (Yerba Buena Island; pg/L)

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

$\phi_{DW} = $ freely dissolved PEST 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)

$\mathcal{V}_{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})

$ResFlux = $ resuspension flux of sediment solids (kg d^{-1})

$ResFlux = 1000(C_{PW} \mathcal{V}_{SS} S_{AW} - C_{SS}V_B S_{AS})$

$C_{SS} = $ concentration of solids in sediment (mg L^{-1})

$V_B = $ sediment burial mass transfer coefficient (m d^{-1})

$\phi_{DS} = $ fraction of freely dissolved PEST 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 2. Percent contribution by mass of individual compounds of ΣDDT and Σchlordane.
Data from five RMP stations represent average percent contributions in RMP water samples collected from 1993 to 1999. Data for technical Chlordane and DDT are from Dearth and Hites (1991) and WHO (1989), respectively.

Particulate Chlordane

Percent	Technical Chlordane	Sacramento River	San Pablo Bay	Yerba Buena Island	Dumbarton Bridge	Coyote Creek
alpha-chlordane	19	16	18	18	26	25
gamma-chlordane	24	28	20	24	27	25
cis-nonachlor	19	2	10	13	11	9
trans-nonachlor	7	20	18	23	23	23
heptachlor	NA	0	1	1	2	1
heptachlor epoxide	NA	19	13	11	9	10
oxychlordane	0	14	20	10	1	6

Dissolved Chlordane

Percent	Technical Chlordane	Sacramento River	San Pablo Bay	Yerba Buena Island	Dumbarton Bridge	Coyote Creek
alpha-chlordane	19	20	22	26	23	25
gamma-chlordane	24	19	16	19	18	18
cis-nonachlor	19	8	7	6	6	7
trans-nonachlor	7	20	17	16	13	14
heptachlor	NA	2	3	5	4	2
heptachlor epoxide	NA	24	27	20	27	25
oxychlordane	0	7	9	8	9	8

Particulate DDT

Percent	Technical DDT	Sacramento River	San Pablo Bay	Yerba Buena Island	Dumbarton Bridge	Coyote Creek
o,p'-DDD	0	4	6	6	6	6
o,p'-DDE	0	4	2	3	3	3
o,p'-DDT	15	2	3	4	5	2
p,p'-DDD	0	11	30	30	34	24
p,p'-DDE	4	73	44	44	40	55
p,p'-DDT	77	7	15	13	12	11

Dissolved DDT

Percent	Technical DDT	Sacramento River	San Pablo Bay	Yerba Buena Island	Dumbarton Bridge	Coyote Creek
o,p'-DDD	0	11	9	12	13	10
o,p'-DDE	0	2	2	2	2	2
o,p'-DDT	15	0	1	0	1	0
p,p'-DDD	0	34	54	54	49	53
p,p'-DDE	4	46	29	26	31	29
P,p'-DDT	77	7	5	5	5	6

Table 3. Properties of San Francisco Bay. Estimates from Davis (2004).

PARAMETER	SYMBOL	BEST ESTIMATE	UNITS
Water surface area	S_{AW}	1.1×10^9	m^2
Sediment surface area	S_{AS}	1.1×10^9	m^2
Depth of active sediment layer		0.15	m
Water volume	X_W	5.5×10^9	m^3
Sediment volume	X_S	1.6×10^8	m^3
Water temperature	T	15	° C
Water outflow	F	7.0×10^{10}	$L\ d^{-1}$
Concentration of particles in water	C_{PW}	8.5×10^{-5}	$kg\ L^{-1}$
Concentration of solids in sediment	C_{SS}	0.5	$kg\ L^{-1}$
Density of suspended solids	d_{PW}	1.1	$kg\ L^{-1}$
Density of sediment solids	d_{SS}	2.7	$kg\ L^{-1}$
Fraction of organic carbon in suspended solids	OC_{PW}	0.03	
Fraction of organic carbon in bottom sediment	OC_{SS}	0.01	
Sediment burial mass transfer coefficient	V_B	0	$m\ d^{-1}$
Solids settling rate	$\mathcal{V}_{SS}$	1	$m\ d^{-1}$
Water-to-sediment diffusion mass transfer coefficient	V_D	2.4×10^{-3}	$m\ d^{-1}$
Average wind speed		10.6	$mi\ hr^{-1}$

Properties of San Francisco Bay

　　　　Descriptive properties of San Francisco Bay used in the model were originally compiled by Davis (2004) based on an extensive literature review and professional judgment by local experts in the Bay Area (Table 3). Derivations of Bay properties are described in detail in Davis (2004). An added component to this model formulation that differed from previous model applications in San Francisco Bay is the inclusion of tidal exchange as part of the overall water budget. Tidal exchange flow was calculated by multiplying freshwater inflow by a factor of 3.75 as discussed in Davis and Oram (2005). It is also important to note that for the modeling studies in San Francisco Bay, the rate of burial (k_B) from the active sediment layer to the underlying buried sediment layer has been modeled with a sediment mass burial mass transfer coefficient (V_B) equal to zero. This is due to recent bathymetric analyses that have shown Bay-wide net erosion of sediment occurring over the past few decades (Jaffe et al., 1998; Capiella et al., 1999; Foxgrover et al., 2004).

Sensitivity analyses from Davis (2004) indicate that the physical properties or rate processes of the Bay that are most influential on PCB model results are outflow through the Golden Gate (k_O) and depth of the active sediment layer. Parameters that are moderately influential on PCB-model sensitivity are the organic carbon content of suspended solids (OC_{PW}) and the sediment burial mass transfer coefficient (V_B), which is an essential parameter for estimating the rate of burial (k_B).

Chemical properties of OC pesticides

Estimates of chemical properties of OC pesticides were derived mainly from values listed in Mackay *et al.* (1997) and Howard *et al.* (1991) and from references cited therein (Table 4). Compilations of exhaustive lists provided a plausible range of values for parameterization of the model; however, values were often derived from studies of varying conditions and methods, which limited their applicability to real environmental systems. Previous reviews of compiled literature and databases have also identified limitations to estimating environmental parameters for hydrophobic organic compounds, including errors in reporting data, poor data quality, and duplication of reported values (Pontolillo and Eganhouse, 2001). To minimize errors associated with data duplication in this study, the compiled datasets were reviewed and data listed in the text as "quoted," "selected," or "averaged" by authors of previous literature reviews and compilations were removed.

Henry's Law Constant

The Henry's Law constant (*H*) is an essential parameter for determining the effective rate constant for volatilization (k_V) of pesticides from the water compartment. Given that *H* is highly dependent on temperature, constants from readily available studies were corrected for a water temperature of 15ºC (288 K). Values of *H* were corrected for temperature using the Clausius-Clapeyron equation and methods described in Rechsteiner (1990). Thermodynamic data used in the calculations are listed in Appendix Table 1. Values of *H* from original studies and their temperature-corrected results are listed in Appendix Table 2. Median values of temperature-corrected *H* were used as best estimates for model input and sensitivity analyses (Table 4).

Octanol-water partition coefficient (K_{OW})

Octanol-water partition coefficients (K_{OW}) are indicators of the hydrophobic nature of organic compounds and the degree to which compounds partition into organic material, such as organic coatings on sediment or lipids in organisms. In this model, partitioning of pesticides between mobile and non-mobile phases, as represented by K_{OW}, is an important parameter required for determining the effective compartment rate constants for processes such as volatilization, solids settling, diffusion between water and sediment, sediment resuspension, and burial in bottom sediment. Values of log K_{OW} were compiled from Mackay *et al.* (1997) and Pontolillo and Eganhouse (2001) (Appendix Table 3). Median values of a compiled list of log K_{OW} values selected from Mackay *et al.* (1997) were used as best estimates for all pesticides, except for p,p'-DDE and p,p'-DDT.

For these parameters, values of 6.23 for p,p'-DDE and 6.24 for p,p'-DDT from Pontolillo and Eganhouse (2001) were used (Table 4).

Mass transfer coefficients

The rate constant for pesticide volatilization from the water column depends on the volatilization mass transfer coefficient (V_E), which is a function of the mass transfer coefficients of evaporation on the water-side (V_{EW}) and air-side (V_{EA}) of the air-water interface (Table 4). The water-side mass transfer coefficients (V_{EW}) were calculated for individual pesticides using input values for wind speed, water temperature, and Schmidt numbers for pesticides and carbon dioxide (CO_2) (discussed below). The air-side mass transfer coefficients (V_{EA}) were calculated for individual pesticides using input values of wind speed and the molecular diffusivities of pesticides in air and water in air.

Schmidt numbers for individual OC pesticides were calculated by dividing the kinematic viscosity of water at 15ºC (288 K) by the molecular diffusivity of each OC pesticide in water. The Schmidt number for CO_2 was calculated using the same equation used by Davis (2004) from Zhang *et al.* (1999) for water temperature of 15ºC (288 K). Diffusivity in water was calculated using the Hayduk and Laudie method at a water temperature of 15ºC (288 K) and wind speed of 4.7 m s^{-1} using equations presented by Tucker and Nelken (1990). Diffusivity in air was calculated using two methods: (1) the Fuller, Schettler, and Giddings Method and (2) the Wilke and Lee Method (with the LeBas molar volume) using equations presented by Tucker and Nelken (1990). For both methods, diffusivities were calculated at a pressure of 1 atmosphere and temperature of 25ºC (298 K). Average values from the two methods were used in calculations of air-side mass transfer coefficients for pesticides.

Degradation rates

Degradation rates listed in Mackay *et al.* (1997), Howard *et al.* (1991), and other references were evaluated to derive best estimates of degradation rates in water (Appendix Table 4) and sediment (Appendix Table 5). For consistency, reported half-lives and degradation rate values were converted to a daily degradation rate (d^{-1}) based on first order kinetics and the following equation:

$$t_{1/2} = -\ln 2/k \tag{5}$$

where: $t_{1/2}$ = half-life of degradation (d)
                     k = daily degradation rate (d^{-1})

Degradation in water

Degradation rates of pesticides in water account for processes of direct and indirect photolysis and hydrolysis. For most of OC pesticides listed in Mackay et al. (1997) and Howard et al. (1991), photolysis rates were higher than hydrolysis rates by orders of magnitude (Appendix Table 4). Studies of pesticide photolysis have typically focused on degradation of dissolved species in distilled water (Miller and Zepp, 1983) and have not accounted for various processes that either enhance or retard photolysis

rates, such as indirect photolysis, light penetration and transmission through water, temperature, and algae (Zepp and Cline, 1977; Miller and Zepp, 1983).

While photolysis rates of DDT and DDD were not expected to be important (Callahan et al., 1979), rates of DDE photolysis have been reported that would essentially remove all DDE from a water body within one day. The persistence of p,p'-DDE and other DDT compounds in the Bay indicate that rates of degradation are probably much slower than these reported values. Persistence of p,p'-DDE in other surface water bodies has been explained by its sorption to sediment (Zepp et al., 1977), which can decrease photolysis rates in the water column (Miller and Zepp, 1979; Oliver et al., 1979). Furthermore, attenuation of sunlight in natural waters has been estimated to decrease photolysis rates of organic contaminants by about 50% within the first 10 to 15 cm or by an order of magnitude at depths of 40-60 cm (Zepp and Cline, 1977). Similar reductions in photolysis rates may occur in the highly turbid waters of San Francisco Bay.

Given the uncertainties of extrapolating degradation rates measured in controlled studies to natural conditions and the observed persistence of OC pesticides in San Francisco Bay, degradation rates were based on either observed rates of degradation or other pathways, such as hydrolysis. A degradation rate of 2×10^{-3} d^{-1} was chosen for DDT compounds and dieldrin based on an observed estimate of degradation in surface waters ($<2.3 \times 10^{-3}$ d^{-1}) compiled by Mackay et al. (1997). This rate for dieldrin was approximately six times slower than a rate selected by Sato and Schnoor (1991) to model the long-term fate of dieldrin in a reservoir. Assuming that the Bay has greater mixing and suspended sediment that screen chemicals from photodegradation compared to the modeled reservoir, a slower rate of photolysis would be expected in the Bay. Other degradation rates selected were 2×10^{-3} d^{-1} for chlordane, 1.5×10^{-1} d^{-1} for heptachlor, and 2.0×10^{-2} d^{-1} for heptachlor epoxide.

Degradation in sediment

Limited data on degradation rates of OC pesticides in sediment and soil were reported under aerobic or anaerobic conditions (Appendix Table 5). Large uncertainties exist in estimating degradation rates, which has been noted in previous modeling studies (*e.g.*, Helm *et al.*, 2002); however, the reported values provide plausible ranges of degradation rates in sediment for incorporation into the model. Degradation rates in sediment were based primarily on median values derived from rates compiled by Mackay et al. (1997). The estimated degradation rate for DDT (2.1×10^{-4} d^{-1}) was also applied for modeling of DDE and DDD isomers since it fell within the range of values reported for those compounds. Degradation rates selected were 8.3×10^{-4} d^{-1} for chlordane, 6.9×10^{-4} d^{-1} for dieldrin, 2.8×10^{-3} d^{-1} for heptachlor, and 1.0×10^{-2} d^{-1} for heptachlor epoxide.

Table 4. Chemical properties of OC pesticides. Bold values are best estimates derived for specific compounds applied to other compounds. Selected data are from sources listed in Appendix Tables 2 through 5.

Parameter	Molecular Weight	log K_{OW}	Henry's Law Constant	Degradation Rate in Water	Degradation Rate in Sediment	Water Side Mass Transfer Coefficient	Air Side Mass Transfer Coefficient
	g mol^{-1}		Pa m^3 mol^{-1}	d^{-1}	d^{-1}	m d^{-1}	m d^{-1}
o,p-DDT	354.5	5.7	0.39	2.0×10^{-3}	2.1×10^{-4}	**0.726**	**396**
p,p-DDT	354.5	6.2	**0.39**	2.0×10^{-3}	2.1×10^{-4}	**0.726**	**396**
DDT	354.5	6.2	0.30	2.0×10^{-3}	**2.1×10^{-4}**	0.726	396
o,p-DDE	318.0	5.6	4.05	2.0×10^{-3}	2.1×10^{-4}	**0.746**	**404**
p,p-DDE	318.0	6.2	**4.05**	2.0×10^{-3}	2.1×10^{-4}	**0.746**	**404**
DDE	318.0	5.9	2.51	2.0×10^{-3}	**2.1×10^{-4}**	0.746	404
o,p-DDD	320.0	5.3	0.58	6.8×10^{-5}	2.1×10^{-4}	**0.740**	**408**
p,p-DDD	320.0	6.0	**0.58**	6.8×10^{-5}	2.1×10^{-4}	**0.740**	**408**
DDD	320.0	6.0	0.30	**6.8×10^{-5}**	**2.1×10^{-4}**	0.740	408
Chlordane		5.5	2.92	**2.0×10^{-3}**	**8.3×10^{-4}**	0.722	394
alpha-chlordane	409.8	6.0	3.6	2.0×10^{-3}	8.3×10^{-4}	0.722	394
gamma-chlordane	409.8	6.1	2.8	2.0×10^{-3}	8.3×10^{-4}	0.722	394
cis-nonachlor	444.2	5.7	3.3	2.0×10^{-3}	8.3×10^{-4}	0.709	378
trans-nonachlor	444.2	5.7	12	2.0×10^{-3}	8.3×10^{-4}	0.709	378
heptachlor	373.3	5.4	50	1.5×10^{-1}	2.8×10^{-3}	0.741	393
heptachlor epoxide	389.3	4.5	0.9	2.0×10^{-2}	1.0×10^{-2}	0.736	391
oxychlordane	423.8	2.6				0.722	384
Dieldrin	380.9	4.6	0.53	2.0×10^{-3}	6.9×10^{-4}	0.727	385

Concentrations of OC pesticides in San Francisco Bay

Best estimates of concentrations of OC pesticides in water and sediment were derived to estimate the current mass of pesticides in each compartment. Estimates were calculated using RMP data from 1993 to 2000 (*e.g.*, SFEI, 2002), Pilot Regional Monitoring Program (PRMP) data from 1991 to 1992 (Flegal *et al.*, 1994), and data from the Bay Protection Toxic Cleanup Program (BPTCP) from 1994 to 1997 (Hunt *et al.*, 1998).

OC pesticide concentrations in water

Average concentrations of ΣDDT, Σchlordane, and dieldrin in water were calculated using data collected by the RMP from 1993 to 2000 from 22 RMP stations throughout the Estuary. The best estimates reflect averages from all RMP stations except Local Effects Monitoring Stations at San Jose (C-3-0) and Sunnyvale (C-1-3) and Estuary Interface Pilot Stations at Guadalupe River (BW15) and Standish Dam (BW10) located in the southern margins of the Lower South Bay. The median values of all site-specific average concentrations were used as best estimates for concentrations of ΣDDT, Σchlordane, and dieldrin in water. Best estimates of Bay-wide pesticide concentrations in water are 660 pg L^{-1} of ΣDDT, 160 pg L^{-1} of Σchlordane, and 77 pg L^{-1} of dieldrin.

OC pesticide concentrations in sediment

Given that contamination in San Francisco Bay sediment is heterogeneous with higher concentrations typically measured near the margins of the Bay (Flegal *et al.*, 1994; Hunt *et al.*, 1998), deriving a Bay-wide average concentration of OC pesticides in sediment is difficult. To estimate average concentrations of pesticides in sediment, a spatially weighted average was calculated following similar methods presented by Davis (2004). Davis (2004) estimated that the shallow marginal regions of the Bay sampled by PRMP, BPTCP, and RMP monitoring accounted for approximately 10% of the entire Bay sediment surface area. Therefore, the contribution of Bay-margin sediment concentrations to the best estimate concentration was derived by multiplying the medians of site-specific average concentrations from monitoring sites near the margins of the Bay by 0.10. The contribution of deeper Bay sediments to the best estimate was derived by multiplying the median site-specific averages of monitoring sites that were located in deeper channels by 0.90. Best estimates of Bay-wide pesticide concentrations in sediment were 4.2 µg kg^{-1} of ΣDDT, 0.54 µg kg^{-1} of Σchlordane, and 0.15 µg kg^{-1} of dieldrin.

III.   MODEL RESULTS AND DISCUSSION

OC PESTICIDE FATE IN SAN FRANCISCO BAY

No external loading

Model results indicate that the overall persistence, measured as overall residence times at steady state, of OC pesticides decreases in the following order: ΣDDT > Σchlordane > dieldrin (Table 5). As previously noted, overall residence time describes the

residence time of a chemical in a multimedia modeled system due to the combined effects of effective loss rates in all compartments. The overall residence times at steady state (T_{OV}) ranged from 3.1 to 6.5 years for DDT compounds and 0.07 to 1.8 years for chlordane compounds. The overall residence time for dieldrin was approximately 0.4 years. Longer residence times (and half-lives) for DDT compounds compared to the other pesticide classes were driven by their greater distribution within the active sediment layer (i.e., relatively high K_{OW}) relative to the water column and slower rates of degradation in sediment used in the model.

The relative importance of degradation or advection as mechanisms of pesticide removal from the Bay was evaluated by comparing overall residence times due solely to degradation (T_{DEG}) or advection (T_{ADV}) (Table 5). Overall residence times were greater for p,p'-isomers of DDT compared to their o,p'-isomer counterparts; however, the residence times due to degradation were similar for all DDT compounds. Accordingly, differences in overall residence times were driven largely by differences in residence times due to advective processes. Similar patterns were observed for alpha- and gamma-chlordane, and cis- and trans-nonachlor. For both pesticide classes, the compounds with comparatively short overall residence times had relatively low K_{OW} and high Henry's Law Constant, which led to greater distribution in the water column and advective removal via Golden Gate outflow and volatilization.

Table 5. Overall persistence of OC pesticides in the Bay. Overall loss rates (k_{OV}), residence times associated with degradation (T_{DEG}), residence times associated with advection processes (T_{ADV}), overall residence times (T_{OV}), and overall half-lives ($t_{1/2}$) were calculated based on a two-compartment model that includes the water column and active sediment layer. Values are weighted by the fraction of pesticide mass distributed between compartments.

	k_{OV}	T_{DEG}	T_{ADV}	T_{OV}	$t_{1/2}$
	yr^{-1}	yr	yr	yr	yr
o,p'-DDT	0.20	12	8.5	4.9	3.4
p,p'-DDT	0.15	12	14	6.5	4.5
o,p'-DDE	0.38	12	3.4	2.6	1.8
p,p'-DDE	0.19	12	9.0	5.2	3.6
o,p'-DDD	0.33	13	4.0	3.1	2.1
p,p'-DDD	0.17	13	11	6.0	4.2
alpha-chlordane	0.60	3.2	3.4	1.7	1.1
gamma-chlordane	0.56	3.2	4.0	1.8	1.2
cis-nonachlor	0.75	3.2	2.3	1.3	0.9
trans-nonachlor	0.88	3.2	1.8	1.1	0.8
heptachlor	6.1	0.27	0.43	0.2	0.1
heptachlor epoxide	15	0.19	0.10	0.066	0.05
dieldrin	2.5	3.3	0.46	0.40	0.3

Long-term model forecasts with no future pesticide loading support findings of greater persistence of DDT than other pesticides (Figure 2). Similar to patterns noted above, the mass of p,p'-isomers of DDT decreased at slower rates than o,p'-isomers. As previously noted, model results for o,p'- and p,p'-DDT in Figure 2 did not necessarily account for the kinetics of transformation to DDE and DDD metabolites. Therefore, the model forecasted removal rates of DDT isomers that were similar to rates of removal for DDE and DDD isomers. Realistically, changes in ΣDDT mass in the Bay more likely follows the predicted change of p,p'-DDD or p,p'-DDE mass than for other compounds.

Model forecasts of chlordane compounds indicate that removal rates followed a decreasing trend for gamma-chlordane > alpha-chordane > cis-nonachlor > trans-nonachlor > heptachlor ≈ heptachlor epoxide. Slower removal rates were observed for gamma-chlordane because of relatively high K_{OW} and lower volatility (*i.e.,* lower *H*) compared to other chlordane components. As with DDT recovery curves, recovery curves were similar between more persistent chlordane components. Dieldrin had relatively fast removal rates compared to other pesticides (Figure 2). Like heptachlor and heptachlor epoxide, dieldrin has a relatively low K_{OW}, which decreases its affinity for organic material on suspended and bed sediment. These compounds also have high degradation rates in sediment that enhance their rates of removal in the Bay.

Forecast recovery curves indicate that prevention of future pesticide loading would eliminate these pesticides from the Bay within a matter of decades. Approximately 95% of the current mass of DDTs, chlordanes, and dieldrin would be removed from the Bay within 25, eight, and six years, respectively. In terms of management of the Bay, efforts that successfully reduce pesticide loading from external pathways, as well as from erosion of historic deposits, may achieve large-scale reductions in pesticide contamination in relatively short time scales.

This study and previous mass budget models of PCBs (Davis, 2004) and PAHs (Greenfield and Davis, 2005) have provided a means for comparing residence times of persistent contaminants in San Francisco Bay. Compared to PCBs and high-molecular weight PAHs, pesticides are less persistent in the Bay, as indicated by a comparison of model forecasts (Figure 3). Results suggest that the mean chemical lifetime in the combined water and sediment system is longer for a high-molecular-weight PAH (benzo[b]fluoranthene) and a moderately high-molecular-weight PCB (PCB 118) than for the OC pesticides. It is important to note that there are considerable uncertainties associated with the estimated rates of removal, especially in determining accurate degradation rates in sediment. However, the comparison indicates that the mass of pesticide in the Bay may be more responsive to reduced loadings than high-molecular weight PAHs and PCBs.

Differences in degradation rates in sediment and chemical properties that enhance the affinity of contaminants to particulate material and sediment were largely responsible for differences in persistence of PCBs, PAHs, and OC pesticides. For example, values of K_{OW} modeled for benzo(b)fluoranthene (6.4) and PCB 118 (6.7) were higher than those modeled for p,p'-DDE (6.2), alpha-chlordane (6.0), and dieldrin (4.6). In addition, alpha-

chlordane and dieldrin were modeled with faster degradation rates in sediment than benzo(b)fluoranthene ($3x10^{-4}$ d^{-1}) and PCB 118 ($3.4x10^{-5}$ d^{-1}). For all of the compared contaminants, rates of degradation in sediment are poorly characterized. Improved characterization of this parameter is essential for comparing the long-term fate of persistent contaminants in the Bay.

   Although the model indicates that the mean chemical lifetime of PCBs and high-molecular weight PAHs are longer than for OC pesticides, comparisons of the overall lifetimes of different contaminants within the Bay require knowledge of the actual magnitudes and trends in loading of each contaminant. Pesticides and PCBs have been banned or restricted for decades, while PAHs are continually introduced to the Bay from various anthropogenic and natural sources of combustion, as well as from crude oil inputs. It follows then that the Bay will probably recover sooner from contamination by OC pesticides and PCBs than by PAHs.

   Differences in sources, transport processes, and chemical characteristics obfuscate comparisons of actual long-term fates between PCBs and pesticides. For example, DDT residues that were widely distributed throughout agricultural regions of the Central Valley continue to enter the Bay thirty years after periods of peak usage (Bergamaschi et al., 2001). Although the model implies that the Bay is much slower in removing PCBs, the large reservoir of pesticides in the Central Valley may take longer to cycle through the major rivers and Bay-Delta system compared to the reservoir of PCBs in the more localized urbanized landscape adjacent to the Bay. Improvements in modeling contaminant fate in San Francisco Bay, combined with more accurate estimates of loading for different contaminants, will better elucidate the impacts of future contaminant loading to the Bay. This will further provide guidance in evaluating the effectiveness of management actions that reduce loads of sediment-associated contaminants from various sources and pathways.
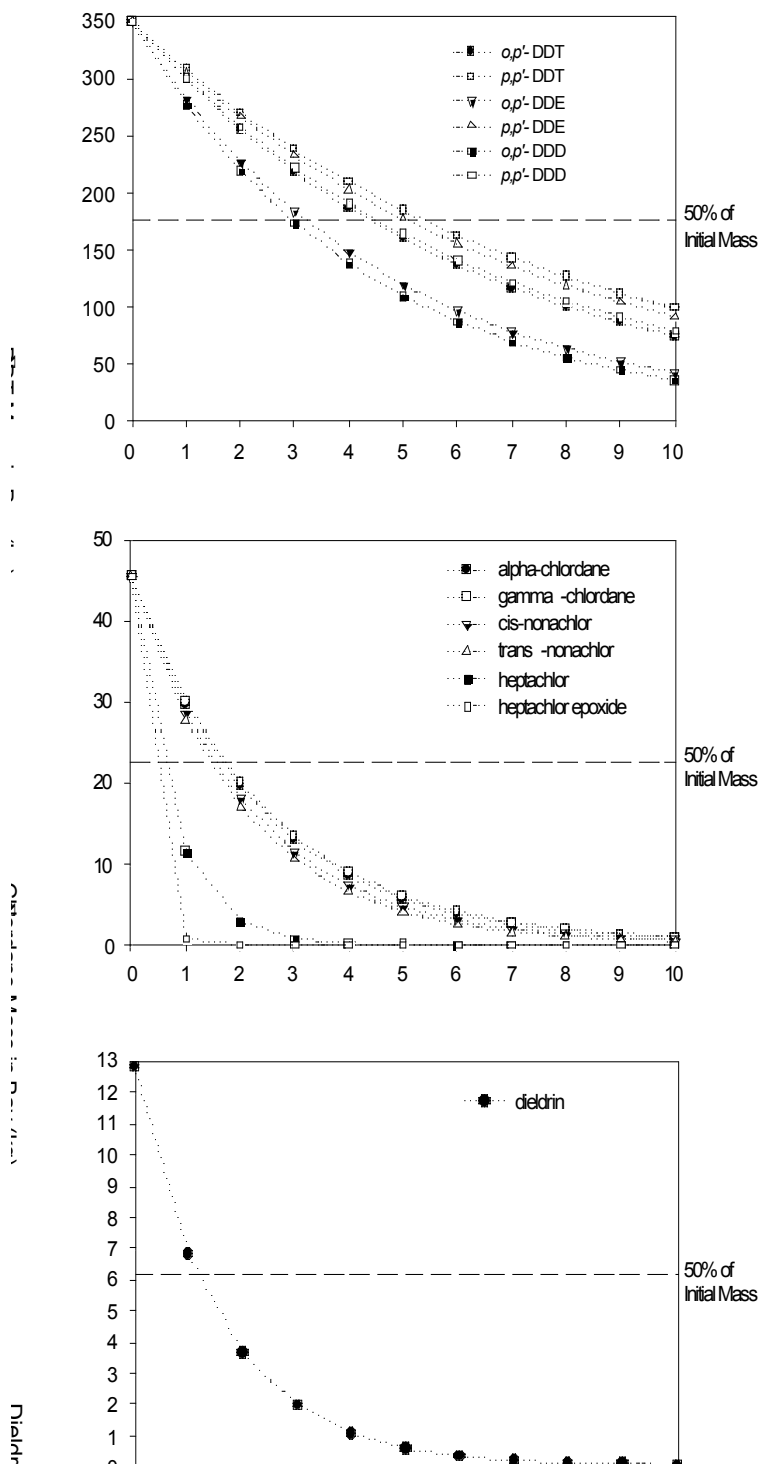
Figure 2.   Model forecast of OC pesticide mass in the Bay with no pesticide loading.
Initial model conditions at time zero represent the current estimated mass of
pesticides in the water column and active sediment layer. Note different scales
on y-axes.

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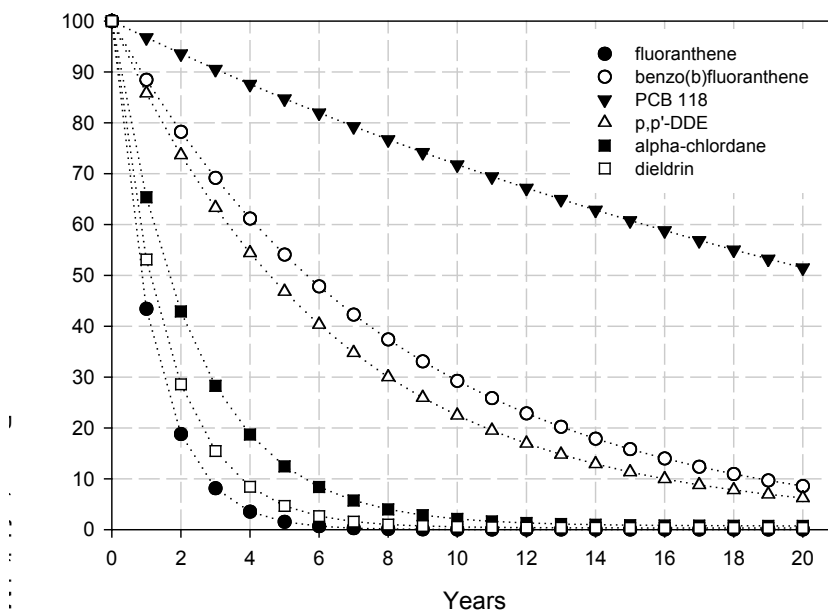
Figure 3. Comparison of model forecasts for OC pesticides, PAHs, and PCBs with no contaminant loading. PCB and PAH modeling results are from Davis (2004) and Greenfield and Davis (2005), respectively. Initial model conditions at time zero represent the current estimated mass of dieldrin in the water column and active sediment layer.

Variable external loading

Given that accurate estimates of annual loading of pesticides (and other contaminants) to the Bay are not available (Davis *et al.*, 2000; KLI, 2002; McKee *et al.*, 2004; Leatherbarrow et al., 2005), model sensitivity to pesticide loading was evaluated by varying the magnitude of annual loads on decadal time scales. The change in ΣDDT mass was modeled using input parameter values for p,p'-DDE and p,p'-DDD (Figure 4). Similarly, the change in Σchlordane mass was modeled using input data for alpha-chlordane, gamma-chlordane, and trans-nonachlor (Figure 5). Dieldrin curves are presented in Figure 6.

For each pesticide, the curve eventually reached an asymptote of steady-state mass in the Bay in response to constant loading. For example, constant loading of approximately 30 kg yr^{-1} of ΣDDT would never allow the mass in the Bay to be reduced by 50% from the initial estimated mass (350 kg; Figure 4). Similarly, approximately 15 kg yr^{-1} would sustain a mass in the Bay approximately half of the current mass of Σchlordane (45 kg; Figure 5). An approximate load of approximately 15 kg yr^{-1} of dieldrin would sustain half of the initial mass of that pesticide (Figure 6).

The model also provided an estimate of the approximate magnitude of constant loading required to maintain the current mass of pesticides in the Bay: 60-70 kg yr^{-1} of ΣDDT, 20-40 kg yr^{-1} of Σchlordane, and 30 kg yr^{-1} of dieldrin. In this context, the model provides upper bounds of pesticide loading to the Bay if it is assumed that pesticide loading is decreasing or at worst remaining constant. Realistically, actual pesticide loading is probably decreasing over time due to degradation and weathering of historic deposits in agricultural soils (Mischke et al., 1985; Spencer et al., 1996) and stream sediment (Pereira et al., 1996), as well as from reductions in sediment loads from the Central Valley (McKee et al., 2002). Therefore, it is reasonable to expect, as a first approximation, that the magnitudes of actual pesticide loading are between zero and the upper bounds estimated by the model.

Figure 4. Model forecast of ΣDDT mass in the Bay with varying pesticide loading.
Model results are based on input values for p,p'-DDE and p,p'-DDD. Initial model conditions at time zero represent the current estimated mass of ΣDDT in the water column and active sediment layer.
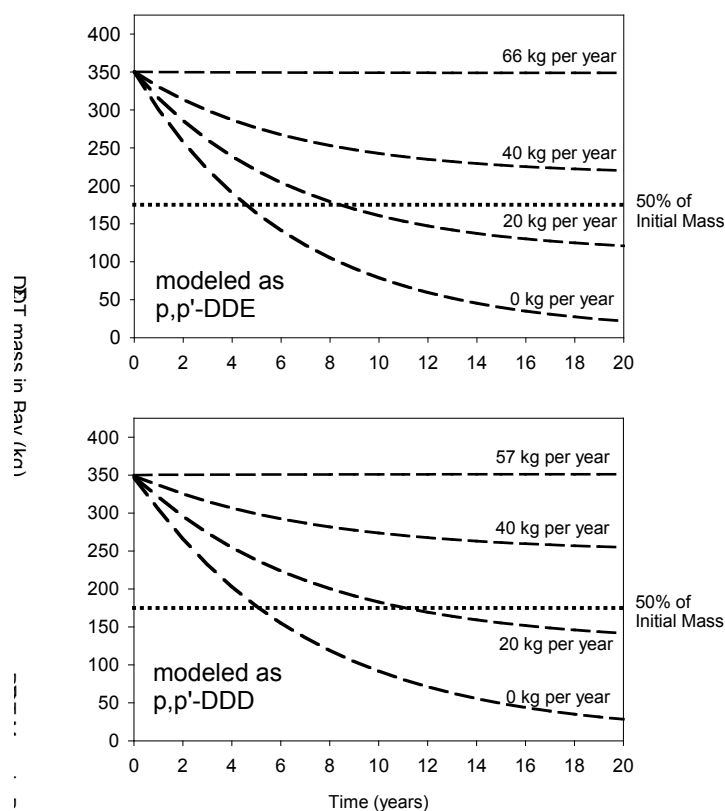
Figure 5. Model forecast of Σchlordane mass in the Bay with varying pesticide loading. Model results are based on input values for alpha- and gamma-chlordane and trans-nonachlor. Initial model conditions at time zero represent the current estimated mass of Σchlordane in the water column and active sediment layer.
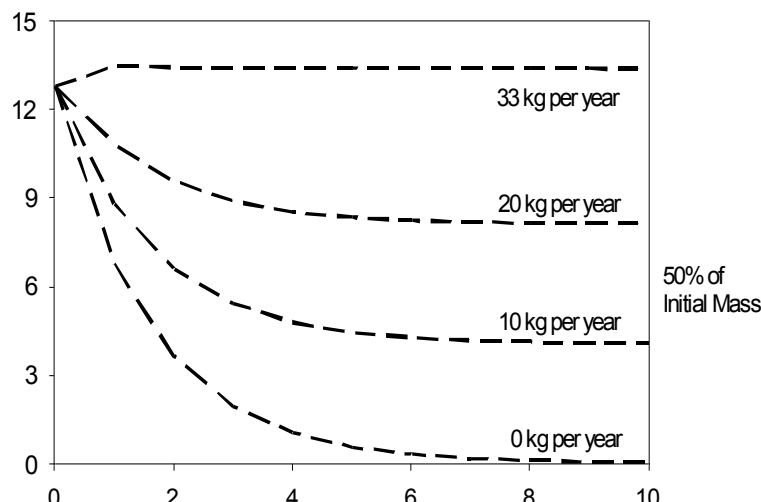
Figure 6. Model forecast of dieldrin mass in the Bay with varying pesticide loading.
Initial model conditions at time zero represent the current estimated mass of dieldrin in the water column and active sediment layer.

Important loss pathways

Model forecasts helped elucidate the importance of the various removal pathways incorporated into the model as specified rate constants. As previously noted, removal pathways in the model include degradation in water and sediment, outflow through the Golden Gate, volatilization, and burial, which was parameterized as being equal to zero on a Bay-wide basis. Model results were evaluated under conditions of no loading for decadal time scales to assess the importance of each major pathway of removal on individual compounds of DDT (Figure 7), chlordane (Figure 8), and dieldrin (Figure 9).

Model forecasts with no continued pesticide loading indicate that degradation in sediment is an important pathway of removal of all pesticides. According to model results, a ten-year forecast with no continued loading showed a reduction of approximately 30 to 40% of the mass of ΣDDT and dieldrin in the Bay due to degradation in sediment. Approximately 60 to 70% of the Σchlordane mass would be removed by degradation over the same time period.

Outflow and volatilization were also important loss pathways for all pesticides, except for heptachlor. The o,p'-isomers of DDT, DDD, and DDE were influenced to a greater extent by volatilization than the p,p'-isomers because of their lower K_{OW}, which enhanced their association with the water column and their accessibility for volatilization. Volatilization of cis- and trans-nonachlor was also more important than for other chlordane components due to lower K_{OW} (and higher H for trans-nonachlor). Heptachlor and heptachlor epoxide were the only compounds that degraded in water to a large extent.

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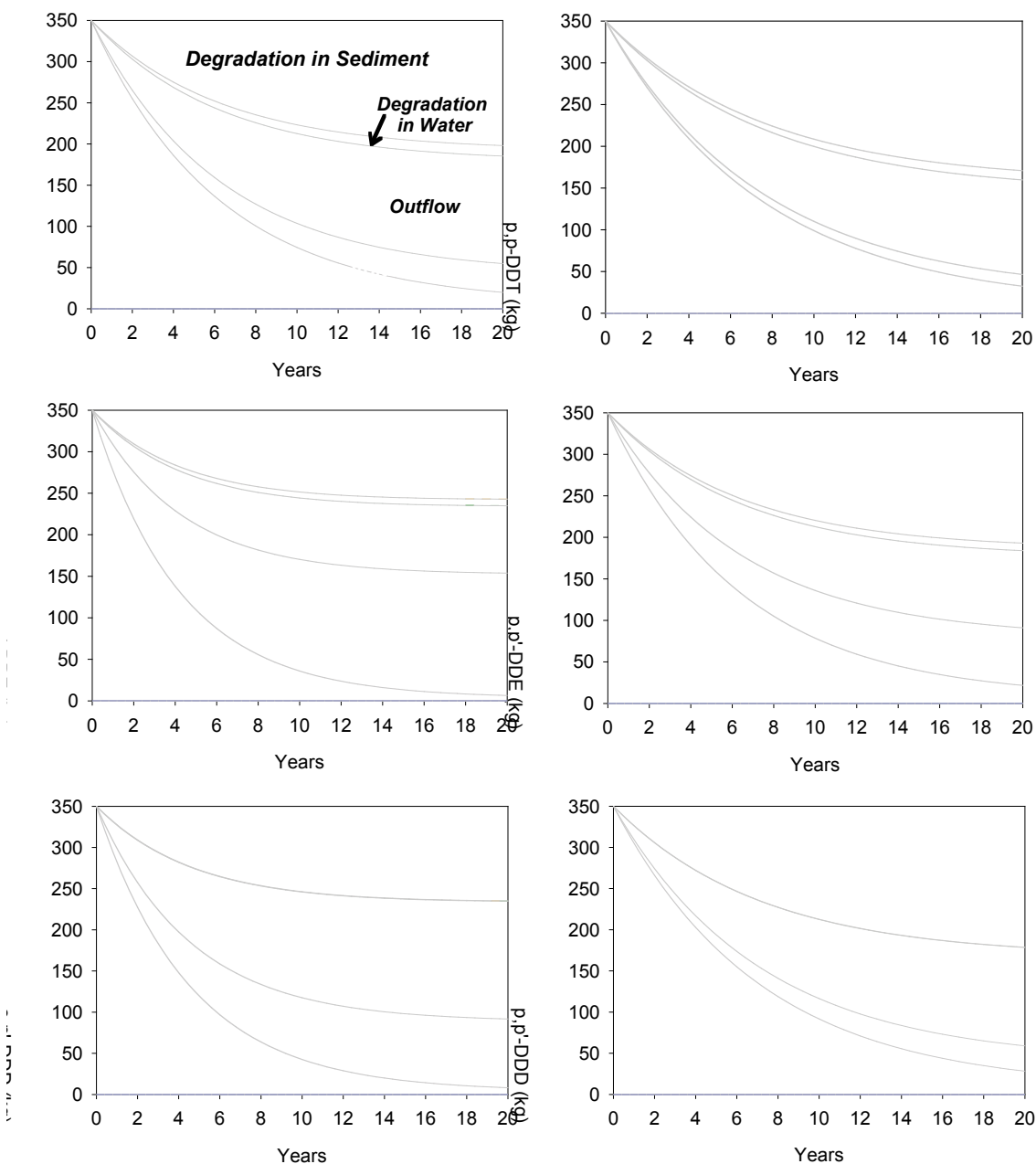
Figure 7. Model forecast of ΣDDT mass removed from the Bay through different pathways for DDT compounds with no pesticide loading. Initial model conditions at time zero represent the current estimated mass of ΣDDT in the water column and active sediment layer.
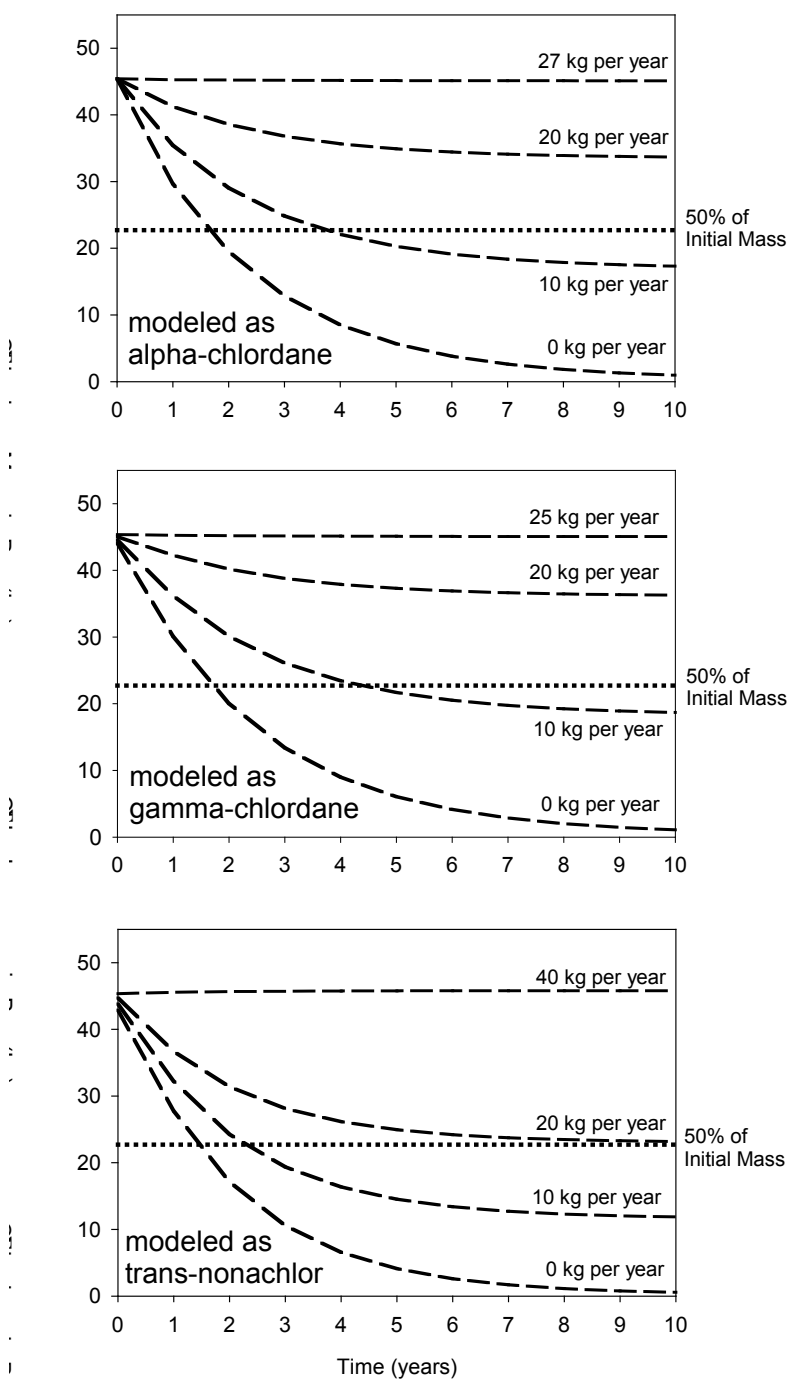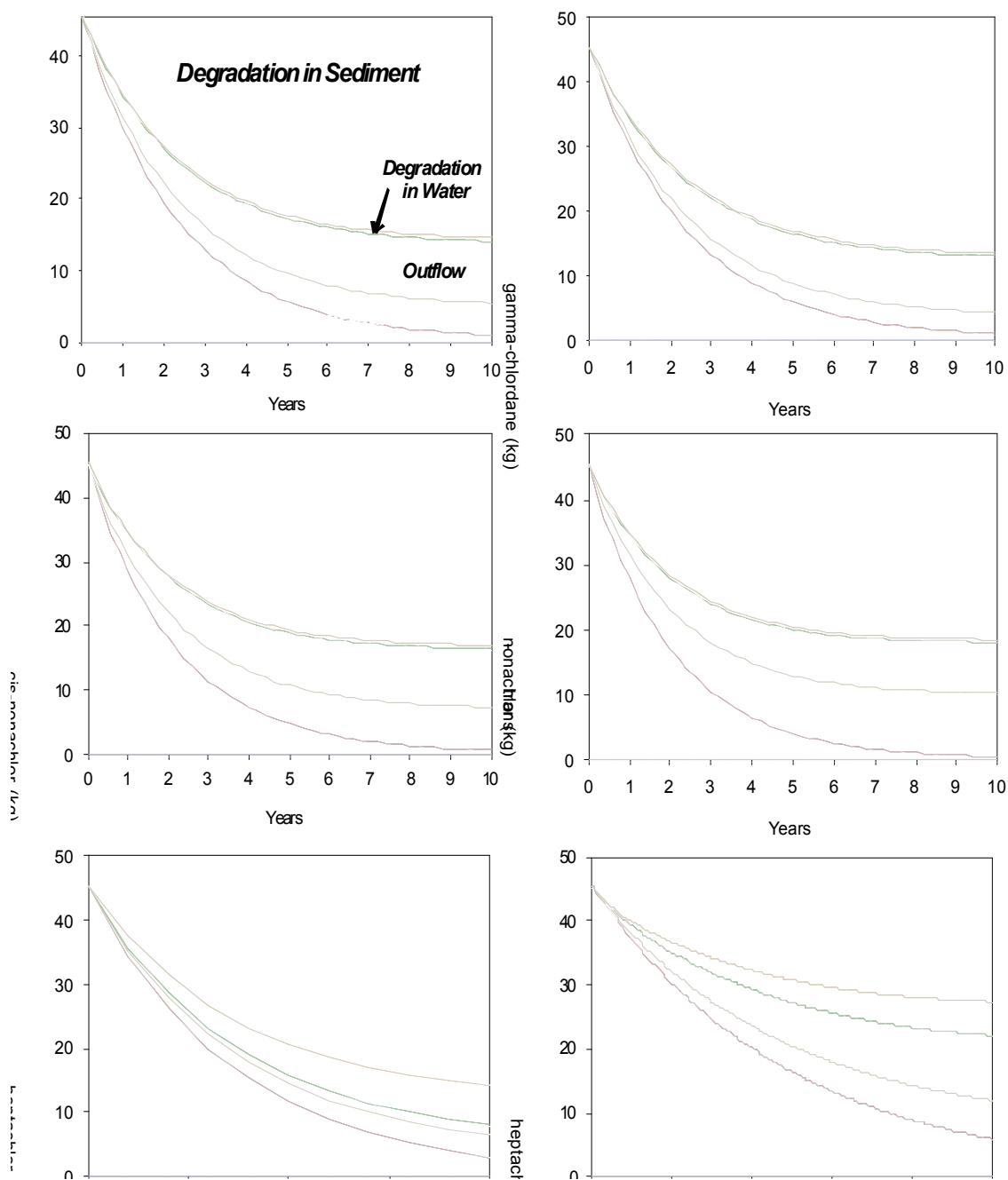
**Figure 8. Model forecast of Σchlordane mass removed from the Bay through
different pathways for chlordane compounds with no pesticide loading.**
Initial model conditions at time zero represent the current estimated mass of
Σchlordane in the water column and active sediment layer.
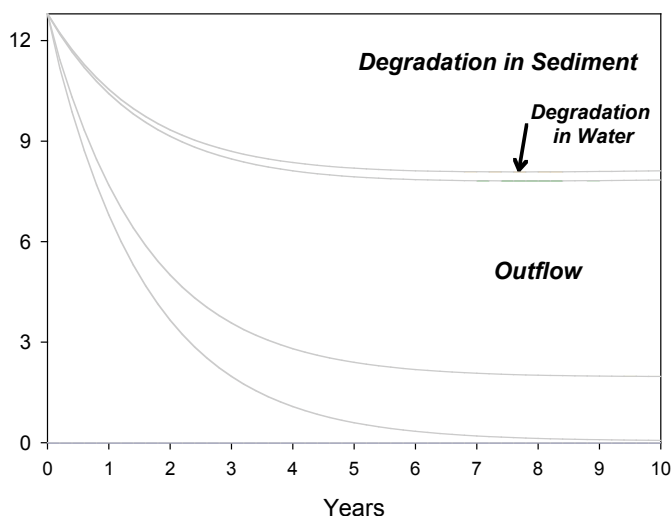
Figure 9. Model forecast of dieldrin mass removed from the Bay through different pathways with no pesticide loading. Initial model conditions at time zero represent the current estimated mass of dieldrin in the water column and active sediment layer.

## Sensitivity analysis

The sensitivity of model outcome to variation in input parameter values was evaluated using local sensitivity analyses performed using two methods. The first method employed approximate partial differences to assess the sensitivity (Δ) of pesticide concentrations in water (C_w) and sediment (C_S) to incremental changes in input parameter values (I) using the following equations:

$$\Delta_S = (\Delta C_S/C_S)/(\Delta I/I) \tag{6}$$

$$\Delta_w = (\Delta C_w/C_w)/(\Delta I/I) \tag{7}$$

Individual input parameters were varied by 0.1% ($\Delta I/I = 0.001$) to evaluate changes in pesticide concentrations in each compartment to small changes in input values. Increasing each parameter by equal proportions helps determine which parameters have the greatest inherent influence on model sensitivity; however, this method does not take into account the sensitivity associated with variability in parameter value estimates.

A second method was used to evaluate model sensitivity to variability in input parameter estimates by varying one parameter at a time over the range of values obtained from the literature and assessing the change in overall pesticide mass in the Bay over time. For both sensitivity analysis methods, physical and chemical parameter values were varied under the conditions of no external loading for 5 years for DDT and 3 years for chlordane and dieldrin. In addition, the second method evaluated model sensitivity under

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the condition of external loading of 10 kg yr^{-1} for 20 years for all pesticide types. It is important to note that a load of 10 kg yr^{-1} was selected for the continuous loading scenarios to represent a magnitude of loading for each pesticide that is reasonable to expect from various loading pathways (Conner et al., 2004). Results of these analyses indicate the difference in percentage of pesticide mass removed in response to the range of input parameter values for p,p'-DDE, alpha-chlordane, and dieldrin.

Based on approximate partial differences, forecasted pesticide concentrations in water and sediment were most influenced by input parameters associated with the active sediment layer (Table 6). For all pesticides, the top four influential parameters were initial pesticide concentration in sediment, degradation rate in sediment (k_{SR}), depth of the active sediment layer, and concentration of solids in sediment (C_{SS}). The ratio of the relative changes in forecasted concentrations to relative changes in input values for these parameters exceeded an absolute value of 0.32. Other parameters that were determined to be highly influential on model sensitivity were directly related to processes that cause partitioning of pesticides into suspended solids and settling out of the water column. These parameters include K_{OW}, density (d_{PW}) and organic carbon content (OC_{PW}) of suspended solids, and solids settling rate (v_{SS}).

Sensitivity analyses based on parameter variability support the results of the methods of approximate partial differences by highlighting the influence of initial pesticide concentrations in sediment, degradation rates and active sediment layer depth on mass removed from the Bay under various conditions (Table 6). For example, the model estimates that in response to no continued loading, only 46% of p,p'-DDE mass would be removed over a 5-year period with an active sediment layer depth of 25 cm compared to 77% removed with a depth of 5 cm. Several important pathways of pesticide removal from the Bay, such as outflow, volatilization, and burial, are independent of the size of the active sediment layer. Therefore, increasing the sediment depth increases the initial mass of pesticides in the sediment and decreases the proportions of pesticides removed from the Bay. As with the first method, other influential parameters were K_{OW} and organic carbon content of suspended solids. It is important to note that increasing the sediment burial mass transfer coefficient from zero to 1.1×10^{-5} m/d had only a slight impact (<5%) on model outcome in the short-term analyses.

In summary, given that the pesticides included in this study are sparingly soluble in the water column and have high affinity for organic material associated with sediment, their rates of removal rely heavily on characteristics of the sediment. Several key parameters had both high influence on model sensitivity and high variability in estimated values. The influence of initial concentrations of pesticide in sediment reflects an important limitation of using single average concentrations to represent the truly heterogeneous concentrations of pesticides measured in water and sediment throughout the Bay. Similarly, treatment of the active sediment layer as a compartment of uniform depth presents another limitation that requires further investigation. Accordingly, future modeling efforts aimed at improving our understanding of pesticide fate require more accurate estimation of input parameters describing processes and properties of the bottom sediment of the Bay.

Table 6. Sensitivity analysis results. Results are given for the ten most influential parameters based on the sediment sensitivity factor. Sensitivity factors represent percent change in pesticide concentrations in water and sediment relative to the percent change in input values in response to no pesticide loading for 5 years for DDT and 3 years for chlordane and dieldrin. Results also indicate the percentage of initial total pesticide mass removed in response to (1) no loading of DDT for 5 years and of chlordane and dieldrin for 3 years and (2) loading of 10 kg per year for 20 years for all pesticides. The sensitivity analysis was performed using lower-bound (low), upper-bound (high), and best estimates of parameter values.

Parameter	Sensitivity Factor for Water	Sensitivity Factor for Sediment	Sensitivity Range			No loading for 5 yrs for DDT and 3 yrs for chlordane and dieldrin (% initial mass lost)			Loading of 10 kg per year for 20 years (% initial mass lost)		
	w	s	Low	Best	High	Low	Best	High	Low	Best	High
DDT											
Concentration in sediment (ng/g)	0.95	0.97	0.42	4.2	44.2	46	53	54	-50	80	94
Degradation rate in sediment (/d)	-0.37	-0.38	1.2×10^{-4}	2.1×10^{-4}	6.9×10^{-3}	45	53	100	72	80	99
Depth of active sediment layer (m)	0.36	0.37	0.05	0.15	0.25	77	53	46	75	80	80
Concentration of solids in sediment (kg/L)	0.36	0.37	0.4	0.5	0.8	57	53	46	79	80	80
log Kow	0.06	0.17	5.3	6.2	7.0	77	53	45	95	80	71
Density of suspended solids (kg/L)	-0.06	-0.17	0.7	1.1	1.5	50	53	56	76	80	82
Organic carbon content of suspended solids	0.06	0.17	0.01	0.03	0.05	65	53	50	89	80	76
Solids settling rate (m/d)	0.10	-0.07	0.4	1	10	49	53	57	80	80	79
Air-side mass transfer coefficient (m/d)	-0.11	-0.07	396	404	408	53	53	53	80	80	80
Henry's Law Constant (Pa-m^3/mol)	-0.11	-0.07	0.3	4.1	4.8	47	53	54	73	80	80
Chlordane											
Concentration in sediment (ng/g)	0.93	0.97	0.054	0.54	5.4	69	72	72	-217	63	96
Degradation rate in sediment (/d)	-0.86	-0.90	2.0×10^{-4}	8.3×10^{-4}	6.9×10^{-3}	44	72	100	19	63	94
Depth of active sediment layer (m)	0.32	0.34	0.05	0.15	0.25	86	72	67	31	63	75
Concentration of solids in sediment (kg/L)	0.32	0.34	0.4	0.5	0.8	74	72	68	57	63	74
log Kow	-0.01	0.14	4.5	6.0	6.2	89	72	70	96	63	59
Density of suspended solids (kg/L)	0.01	-0.14	0.7	1.1	1.5	70	72	73	59	63	66
Organic carbon content of suspended solids	-0.01	0.14	0.01	0.03	0.05	77	72	70	76	63	58
Solids settling rate (m/d)	0.16	-0.10	0.4	1	10	69	72	75	72	63	54
Air-side mass transfer coefficient (m/d)	-0.10	-0.05	384	394	404	72	72	72	63	63	63
Henry's Law Constant (Pa-m^3/mol)	-0.10	-0.05	0.9	3.6	50	70	72	74	58	63	68
Dieldrin											
Depth of active sediment layer (m)	0.97	1.08	0.05	0.15	0.25	98	85	76	53	68	75
Concentration of solids in sediment (kg/L)	0.96	1.07	0.4	0.5	0.8	88	85	77	65	68	75
Concentration in sediment (ng/g)	0.88	0.98	0.015	0.15	1.5	85	85	84	-146	68	97
Degradation rate in sediment (/d)	-0.66	-0.74	2.7×10^{-4}	6.9×10^{4}	6.9×10^{-3}	76	85	100	59	68	91
Solids settling rate (m/d)	-0.06	-0.66	0.4	1	10	76	85	97	78	68	53
log Kow	0.04	0.41	2.6	4.6	6.2	100	85	64	96	68	-75
Density of suspended solids (kg/L)	-0.03	-0.25	0.7	1.1	1.5	83	85	86	56	68	75
Organic carbon content of suspended solids	0.03	0.25	0.01	0.03	0.05	87	85	82	85	68	54
Density of sediment solids (kg/L)	-0.01	-0.16	1.5	2.7	3.5	83	85	85	67	68	69
Organic carbon content of bottom sediment	0.01	0.16	0.005	0.01	0.02	87	85	83	70	68	67

MODEL RESULTS IN THE CONTEXT OF EXISTING DATA

Model results are most informative when evaluated in the context of estimates of pesticide loading to the Bay and actual data on trends in pesticide concentration (or mass). Comparisons of model results to observed trends in contamination provide general understanding of the implications of continued pesticide loading on future trends. As previously noted, the potential effects of exposure of humans and wildlife to OC pesticides in fish has been a primary concern for these chemicals and contributed to the current consumption advisories for fish caught in San Francisco Bay (OEHHA, 1994). Model results also assist in making hypotheses about realistic time scales of recovery in the Bay and subsequent reductions in pesticide concentrations in Bay fish.

Loading estimates

Using the model as a tool to develop reasonable hypotheses about time scales of water quality recovery with respect to pesticide contamination requires an assessment of pesticide loading from major pathways: atmospheric deposition, wastewater effluent, erosion of buried contaminated sediment, agricultural and urban runoff from local watersheds, and inputs from the Central Valley. Conner et al. (2004) summarized the existing state of knowledge on pesticide emissions to the Bay to approximate best estimates and probable ranges of annual pesticide loading. Based on estimates by Conner et al. (2004), best estimate loads (and ranges) are 60 kg (10-250 kg) of ΣDDT, 30 (10-170 kg) of Σchlordane, and 10 kg (3-30 kg) of dieldrin. The order-of-magnitude range in estimated loads exemplifies the difficulty in deriving accurate estimates of annual pesticide loading due to significant spatial and temporal variability in pesticide distribution and transport. Uncertainties in loading estimates are driven primarily by the great uncertainty in pesticide loads from the local watersheds surrounding the Bay.

Compared to model forecasts in Figures 4 and 5, the best estimate loads of ΣDDT and Σchlordane are of similar magnitude to the modeled loads that would sustain the mass of these pesticides at steady state. With respect to dieldrin, the best estimate loads are approximately one-third of the steady-state modeled load (Figure 6). This general agreement between estimated loads and the range of forecasted model loads suggests that the model presents plausible scenarios of how the Bay responds to continued inputs of OC pesticides. As a result, the model forecasts lend themselves to the hypothesis that the mass of ΣDDT and Σchlordane will remain elevated if currently estimated loads are sustained over the long term, while dieldrin mass will decline more readily; however, the use of loading estimates to accurately predict whether pesticide mass in the Bay is changing (*i.e.*, decreasing or increasing) or staying constant would require a much greater degree of accuracy in the model and estimated loads than is currently available.

Trends in bivalve contamination

Pesticide concentration data collected through routine monitoring of the Bay enables an evaluation of current temporal trends in contamination that further assists in interpreting model results and understanding the implications of continued OC pesticide

loading. One of the best records of decadal and annual trends in pesticide concentrations in the Bay has been compiled from long-term continuous monitoring of transplanted bivalves. From 1979 to 1993, the State Mussel Watch (SMW) Program monitored bivalves at several locations in the Bay (Stephenson *et al.*, 1995). In 1993, the RMP began monitoring at several locations in close proximity to SMW stations to extend the long-term record of contaminant concentrations in bivalves (SFEI, 2002). Data from the two studies are not strictly comparable due to different participating laboratories and inconsistencies in seasonal collection times; however, the data are valuable for evaluating large-scale changes in concentrations during the last two decades.

Bivalve data collected at Pinole Point and Yerba Buena Island (previously called Treasure Island in the SMW study) provided the most complete record of decreasing trends in OC pesticide concentrations from 1980 to 2001 (Gunther *et al.*, 1999; SFEI, 2003). Gunther *et al.* (1999) determined that concentrations of p,p'-DDE, alpha-chlordane, and dieldrin significantly decreased at Yerba Buena Island from 1980 to 1996. Although sharp decreases occurred over that period, concentrations were relatively constant since the early to mid-1990s (Gunther *et al.*, 1999). One potential reason for less apparent trends in pesticide concentrations in bivalves is that the concentrations in the Bay are being controlled by two major sources: internal sources of stored pesticides within Bay sediment and external sources that provide continued inputs.

For comparison to model results, decadal rates of decline in bivalve pesticide concentrations were evaluated (Figure 10). Annual average concentrations of p,p'-DDE, alpha-chlordane, and dieldrin in mussels (*Mytilus californianus*) were calculated from pooled data collected from seven SMW/RMP stations: Pinole Point, Richmond Bridge, Fort Baker/Horseshoe Bay, Treasure Island/Yerba Buena Island, Hunters Point/Alameda, Redwood Creek, and Dumbarton Bridge. Fitting the bivalve trends to first-order decay curves yielded apparent removal rates of 0.053 yr^{-1}, 0.11 yr^{-1}, and 0.065 yr^{-1} for p,p'-DDE, alpha-chlordane, and dieldrin respectively. Corresponding apparent half-lives are approximately 13 yrs, 6.3 yrs, and 8.4 yrs, respectively. These apparent half-lives are longer than the steady-state half-lives determined by the model in Table 5. Although there are numerous complexities in relating pesticide concentrations in water and sediment to concentrations in biota, the longer apparent half-lives estimated using bivalve data contribute to the hypothesis that the observed decadal trends are a result of the combined influences of continued inputs and a dampened response by internal recycling of pesticides within the Bay.

This highlights the uncertainties associated with our current ability to use the model to predict whether pesticide contamination is at steady state or continues to decrease and identify causes of observed trends. The regional model of the Bay is incapable of discerning between the effects of internal cycling and continued external inputs on pesticide contamination in various media within the Bay. Furthermore, current trends in contamination are not readily apparent. Accordingly, a more spatially and temporally explicit model of the Bay, combined with future monitoring of potential trends, is required to accurately relate model forecasts to actual trends in pesticide contamination in water, sediment, and biota in the Bay.
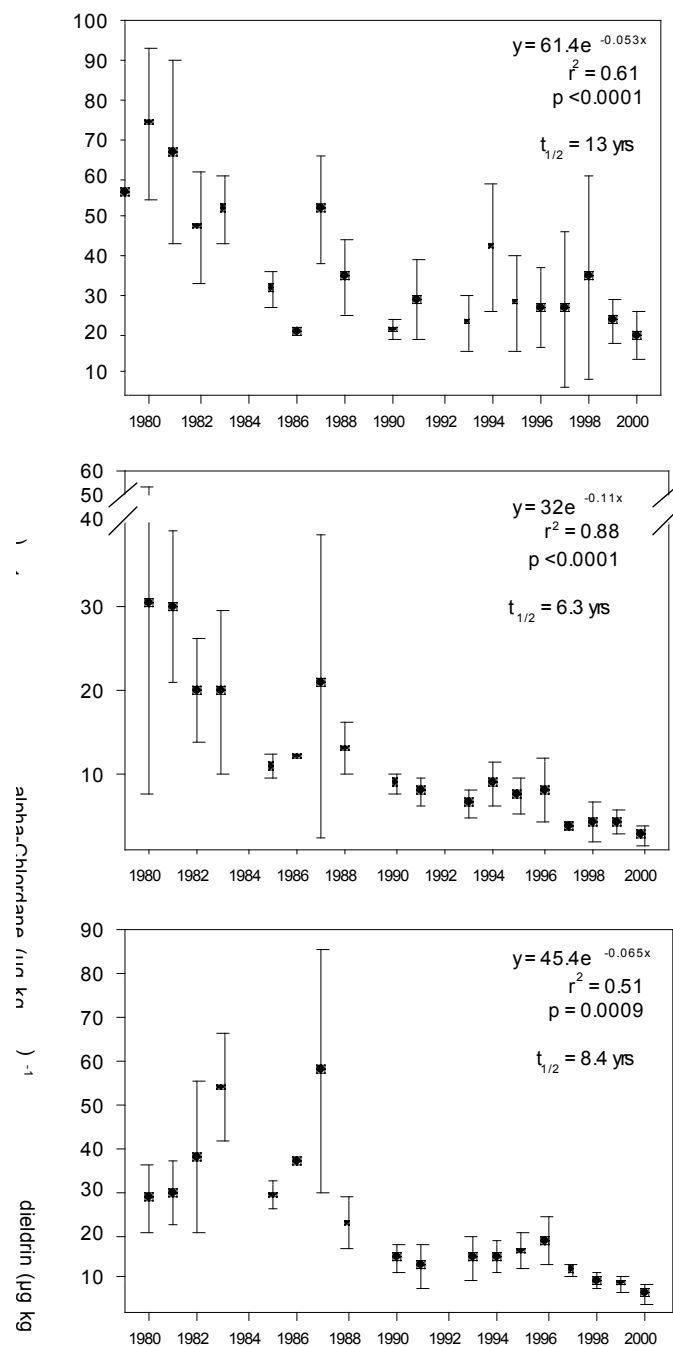
Figure 10. Pesticide concentrations in transplanted bivalves from 1979 to 2000. Bivalve data were averaged on an annual basis. Data from 1979 to 1993 are from the State Mussel Watch Program (SMW). Data from 1993 to 2000 are from the Regional Monitoring Program for Trace Substances (RMP).

Concentrations in fish

Human health concerns associated with exposure to bioaccumulative contaminants in sport fish caught in the Bay has led to routine monitoring of fish by the RMP on a triennial basis (i.e., sampling in 1994, 1997, 2000, and 2003) to assess the extent to which concentrations in fish exceed screening values developed to protect human health (Fairey *et al.*, 1997; Davis *et al.*, 2002; Greenfield *et al.*, 2002). Data collected in 2000 showed that median concentrations of all pesticides in individual species were below screening values (Greenfield *et al.*, 2002). The maximum concentration of ΣDDT in white croaker was only 13% above the screening value, while the maximum concentration of dieldrin was approximately 2.2 times greater than the screening value (Greenfield *et al.*, 2002). ΣChlordane concentrations in all samples were below the screening value of 30 ng g^{-1} in 2000.

Recent fish monitoring by the RMP provides goals for reduction in pesticide contamination in the Bay. A first approximation is that pesticide concentrations in Bay fish are linearly correlated to the mass of pesticides in the Bay; therefore, an approximate 50% reduction would be sufficient to reduce concentrations in the most contaminated fish to below the screening values. A food web PCB model was developed that established a quantitative linkage between persistent contaminant concentrations (and mass) in Bay sediments to concentrations in fish (Gobas and Wilcockson, 2002). Food web modeling for OC pesticides would enhance predictions of concentrations in fish and establish more accurate goals for contaminant reduction efforts.

IV.   CONCLUSIONS

This study represents an initial attempt to model the long-term fate of OC pesticide fate in San Francisco Bay and understand the key processes that facilitate reduction of pesticides in the ecosystem. The model was used to: (1) summarize the current state of knowledge of OC pesticides in San Francisco Bay, (2) estimate the response of the Bay to varying magnitudes of loading, (3) estimate upper bounds on current pesticide loading to the Bay, and (4) identify important characteristics, processes, and pathways of removal that require further investigation and evaluation for improving our modeling capability. Although there are considerable uncertainties associated with applying the regional model to the Bay, it is a valuable tool for environmental scientists and managers to use in understanding major processes affecting the fate of pesticides and the time scales of recovery in the Bay.

The primary value of this modeling exercise has been in evaluating the overall persistence of individual pesticides and implications of future pesticide loading on time scales of recovery of the Bay. The model estimated that if all future pesticide loading were eliminated, the mass of OC pesticides in the Bay would be mostly removed within one to two decades. In contrast, continued loading scenarios resulted in forecasts of long-term steady-state condition where the total mass of pesticides in the Bay would never fall below a certain level. The extent to which pesticide mass in the Bay continues to decline

or approaches a steady state condition is ultimately dependent on the extent to which rates of pesticide inputs (i.e., loads) equal rates of output (i.e., degradation and advection).

Monitoring data suggest that past decreases in pesticide loading led to subsequent declines in concentrations in biota; however, more recent trends are less apparent. Thus, the question remains as to whether reductions in loading and contamination are still occurring and what effect does internal cycling of pesticides have on dampened trends in recent years. Answering these questions is especially important with respect to using a multimedia model to accurately predict the long-term fate of pesticides based on recent trends in contamination. Furthermore, a more spatially and temporally explicit modeling approach is needed to make proper management decisions between source reduction efforts aimed at internal and/or external sources and allowing for natural attenuation of pesticide contamination in the Bay.

V.   LITERATURE CITED

Anderson, B.S., J.W. Hunt, B.M. Phillips, M. Stoelting, J. Becker, R. Fairey, H.M. Puckett, M Stephenson, R.S. Tjeerdema, and M. Martin. 2000. Ecotoxicological change at a remediated Superfund site in San Francisco, California, USA. Environmental Toxicology and Chemistry. 19 (4). pp. 879-887.

Arnold, S. F., D.M. Klotz, B.M. Collins, P.M. Vonier, L.J. Guillette, Jr., and J.A. McLachlan. 1996. Synergistic activation of estrogen receptor with combinations of environmental chemicals. Science 272, 1489-1492.

Bennett, D.H., W.E. Kastenberg, and T.E. McKone. 1999. General formulation of characteristic time for persistent chemicals in a multimedia environment. Environmental Science and Technology. 33 (3): 503-509.

Bergamaschi, B.A., K.M. Kuivila, and M.S. Fram. 2001. Pesticides associated with suspended sediments entering San Francisco Bay following the first major storm of water year 1996. Estuaries. 24 (3). pp. 368-380.

Bernstein, B. and J. O'Connor. 1997. Five-Year Program Review: Regional Monitoring Program for Trace Substances in the San Francisco Estuary. RMP Contribution #28. San Francisco Estuary Institute. Richmond, CA.

Callahan, M.A., M.W. Slimak, N.W. Gabel, I.P. May, C.F. Fowler, J.R. Freed, P. Jennings, R.L. Durfee, F.C. Whitmore, B. Maestri, W.R. Mabey, B.R. Holt and C. Gould. 1979. Water-related environmental fate of 129 priority pollutants. Vol. 1. EPA-440/4-79-029a. National Technical Information Service, Springfield, VA. pp. 17-1 to 17-11.

Cappiella, K., C. Malzone, R.E. Smith, and B.E. Jaffe. 1999. Historical Bathymetric Change in Suisun Bay: 1867-1990. U.S. Geological Survey, Open-File Report 99-563. Menlo Park, CA.

Davis, J.A., L.J. McKee, J.E. Leatherbarrow, and T.H. Daum. 2000. Contaminant loads from stormwater to coastal waters in the San Francisco Bay region: Comparison to other pathways and recommended approach for future evaluation. San Francisco Estuary Institute. Richmond, CA.

Davis, J.A., M.D. May, B.K. Greenfield, R. Fairey, C. Roberts, G. Ichikawa, M.S. Stoelting, J.S. Becker, and R.S. Tjeerdema. 2002. Contaminant concentrations in sport fish from San Francisco Bay, 1997. Marine Pollution Bulletin. 44. pp. 1117-1129.

Davis, J.A. 2004. The long term fate of PCBs in San Francisco Bay. Environmental Toxicology and Chemistry. 23 (10): 2396-2409.

Davis, J.A. and J.J. Oram. 2005. Comment on "The long-term fate of polychlorinated biphenyls in San Francisco Bay (USA)." Letter to the Editor. Environmental Toxicology and Chemistry. 24 (10): 2397-2400.

Dearth, M.A. and R.M. Hites. 1991. Complete analysis of technical chlordane using negative ionization mass spectrometry. Environmental Science and Technology. 25 (2). pp. 245-254.

Fairey, R., K. Taberski, S. Lamerdin, E. Johnson, R.P. Clark, J.W. Downing, J. Newman, and M. Petreas. 1997. Organochlorines and other environmental contaminants in muscle tissues of sportfish collected from San Francisco Bay. Marine Pollution Bulletin. 34 (12): 1058-1071.

Flegal, A.R., R.W. Risebrough, B.A. Anderson, J. Hunt, S. Anderson, J. Oliver, M. Stephensen, and R. Packard. 1994. San Francisco Estuary Regional Monitoring Program: sediment studies. Submitted to San Francisco Bay Regional Water Quality Control Board.

Foxgrover, A.C., S.A. Higgins, M.K. Ingraca, B.E. Jaffe, and R.E. Smith. 2004. Deposition, Erosion, and Bathymetric Change in South San Francisco Bay: 1858-1983. U.S. Geological Survey, Open-File Report 2004-1192. Santa Cruz, CA.

Gilliom, R.J. and D.G. Clifton. 1990. Organochlorine pesticide residues in bed sediments of the San Joaquin River, California. Water Resources Bulletin. American Water Resources Association. 26 (1). pp. 11-24.

Gobas, F.A.P.C., M. N. Z'graggen, and X. Zhang. 1995. Time response of the Lake Ontario ecosystem to virtual elimination of PCBs. Environmental Science and Technology. 29. pp. 2038-2046.

Gobas, F.A.P.C and J. Wilcockson, 2002. San Francisco Bay PCB food-web model. Prepared for the Regional Monitoring Program for Trace Substances.

Greenfield, B.K. and J.A. Davis. 2005. A PAH fate model for San Francisco Bay. Chemosphere. 60 (4): 515-530.

Greenfield, B.K, J. A. Davis, R. Fairey, C. Roberts, D. Crane, G. Ichikawa, M. Petreas, and H. Lee. 2002. Contaminant concentrations in fish from San Francisco Bay, 2000. San Francisco Estuary Institute. Oakland, CA.

Gunther, A.J., J.A. Davis, D.D. Hardin, J. Gold, D. Bell, J.R. Crick, G.M Scelfo, J. Sericano, and M. Stephenson. 1999. Long-term bioaccumulation monitoring with transplanted bivalves in the San Francisco Estuary. Marine Pollution Bulletin. 38 (3): 170-181.

Helm, P.A., M.L. Diamond, R. Semkin, W.M.J. Strachan, C. Teixeira, and D. Gregor. 2002. A mass balance model describing multiyear fate of organochlorine compounds in a high Arctic lake. Environmental Science and Technology. 36. pp. 996-1003.

Howard, P.H., R.S. Boethling, W.F. Jarvis, W.M. Meylan, and E.M. Michalenko. 1991. Handbook of Environmental Degradation Rates. Ed. Heather Taub Printup. Lewis Publishers. Chelsea, MI.

Hunt, J.W., B.S. Anderson, B.M. Phillips, J. Newman, R.S. Tjeerdema, K. Taberski, C.J. Wilson, M. Stephenson, H.M. Puckett, R. Fairey, and J. Oakden. 1998. Bay Protection and Toxic Cleanup Program Final Technical Report: Sediment quality and biological effects in San Francisco Bay. California State Water Resources Control Board. Sacramento, CA.

Jaffe, B.E., R.E. Smith, and L. Torresan. 1998. Sedimentation and bathymetric change in San Pablo Bay, 1856-1983: U.S. Geological Survey, Open-File Report 98-759. Menlo Park, CA.

KLI. 2002. Joint stormwater agency project to study urban sources of mercury, PCBs, and organochlorine pesticides. Report prepared by Kinnetic Laboratories, Inc. for Santa Clara Valley Urban Runoff Pollution Prevention Program, Contra Costa Clean Water Program, San Mateo Countywide Stormwater Pollution Prevention Program, Marin County Stormwater Pollution Prevention Program, Vallejo Flood Control and Sanitation District, Fairfield-Suisun Sewer District. 71pp.

Law, L.M. and D.F Goerlitz. 1974. Selected chlorinated hydrocarbons in bottom material from streams tributary to San Francisco Bay. Pesticides Monitoring Journal. 8(1):PAGES

Leatherbarrow, J.E., R. Hoenicke, and L.J. McKee. 2002. Results of the Estuary Interface Pilot Study, 1996-1999. RMP Technical Report. San Francisco Estuary Regional Monitoring Program. SFEI Contribution 50. San Francisco Estuary Institute. Oakland, CA. Available online at :http://www.sfei.org/rmp/reports/eip/EIP_FINAL.pdf

Leatherbarrow, J.E., L.J. McKee, D.H. Schoellhamer, N.K. Ganju, and A.R. Flegal. 2005. Concentrations and loads of organic contaminants and mercury associated with suspended sediment discharged to San Francisco Bay from the Sacramento-San Joaquin River Delta, California. RMP Technical Report. San Francisco Estuary Regional Monitoring Program. SFEI Contribution 405. San Francisco Estuary Institute. Oakland, CA. Available online at: http://www.sfei.org/rmp/Technical_Reports/MallardIslandReport_2002_03.pdf

Mackay, D., S. Sang, P. Vlahos, M. Diamond, F. Gobas, and D. Dolan. 1994. A rate constant model of chemical dynamics in a lake ecosystem: PCBs in Lake Ontario. J. Great Lakes Res. 20 (4): 625-642.

Mackay, D., W. Shiu, and K. Ma. 1997. Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals. Volume V: Pesticide chemicals. Lewis Publishers. Boca Raton, FL.

MacLeod, M. and T.E. McKone. 2004. Multimedia persistence as an indicator of potential for population-level intake of environmental contaminants. Environmental Toxicology and Chemistry. 23 (10): 2465-2472.

McKee, L.J., N. Ganju, D. Schoellhamer, D. Yee, J.A. Davis, J.E. Leatherbarrow, and R. Hoenicke. 2002. Estimates of suspended-sediment flux entering San Francisco Bay from the Sacramento and San Joaquin Delta. RMP Technical Report. San Francisco Estuary Regional Monitoring Program. SFEI Contribution 65. San Francisco Estuary Institute. Oakland, CA. Available online at http://www.sfei.org/rmp/reports/Sediment_loads_report.pdf

McKee, L.J., J.E. Leatherbarrow, and R. Eads. 2004. The concentration and load of PCBs, OC pesticides, and mercury associated with suspended sediments in the lower Guadalupe River, San Jose, California. SFEI Contribution #86. San Francisco Estuary Institute. Oakland, CA.

Mischke, T., K. Brunetti, V. Acosta, D. Weaver, and M. Brown. 1985. Agricultural sources of DDT residues in California's environment. Environmental Hazards Assessment Program. California Department of Food and Agriculture. Sacramento. CA.

Miller, G.C. and R.G. Zepp. 1979. Effects of suspended sediments on photolysis rates of dissolved pollutants. Water Resources, 13, 453 459.

Miller, G.M. and R.G. Zepp. 1983. Extrapolating photolysis rates from the laboratory to the environment. Residue Reviews. 85: 89-110.

OEHHA. 1994. Health advisory on catching and eating fish: interim sport fish advisory for San Francisco Bay. Office of Environmental Health Hazard Assessment. California Environmental Protection Agency. Sacramento. CA. http://www.oehha.org/fish/general/99fish.html

Oliver, B.G., E.G. Cosgrove, and J.H. Carey. 1979. Effect of suspended sediments on the photolysis or organics in water. Environmental Science and Technology. 13 (9): 1075-1077.

Pereira, W.E., F.D. Hostettler, and J.B. Rapp. 1996. Distributions and fate of chlorinated pesticides, biomarkers, and polycyclic aromatic hydrocarbons in sediments along a contamination gradient from a point-source in San Francisco Bay, CA. Marine Environmental Research. 41 (3): 299-314.

Pontolillo, J. and R.P. Eganhouse. 2001. The search for reliable aqueous solubility (SW) and octanol-water partition coefficient (KOW) data for hydrophobic organic compounds: DDT and DDE as a case study. U.S. Geological Survey. Water-Resources Investigations Report 01-4201.

Rechsteiner, Jr., C.E. 1990. Heat of vaporization. In W.J. Lyman, W.F. Reehl, and D.H. Rosenblatt, eds. Handbook of Chemical Property Estimation Methods: Environmental behavior of organic compounds. American Chemical Society. Washington, D.C.

Sato, C. and J.L. Schnoor. 1991. Applications of three completely mixed compartment models to the long-term fate of dieldrin in a reservoir. Water Research. 25 (6): 621- 631.

Soto, A. M., C. Sonnenschein, K.L. Chung, M.F. Fernandez, N. Olea, and F.O. Serrano. 1995. The E-Screen Assay as a tool to identify estrogens: an update on estrogenic environmental pollutants. Environmental Health Perspectives. 103. pp. 113-122.

SFEI. 2002. 2000 RMP Annual Results. San Francisco Estuary Regional Monitoring Program for Trace Substances. San Francisco Estuary Institute. Oakland, CA.

Spencer, W.F., G. Singh, C.D. Taylor, R.A. LeMert, M.M. Cliath, and W.J. Farmer. 1996. DDT persistence and volatility as affected by management practices after 23 years. Journal of Environmental Quality. 25. pp. 815-821.

Stephenson, M.D., M. Martin, and R.S. Tjerdeema. 1995. Long-term trends in DDT, polychlorinated biphenyls, and chlordane in California mussels. Archives of Environmental Contamination and Toxicology. 28 (4): 443-450.

SWRCB. 2003. Revision of the Clean Water Act Section 303(d) list of water quality limited segments. Staff Report: Volume 1. State Water Resources Control Board. Sacramento, CA.

Tucker, W.A. and L.H. Nelken. 1990. Diffusion coefficients in air and water. In W.J. Lyman, W.F. Reehl, and D.H. Rosenblatt, eds. Handbook of Chemical Property Estimation Methods: Environmental behavior of organic compounds. American Chemical Society. Washington, D.C.

USEPA. 1988. Chlordane/heptachlor termiticides: notification of cancellation and amendment of existing stocks determination. Federal Register. 53:11798-l 1805.

USEPA. 1990. Suspended, canceled, and restrict pesticides. United States Environmental Protection Agency, Office of Pesticides and Toxic Substances, and Office of Compliance Monitoring. EPA/20T-1002.

USEPA. 2000. Guidance for assessing chemical contaminant data for use in fish advisories. Volume 1. Fish sampling and analysis. 3rd edition. United States Environmental Protection Agency.

Venkatesan, M.I., R.P. de Leon, A. van Geen, and S.N. Luoma. 1999. Chlorinated hydrocarbon pesticides and polychlorinated biphenyls in sediment cores from San Francisco Bay. Marine Chemistry. 64: 85-97.

Webster, E., D. Mackay, and F. Wania. 1998. Evaluating environmental persistence. Environmental Toxicology and Chemistry. 17 (11): 2148-2158.

WHO. 1989. DDT and its derivatives – environmental aspects. Environmental Health Criteria 83. World Health Organization. Geneva.

Yee, D., J.E Leatherbarrow, and J.A Davis. 2001. South Bay/Fairfield-Suisun Trace Organic Contaminants in Effluent Study. Prepared for the San Jose/Santa Clara Water Pollution Control Plant, Sunnyvale Water Pollution Control Plant, Palo Alto Water Quality Control Plant, and Fairfield-Suisun Sewer District. San Francisco Estuary Institute. Richmond, CA.

Zepp, R.G. and D.M. Cline. 1977. Rates of direct photolysis in aquatic environment. Environmental Science and Technology. 11 (4): 359-366.

Zepp, R.G., N.L. Wolfe, L.V. Azarraga, R.H. Cox, and C.W. Pape. 1977. Photochemical transformation of DDT and methoxychlor degradation products, DDE and DMDE, by sunlight. Archives of Environmental Contamination and Toxicology. 6: 305-314.

Zhang, H., S.J. Eisenreich, T.R. Franz, J.E. Baker, and J.H. Offenberg. 1999. Evidence for increased gaseous PCB fluxes to Lake Michigan from Chicago. Environmental Science and Technology. 33: 2129-2137.

VI.   ACKNOWLEDGMENTS

Appendix Table 1. Input data for converting Henry's Law Constants.

Compound	T_B K	T_C K	ΔH_V at T_B cal mol^{-1}	ΔH_V at T_B kJ mol^{-1}	ΔH_V at 288 K kJ mol^{-1}
DDT[a]	533.15	720.75	22000	92.1	130
DDD[a]	639.90	863.77	17000	71.1	105
DDE[a]	636.44	860.38	15000	62.8	92.2
chlordane	624.24	885.73	14000	58.6	79.0
alpha-chlordane[b]	624.24	885.73	14000	58.6	79.0
gamma-chlordane[b]	624.24	885.73	14000	58.6	79.0
trans-nonachlor[c]	624.24	885.73	15125	63.3	85.3
heptachlor	603.69	846.31	13000	54.4	76.6
heptachlor epoxide	613.96	848.76	16000	67.0	95.7
dieldrin	613.32	842.25	17000	71.1	102

a = values were applied to individual isomers for converting H constants
b = chlordane data were used for these compounds
c = boiling point and critical temperature were applied from chlordane values; Enthalpy from Miller et al., 2001

Appendix Table 2. Temperature converted Henry's Law Constants. Selected data are from listed sources compiled by Mackay et al. (1997).

	Henrys Law Constant reported in study	T (deg C)	Henrys Law Constant corrected for 15	SOURCE
	Pa m3 mol-1	deg C	Pa m3 mol-1	
Chlordane	9.02	20	5.05	Suntio et al., 1988
Chlordane	9.64	25	3.08	Mackay et al., 1986
Chlordane	9.12	25	2.92	Mabey et al., 1982
Chlordane	6.60	23	2.64	Bidleman and McConnell, 1995
Chlordane	4.90	25	1.57	Warner et al., 1987
Chlordane	3.44	25	1.10	Hine and Mookerjee, 1975
alpha-Chlordane	11.2	25	3.58	Iwata et al., 1995
gamma-Chlordane	16.5	25	5.28	Iwata et al., 1995
gamma-Chlordane	8.37	23	3.34	Fendinger et al., 1989
gamma-Chlordane	5.91	23	2.36	Fendinger et al., 1989
gamma-Chlordane	5.41	23	2.16	Fendinger et al., 1989
trans-Nonachlor	49.5	25	14.5	Iwata et al., 1995
trans-Nonachlor	31.4	25	9.20	Miller et al., 2001
Heptachlor	845	25	280	Jury et al. 1990
Heptachlor	233	25	77	Montgomery 1993
Heptachlor	150	25	50	Meylan and Howard 1991
Heptachlor	150	25	50	Warner et al. 1980
Heptachlor	30	25	9.8	Altschuh et al., 1999
Heptachlor	18	25	5.9	Meylan and Howard 1991
Heptachlor Epoxide	395	25	102	Mabey et al. 1982
Heptachlor Epoxide	66	20	33	Majewski and Capel 1995
Heptachlor Epoxide	3.4	25	0.88	Warner et al. 1980
Heptachlor Epoxide	3.3	25	0.84	Montgomery 1993
Heptachlor Epoxide	2.1	25	0.55	Altschuh et al., 1999
p,p'-DDD	9.00	30	0.98	Ballschmitter and Wittlinger, 1991
p,p'-DDD	0.84	25	0.19	Altschuh et al., 1999
DDD	0.64	20	0.30	Suntio et al., 1988
p,p'-DDE	34.00	30	4.81	Ballschmitter and Wittlinger, 1993
p,p'-DDE	7.95	20	4.05	Suntio et al., 1988
p,p'-DDE	4.18	25	1.11	Altschuh et al., 1999
DDE	1.25	10	2.51	McLachlin et al., 1990
DDE	6.89	25	1.83	Mabey et al., 1982
p,p'-DDT	6.00	25	0.94	Ballschmitter and Wittlinger, 1991
p,p'-DDT	2.36	20	0.92	Suntio et al., 1988
p,p'-DDT	1.30	20	0.51	Atkins and Eggleton, 1971
p,p'-DDT	1.20	23	0.27	Bidleman and McConnell, 1995
p,p'-DDT	1.31	25	0.21	Mackay et al., 1986
p,p'-DDT	0.66	25	0.10	Altschuh et al., 1999
DDT	6.02	20	2.35	Thibodeaux, 1979
DDT	5.30	20	2.07	Mackay and Shiu, 1981
DDT	1.33	23	0.30	Fendinger et al., 1989
DDT	1.31	23	0.30	Montgomery, 1993
DDT	1.28	23	0.29	Fendinger et al., 1989
DDT	1.60	25	0.25	Mabey et al., 1982
DDT	0.86	23	0.19	Fendinger et al., 1989
Dieldrin	4.59	20	2.18	Atkins and Eggleton, 1971
Dieldrin	2.94	20	1.40	Slater and Spedding, 1981
Dieldrin	5.90	25	1.36	Warner et al., 1987
Dieldrin	1.12	20	0.53	Suntio et al., 1988
Dieldrin	1.10	20	0.52	Mackay and Shiu, 1981
Dieldrin	1.01	25	0.23	Altschuh et al., 1999
Dieldrin	0.78	25	0.18	Mackay et al., 1986

Appendix Table 3. Octanol-water partition coefficients. Selected data are from listed sources compiled by Mackay et al. (1997).

Pesticide	log Kow	Source
Chlordane	6.21	Kollig, 1993
Chlordane	6.0	Veith and Kosian, 1983
Chlordane	6.0	Travis and Arms, 1988; Thomann, 1989
Chlordane	6.0	Endicott and Richardson, 1989
Chlordane	6.0	Montgomery, 1993; Devillers et al., 1996
Chlordane	5.8	Finizio et al., 1997
Chlordane	5.54	CLOGP, 1986
Chlordane	5.54	Thor, 1989
Chlordane	5.48	Schnoor et al., 1987
Chlordane	5.16	Kenaga 1980a, b
Chlordane	5.08	Sicbaldi and Finizio, 1993
Chlordane	5.08	Finizio et al., 1997
Chlordane	4.75	Finizio et al., 1997
Chlordane	4.3	Ryan et al., 1988
Chlordane	3.3	ATSDR, 1988
Chlordane	2.78	Sanborn et al., 1976
Chlordane	2.78	Schnoor et al., 1987
alpha-Chlordane	5.9	Kawano et al., 1988
alpha-Chlordane	6.0	Isnard and Lambert, 1988
gamma-Chlordane	6.1	Kawano et al., 1988
gamma-Chlordane	6.0	Markwell et al., 1989
cis-Nonachlor	5.7	Nowell et al., 1999
trans-Nonachlor	5.7	Nowell et al., 1999
Oxychlordane	2.6	Nowell et al., 1999
Heptachlor	8.25	Patil, 1994
Heptachlor	5.58	Hansch et al., 1995
Heptachlor	5.53	Kollig, 1993
Heptachlor	5.46	Finizio et al., 1997
Heptachlor	5.44	Veith et al. 1979, Veith and Kosian 1983
Heptachlor	5.34	Noegrohati and Hammers 1992
Heptachlor	5.27	Schuurmann and Klein 1988
Heptachlor	5.24	Finizio et al., 1997
Heptachlor	4.92	Finizio et al., 1997
Heptachlor	4.61	Thor 1989
Heptachlor	3.9	US EPA 1984
Heptachlor	5.44	Isnard and Lambert, 1988
Heptachlor Epoxide	4.43	Briggs, 1981
Heptachlor Epoxide	5.4	Veith et al., 1979
Heptachlor Epoxide	2.65	Mabey et al., 1982
Heptachlor Epoxide	4.56	Noegrohati and Hammers, 1992
Heptachlor Epoxide	3.65	Montgomery, 1993
Heptachlor Epoxide	5.4	Isnard and Lambert, 1988
p,p-DDT	6.06	Finizio et al., 1997
p,p-DDT	5.53	Finizio et al., 1997
p,p-DDT	4.82	Finizio et al., 1997
p,p-DDT	5.98	Isnard and Lambert, 1988

Appendix Table 3 (continued). Octanol-water partition coefficients. Selected data are from listed sources compiled by Mackay et al. (1997).

Pesticide	log Kow	Source
o,p-DDT	6.76	Finizio et al., 1997
o,p-DDT	5.65	Finizio et al., 1997
o,p-DDT	5.53	Finizio et al., 1997
o,p-DDT	5.75	Isnard and Lambert, 1988
DDT	7.48	Brooke et al., 1990
DDT	7.35	Harnisch et al., 1983
DDT	6.91	Brooke et al., 1990
DDT	6.91	De Bruijn et al., 1989
DDT	6.91	Kollig, 1993
DDT	6.91	Eadsforth and Moser, 1983
DDT	6.91	Mabey et al., 1982
DDT	6.91	Burkhard et al., 1985
DDT	6.91	Brooke et al., 1990
DDT	6.84	Karickhoff et al., 1989
DDT	6.82	Patil, 1994
DDT	6.69	Belluck and Felsot, 1981
DDT	6.613	Rekker et al., 1993
DDT	6.38	Hammers et al., 1982
DDT	6.37	Brooke et al., 1990
DDT	6.36	Chiou et al., 1977; 1982
DDT	6.36	Karickhoff et al., 1989
DDT	6.36	Brooke et al., 1986
DDT	6.36	Medchem, 1988
DDT	6.36	Thor, 1989
DDT	6.31	Brooke et al., 1990
DDT	6.21	Eadsforth and Moser, 1983
DDT	6.2	Elgar, 1983
DDT	6.2	ATSDR, 1988
DDT	6.19	Freed et al., 1979
DDT	6.19	De Kock and Lord, 1987
DDT	6.19	O'Brien, 1975
DDT	6.12	Eadsforth and Moser, 1983
DDT	6.08	Yalkowsky and Dannenfelser, 1994
DDT	6.06	Chin et al., 1986
DDT	5.98	Callahan et al., 1979
DDT	5.98	Pavlou and Weston, 1983; 1984
DDT	5.94	Ellgehausen et al,. 1981, Sicbaldi and Finizio 1993
DDT	5.9	Eadsforth and Moser, 1983
DDT	5.75	Veith and Kosian, 1982
DDT	5.55	McDuffie, 1981
DDT	5.5	Sicbaldi and Finizio, 1993
DDT	5.44	Gerstl and Mingelgrin, 1984
DDT	5.44	Burkhard et al., 1985
DDT	5.1	Platford et al., 1982
DDT	5.1	Platford, 1982; 1983
DDT	4.98	Clement Associates, 1983

Appendix Table 3 (continued). Octanol-water partition coefficients. Selected data are from listed sources compiled by Mackay et al. (1997).

Pesticide	log Kow	Source
DDT	3.98	Kapoor et al., 1973
DDT	3.98	Lu and Metcalf, 1975
o,p-DDE	6.94	Finizio et al., 1997
o,p-DDE	5.8	O'Brien, 1974
o,p-DDE	5.45	Finizio et al., 1997
o,p-DDE	5.43	Finizio et al., 1997
p,p-DDE	6.956	De Bruijn et al., 1989
p,p-DDE	6.89	Connell et al., 1988; Markwell et al., 1989
p,p-DDE	6.72	Noegrohati and Hammers, 1992
p,p-DDE	5.69	O'Brien, 1975
p,p-DDE	5.69	Veith et al., 1979
p,p-DDE	5.69	Isnard and Lambert, 1988
DDE	6.96	Mabey et al., 1982
DDE	6.94	De Bruijn et al., 1989
DDE	6.51	Medchem, 1988
DDE	6.51	Thor, 1989
DDE	6.36	Karickhoff et al., 1989
DDE	6.29	Chin et al., 1986
DDE	6.09	De Kock and Lord, 1987
DDE	5.89	Burkhard et al., 1985
DDE	5.83	Garten and Trabalka, 1983
DDE	5.78	Sicbaldi and Finizio, 1993
DDE	5.77	Kenaga and Goring, 1980
DDE	5.63	Swann et al., 1983
DDE	5	Calamari et al. 1991
DDE	4.28	Metcalf et al. 1975
o,p-DDD	6.06	Finizio et al., 1997
o,p-DDD	5.34	Finizio et al., 1997
o,p-DDD	4.87	Finizio et al., 1997
p,p'-DDD	6.02	Veith and Morris, 1978; Veith et al., 1989
p,p'-DDD	6.02	Isnard and Lambert, 1988
DDD	6.7	Karickhoff et al. 1989
DDD	6.26	Belluck and Felsot, 1981
DDD	6.217	De Bruijn et al. 1989, Sicbaldi and Finizio 1993
DDD	6.21	Kollig 1993
DDD	6.2	ATSDR 1988
DDD	6.02	Ernst, 1977
DDD	6	Kenaga and Goring 1980
DDD	5.99	O'Brien, 1974
DDD	5.8	De Kock and Lord 1987
DDD	5.69	Hansch and Leo, 1979
DDD	5.59	Noegrohati and Hammers, 1992
DDD	5.19	Chin et al. 1986
DDD	5	De Kock and Lord 1987
DDD	4.82	Sicbaldi and Finizio 1993
Dieldrin	6.2	Briggs 1981

Appendix Table 3 (continued). Octanol-water partition coefficients. Selected data are from listed sources compiled by Mackay et al. (1997).

Pesticide	log Kow	Source
Dieldrin	5.88	Patil 1994
Dieldrin	5.48	Kenaga 1980a, b
Dieldrin	5.4	De Bruijn et al. 1989
Dieldrin	5.4	Kollig 1993
Dieldrin	5.3	Hermens and Leeuwangh 1982
Dieldrin	5.21	Belluck and Felsot 1981
Dieldrin	5.17	Finizio et al., 1997
Dieldrin	5.11	Hammers et al. 1982
Dieldrin	5.109	Yalkowsky and Dannenfelser 1994
Dieldrin	5.1	Platford 1982
Dieldrin	4.76	Sicbaldi and Finizio 1993
Dieldrin	4.76	Finizio et al., 1997
Dieldrin	4.6	Brooke et al. 1986
Dieldrin	4.6	Devillers et al. 1991
Dieldrin	4.55	Brooke et al. 1986
Dieldrin	4.51	Brooke et al. 1986
Dieldrin	4.51	De Kock and Lord 1987
Dieldrin	4.49	Brooke et al. 1986
Dieldrin	4.32	Kanazawa 1981
Dieldrin	4.32	Hansch and Leo 1985
Dieldrin	4.32	Medchem 1988
Dieldrin	4.32	Thor 1989
Dieldrin	3.69	Montgomery 1993
Dieldrin	3.63	Finizio et al., 1997
Dieldrin	3.176	Pinsuwan et al. 1995
Dieldrin	2.6	Hansch and Leo 1979

Appendix Table 4. Degradation rates in water. Original data were converted to first order decay rates (k) in units of d^{-1}.

k (d^{-1})	Pathway	Study Comments	Primary Source	Summarized By
DDT				
2.0×10^{-3} - 9.9×10^{-2}	Photooxidation	estimated photooxidation	Callahan et al., 1979	Howard et al., 1991; Mackay et al., 1997
	Photolysis	NOT SIGNIFICANT	Callahan et al., 1979; Zepp et al., 1977	Howard et al., 1991
8.6×10^{-5}	Hydrolysis	pH 7 and 27 deg C	Wolfe et al., 1977	Howard et al., 1991; Mackay et al., 1997
1.6×10^{-4}	Hydrolysis	pH 7 and 25 deg C	Kollig, 1993	Mackay et al., 1997
3.8×10^{-3}	Hydrolysis	pH 7	Neely and Blau, 1985	Mackay et al., 1997
DDE				
1.1×10^{-1} - 1.1×10^{1}	Photolysis	scientific judgment	Zepp and Cline, 1977; Draper, 1985	Howard et al., 1991
1.9×10^{-1}	Photolysis	irradiation of aqueous solution of p,p'-DDE in natural water	Ross and Crosby, 1995	Montgomery et al., 1993
4.6×10^{-1}	Photolysis	sunlight irradiation	Mansour et al., 1989	Montgomery et al., 1993
< 1.6×10^{-5}	Hydrolysis	27 deg C	Wolfe et al., 1977	Mackay et al., 1997
< 2.3×10^{-3}	Surface water	estimated half-life in lake water	Zoeteman et al., 1980	Mackay et al., 1997
DDD				
6.8×10^{-5}	Hydrolysis	pH 7 and 25 deg C	Ellington et al. 1987	Howard et al., 1991
6.8×10^{-5}	Hydrolysis	pH 7 and 25 deg C	Ellington et al. 1988	Montgomery et al., 1993

Appendix Table 4 (cont.). Degradation rates in water. Original data were converted to first order decay rates (k) in units of d^{-1}.

k (d^{-1})	Pathway	Study Comments	Primary Source	Summarized By
Dieldrin				
1.1x10^{-2}	Photolysis	direct sunlight at 40 deg latitude	Mabey et al., 1982	Mackay et al., 1997
1.7x10^{-4}	Hydrolysis	pH 7; 25 deg C	Kollig, 1993	Mackay et al., 1997
1.8x10^{-4}	Hydrolysis	pH 7; 25 deg C	Ellington et al., 1987	Howard et al., 1991; Mackay et al., 1997
< 2.3x10^{-3}	Surface water	estimated half-life in lake water	Zoeteman et al., 1980	Mackay et al., 1997
Chlordane				
< 4.6x10^{-3}	Photolysis	summarized	Callahan et al., 1979	Mackay et al., 1997
< 9.6x10^{-9}	Hydrolysis	pH 7, 25 deg C	Ellington et al., 1987	Howard et al., 1991; Mackay et al., 1997
< 9.6x10^{-9}	Hydrolysis	pH 7, 25 deg C (cis-chlordane)	Ellington et al., 1988	Montgomery et al., 1993
8.6x10^{-5}	Oxidation	summarized	Callahan et al., 1979	Mackay et al., 1997
Heptachlor and Heptachlor Epoxide				
1.5x10^{-1}	Hydrolysis	Heptachlor; 1% ethanol/water phosphate buffered solution at 25 deg C, pH 7	Chapman and Cole, 1982	Montgomery et al., 1993
1.3x10^{-1} - 7.2x10^{-1}	Hydrolysis	Heptachlor; half-lives	Kollig et al., 1987; Chapman and Cole, 1982	Mackay et al., 1997
1.7x10^{-1}	Hydrolysis	Heptachlor; pH 7, 25 deg C	Kollig, 1993	Mackay et al., 1997
2.0x10^{-2}	Surface water	H. Epoxide; half-life in lower Rhine River	Zoeteman et al., 1980	Mackay et al., 1997

Appendix Table 5. Degradation rates in soil and sediment. Original data were converted to first order decay rates (k) in units of d^{-1}.

k (d^{-1})	Matrix	Study Comments	Cited Source	Summarized By
DDT				
1.2×10^{-4} - 6.3×10^{-3} (7.5×10^{-4})	Soil	various studies	various	Agricultural Research Service, 2003
1.2×10^{-4} - 9.5×10^{-4}	Soil	aerobic field conditions	Lichtenstein and Schultz, 1959; Stewart and Chisholm, 1971	Howard et al., 1991; Mackay et al., 1997
1.3×10^{-4}	Soil	aerobic; biodegradation in soil incubation studies	Rao and Davidson, 1980	Mackay et al., 1997
1.6×10^{-4}	Soil	avg. half-life in 3 soils of ~ 50 ppm DDT; field study	Nash and Woolson, 1967	Mackay et al., 1997
1.8×10^{-4}	Soil	half-life in soil	Jury et al. 1987	Montgomery et al., 1993; Mackay et al., 1997
2.0×10^{-4}	Soil	half-life in soil	Mackay and Stiver, 1991	Mackay et al., 1997
2.1×10^{-4}	Sediment	quoted mean value from Howard et al., 1991	Howard et al., 1991	Mackay et al., 1997
3.0×10^{-4}	Soil	estimated field half-life	Augustijm-Beckers et al., 1994; Hornsby et al. 1996	Mackay et al., 1997
3.5×10^{-4}	Soil	anaerobic flooded soil incubation	Rao and Davidson, 1980	Mackay et al., 1997
4.0×10^{-4}	Soil	incorporated into soil	Willis et al., 1971	Mackay et al., 1997
6.9×10^{-4}	Soil	half-life in soil	Willis and McDowell, 1982	Mackay et al., 1997
DDD				
1.2×10^{4} - 9.5×10^{4}	Soil	various studies	various	Agricultural Research Service, 2003
1.2×10^{4} - 9.5×10^{4}	Soil	aerobic field conditions	Lichtenstein and Schultz, 1959; Stewart and Chisholm, 1971	Howard et al., 1991; Mackay et al., 1997
6.9×10^{-4}	Soil	estimated field-half life, 20-25 deg C	Hornsby et al., 1996	Mackay et al., 1997

Appendix Table 5 (cont.). Degradation rates in soil and sediment. Original data were converted to first order decay rates (k) in units of d^{-1}.

k (d^{-1})	Matrix	Study Comments	Cited Source	Summarized By
DDE				
1.2×10^{-4} - 9.5×10^{-4}	Soil	various studies	various	Agricultural Research Service, 2003
1.2×10^{-4} - 9.5×10^{-4}	Soil	aerobic field conditions	Lichtenstein and Schultz, 1959; Stewart and Chisholm, 1971	Howard et al., 1991
6.9×10^{-4}	Soil	estimated field-half life, 20-25 deg C	Hornsby et al., 1996	Mackay et al., 1997
4.8×10^{-4} - 3.9×10^{-3}	Sediment	anaerobic; methanogenic treatment	Quensen et al., 1998	
4.7×10^{-4} - 1.2×10^{-3}	Sediment	anaerobic; sulfidogenic treatment	Quensen et al., 1998	
Dieldrin				
5.5×10^{-4} - 3.1×10^{-3}	Soil	various studies	various	Agricultural Research Service, 2003
6.3×10^{-4} - 4.0×10^{-3}	Soil	aerobic; soil grab sample and reported half-life in soil based on field data	Castro and Yoshida, 1971; Kearney et al., 1969	Howard et al., 1991; Mackay et al., 1997
2.7×10^{-4}	Soil	half-life in soil, field study	Nash and Woolson, 1967	Mackay et al., 1997
6.9×10^{-4}	Soil	estimated half-life	Augustijn-Beckers et al., 1994; Hornsby et al., 1996	Mackay et al., 1997
6.9×10^{-3} - 3.5×10^{-2}	Soil	half-life in soils	Willis and McDowell, 1982	Mackay et al., 1997
1.3×10^{-2}	Soil	aerobic; soil incubation studies	Rao and Davidson 1980	Mackay et al., 1997
9.9×10^{-2} - 6.9×10^{-1}	Soil	anaerobic; soil and freshwater mud grab sample	Maule et al., 1987	Howard et al., 1991

Appendix Table 5 (cont.). Degradation rates in soil and sediment. Original data were converted to first order decay rates (k) in units of d^{-1}.

k (d^{-1})	Matrix	Study Comments	Cited Source	Summarized By
Chlordane				
$2.0x10^{-4}$ - $2.5x10^{-3}$	Soil	various studies	various	Agricultural Research Service, 2003
$5.0x10^{-4}$ - $2.4x10^{-3}$	Soil	unacclimated aerobic river die-away test and reported soil grab sample	Eichelberger and Lichtenberg, 1971; Castro and Yoshida, 1971	Howard et al., 1991
$3.2x10^{-4}$	Soil	half-life in soil	Nash and Woolson, 1967	Mackay et al., 1997
$5.7x10^{-4}$	Soil	field conditions in soil	Rao and Davidson, 1980	Mackay et al., 1997
$5.8x10^{-4}$	Soil	field conditions in soil	Howard et al., 1991	Mackay et al., 1997
$8.3x10^{-4}$	Sediment	quoted mean value from Howard et al., 1991	Howard et al., 1991	Mackay et al., 1997
$1.9x10^{-3}$	Soil	half-life in soil	Hartley and Kidd, 1987	Montgomery et al., 1993, Mackay et al., 1997
$2.0x10^{-3}$	Soil	estimated field half-life	Augustijm-Beckers et al. 1994; Tomlin 1994; Hornsby et al. 1996	Mackay et al., 1997
$6.9x10^{-3}$	Soil	half-life in soil	Jury et al., 1990; Willis and McDowell, 1982	Mackay et al., 1997
Heptachlor				
$3.5x10^{-4}$ - $1.7x10^{-2}$	Soil	various studies	various	Agricultural Research Service, 2003
$3.8x10^{-4}$ - $9.5x10^{-4}$	Soil	estimated half-life in soil	Nash and Woolson, 1967	Mackay et al., 1997
$2.4x10^{-3}$	Soil	reported half-life of 9 to 10 months in soil	Hartley and Kidd, 1987	Mackay et al., 1997; Montgomery et al., 1993
$2.8x10^{-3}$	Soil	field half-life	Augustijm-Beckers et al. 1994; Hornsby et al. 1996	Mackay et al., 1997
$3.2x10^{-3}$	Soil	biodegradation half-life	Jury et al. 1980	Mackay et al., 1997
$1.1x10^{-2}$	Soil	biodegradation in die-away test in soil	Rao and Davidson, 1980	Mackay et al., 1997

Appendix Table 5 (cont.). Degradation rates in soil and sediment. Original data were converted to first order decay rates (k) in units of d^{-1}.

k (d^{-1})	Matrix	Study Comments	Cited Source	Summarized By
Heptachlor Epoxide				
8.8x10^{-3} - 1.47x10^{-1}	Soil	various studies	Agricultural Research Service, 1997	Nowell et al., 1999
9.9x10^{-2}	Soil	Anaerobic; soil and freshwater mud grab sample data for aldrin, dieldrin, endrin and heptachlor epoxide	Maule et al. 1987	Howard
6.9x10^{-1}	Soil	Anaerobic; soil and freshwater mud grab sample data for aldrin, dieldrin, endrin and heptachlor epoxide	Maule et al. 1987	Howard