**US Army Corps
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Waterways Experiment
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Water Quality Research Program

Description of Contaminant Sediment-Water Interactions Using RECOVERY

by   Thomas C. Sturgis, Carlos Ruiz,
      Douglas Gunnison, Judith C. Pennington
      Environmental Laboratory

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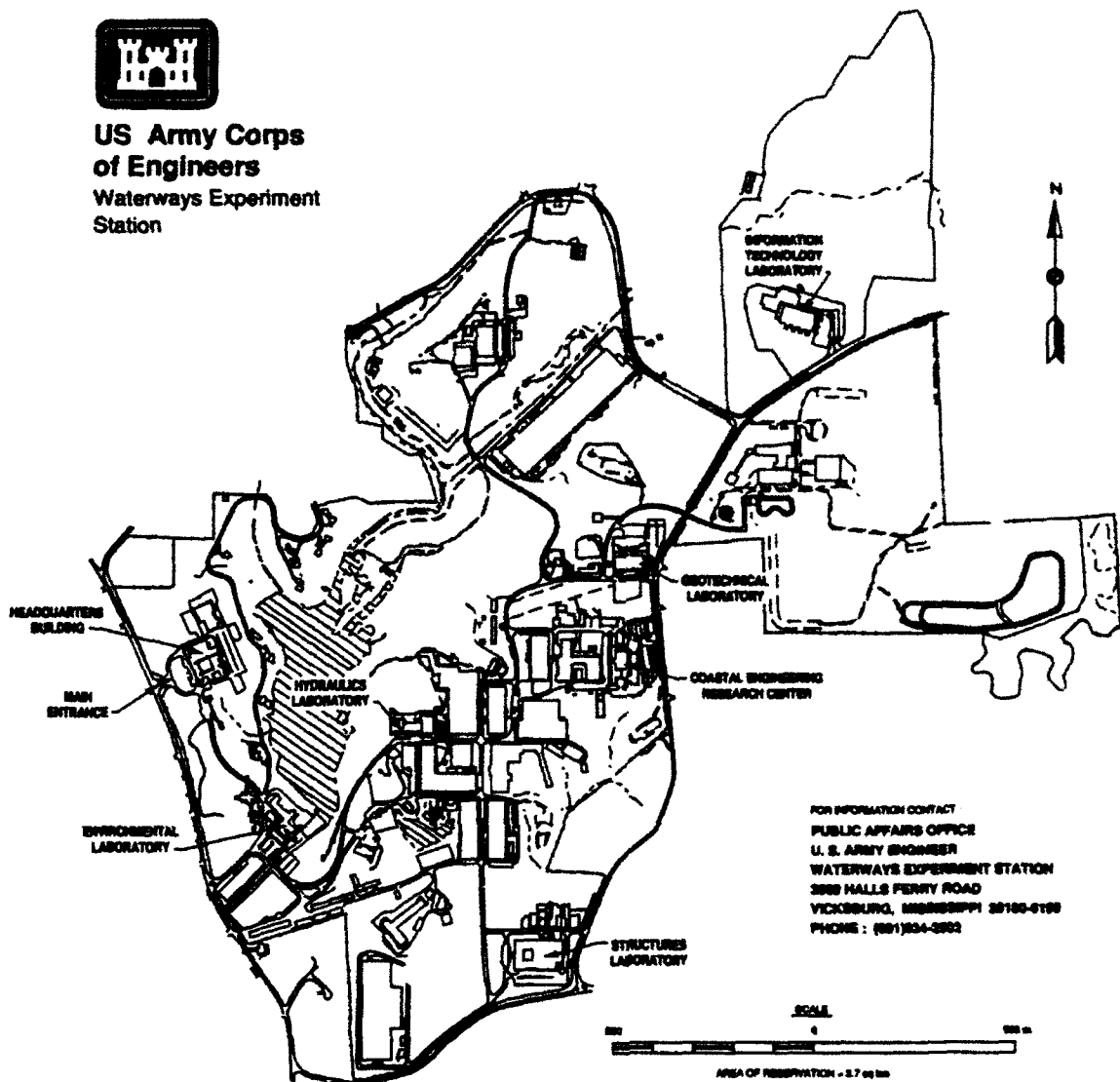   Douglas Gunnison, Judith C. Pennington

Environmental Laboratory

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Final report

**US Army Corps
of Engineers**
Waterways Experiment
Station

PREFACE

The work reported herein was conducted as part of the Water Quality Research Program (WQRP), Work Unit 32513, "Sediment-Water Interactions and Contaminant Processes in Reservoirs." The WQRP is sponsored by the Headquarters, US Army Corps of Engineers (HQUSACE), and is assigned to the US Army Engineer Waterways Experiment Station (WES) under the purview of the Environmental Laboratory (EL). Funding was provided under Department of the Army Appropriation No. 96X3121, General Investigation. The WQRP is managed under the Environmental Resources Research and Assistance Programs (ERRAP), Mr. J. L. Decell, Manager. Mr. Robert C. Gunkel was Assistant Manager, ERRAP, for the WQRP. Technical Monitors during the study were Mr. Frederick B. Juhle, Mr. James Gottesman, and Dr. John Bushman, HQUSACE.

The study was conducted and the report prepared by Mr. Thomas C. Sturgis and Drs. Douglas Gunnison and Judith C. Pennington, Ecosystem Processes and Effects Branch (EPEB), and Dr. Carlos Ruiz, Water Quality and Contaminant Modeling Branch, Environmental Processes and Effects Division (EPED), EL.

The study was conducted under the direct supervision of Dr. Richard E. Price, Chief, EPEB, and under the general supervision of Mr. Donald L. Robey, Chief, EPED, and Dr. John Harrison, Director, EL. Technical reviews of the report were provided by Dr. James M. Brannon and Mr. Dennis Brandon, EPED.

At the time of publication of this report, Director of WES was Dr. Robert W. Whalin. Commander was COL Leonard G. Hassell, EN.

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CONVERSION FACTORS, NON-SI TO SI
UNITS OF MEASUREMENT

Non-SI units of measurement used in this report can be converted to SI units
as follows:

Multiply	By	To Obtain
acres	4,046.873	square meters
feet	0.3048	meters
miles (US statute)	1.609347	kilometers
tons (2,000 pounds, mass)	907.1847	kilograms

DESCRIPTION OF CONTAMINANT SEDIMENT-WATER INTERACTIONS USING RECOVERY

PART I: INTRODUCTION

1. Bedded sediments serve as sinks for many contaminants. Deposition of contaminants into the sediment begins a series of processes that may cycle contaminants back into the water column creating potentially adverse ecological impacts on aquatic biota. Sorption processes influence the mobility of contaminants from the sediment. Sorption is a general term referring to chemical binding that may be both reversible and irreversible. Desorption quantifies the reversibility of contaminants and is important because the availability of contaminants for uptake depends on the rate of desorption. The partitioning of contaminants between sediment and aqueous phases influences sorption processes and can be mathematically written as:

$$K_d = C_s/C_w \tag{1}$$

where

K_d = the distribution coefficient, ℓ/kg

C_s = the concentration of contaminant sorbed to sediment solids, mg/kg

C_w = the concentration of contaminant in aqueous phase, mg/ℓ

Because the distribution coefficient of nonpolar organic compounds such as polycyclic aromatic hydrocarbons (PAHs) is strongly dependent on sediment organic-matter content, the distribution coefficient is usually normalized for organic content of the sediment:

$$K_{oc} = K_d/f_{oc} \tag{2}$$

where

K_{oc} = the normalized partition coefficient

f_{oc} = the fraction of organic carbon in the sediment

Partitioning and sorption are key processes that must be understood to determine the role and potential impacts of the sediment in contaminant mobilization on the aquatic biota.

2. The overall objective of this study was to use experimental data and a model simulation to predict desorption kinetics of organic contaminants and to assess the potential effect of contaminated sediment on the overlying water. In the experimental phase, several PAHs and polychlorinated biphenyl (PCB) 153 were quantified. Radiolabeled PAHs and PCB 153 were selected as tracers to determine the rate and magnitude of contaminant mobilization from five reservoir sediments. Data from the experimental phase will be used to verify and assess the applicability of the RECOVERY model in predicting desorption.

3. Concern about environmental exposure to contaminants has increased the need to predict the fate of anthropogenic organic contaminants entering aquatic systems. A primary sink for contaminants is the sediment. The RECOVERY model permits estimation of desorption rates and allows assessment of the potential adverse impact of contaminated sediments on the overlying water and biota. The model assumes that the contaminants follow linear equilibrium sorption and first-order decay kinetics. Partitioning models in which equilibrium between sorbed and dissolved species is assumed are often sufficient to describe the transport fate of contaminants, particularly when incubation periods are relatively long (days to months) (Neeley and Blau 1977; Watanbe 1985). Once desorption rates are predicted, a hazard assessment can be made on a given reservoir project.

PART II: MATERIALS AND METHODS

Organic Chemicals

4. To demonstrate the impact of sediment-water interactions on contaminant levels in US Army Corps of Engineer (USACE) reservoir projects, radio-labeled contaminants such as 2,2',4,4',5,5'-Hexachlorobiphenyl-UL-^{14}C (PCB 153),[3-^{14}C]fluoranthene and naphthalene-1-^{14}C were used as model chemicals (Figure 1). Information obtained using these chemicals can provide insight into the impact of other PCBs (e.g., pentachlorobiphenyl) and PAHs (e.g., fluorene, anthracene, and phenanthrene). Fluoranthene and naphthalene represent a wide range of solubilities and log octanol/water coefficients. Fluoranthene is a three-ring aromatic hydrocarbon that is sparingly soluble in
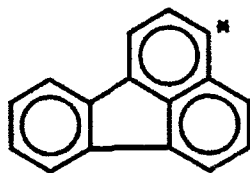
a. Fluoranthene
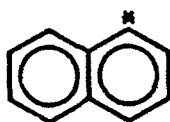
b. Naphthalene
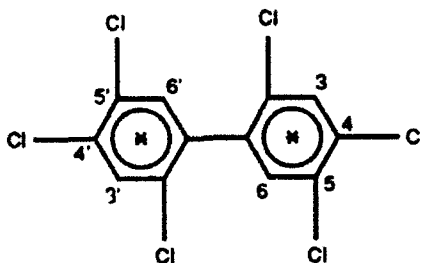
c. Polychlorinated biphenyl

Figure 1. Molecular structures for fluoranthene, naphthalene, and polychlorinated biphenyl and location of [^{14}C]

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water (0.26 mg/ℓ). Naphthalene is a two-ring aromatic hydrocarbon having an aqueous solubility of 34 mg/ℓ. Fluoranthene and naphthalene have log octanol/water coefficients of 5.33 and 3.37, respectively (Radding et al. 1976; Leo and Elkins 1971).

5. PCB is the generic name for a group of related compounds (congeners) having 209 possible individual configurations (McFarland, Clarke, and Gibson 1986). The congeners differ in number and position of chlorine atoms substituted for hydrogen on the biphenyl molecule. PCB 153 has a low water solubility (0.04 to 0.2 mg/ℓ) and a log octanol/water coefficient of 6.03.

Sediments

6. Five sediments with organic carbon ranging from 1.2 to 9 percent were selected. They were Mark Twain Lake (Missouri), Louisville (Kentucky), Brown's Lake (Mississippi), Wayne County (Iowa), and Oakland Inner Harbor (California) (Table 1).

Table 1

Physical Characteristics of Sediments

	Concentration of Constituent, percent				
Constituent	Louisville Lake Sediment	Mark Twain Lake Sediment	Oakland Inner Harbor Sediment	Brown's Lake Sediment	Wayne County Sediment
Sand	10.0	45.0	72.5	5.0	57.5
Silt	75.0	37.5	10.0	7.0	27.5
Clay	15.0	17.5	17.5	25.0	15.0
Organic Matter	5.7	3.7	2.7	3.1	5.5
Organic Carbon	2.6	1.2	1.8	2.8	9.0

Batch Studies

7. Batch studies to assess the release of organic contaminants from sediment were determined in 25-ml glass centrifuge tubes. These experiments were conducted in the laboratory where the temperature was maintained at

20 °C ± 0.5 °C. Each sediment was spiked with 1 ppm 2,2',4,4',5'- Hexachlor-obiphenyl-UL-^{14}C (PCB 153), [3-^{14}C]fluoranthene, and naphthalene-1-^{14}C. The specific activities of PCB 153, fluoranthene, and naphthalene are 12.2, 55.0, and 10.1 mCi/mmol, respectively; chemical and radiological purities were greater than 98 percent by high performance liquid chromatography and radio thin layer chromatography, respectively. Sediments were spiked with PCB 153 and fluoranthene by coating the side walls of glass centrifuge tubes with toluene and benzene solution of the contaminants, respectively. Tubes were allowed to turn on their sides on an electrical roller drum until the solvents evaporated. A sediment slurry with a 2:1 water to sediment ratio was then added to the glass centrifuge tubes. Naphthalene was added directly to the sediment slurry.

8. All glass centrifuge tubes were placed on a reciprocating box shaker and allowed to shake for 24 hr at a speed of 280 excursions/min. This allowed the contaminants to partition from the walls of the glass centrifuge tubes to the sediment and aqueous phases. This technique produced a more uniform chemical distribution among suspended sediment particles (Karickhoff and Morris 1985). After 24 hr, the tubes were removed from the shaker. The upper inside walls of all tubes were cleaned, capped with foam plugs, and the contents allowed to settle for 3 days.

9. After 3 days, the overlying water was removed and centrifuged at 12,000 rpm (7,400 x g) for 30 min. One milliliter of the supernatant was counted in 20 ml of Aquasol (Cole-Palmer, Chicago, IL) in a Packard TriCarb 2500 Liquid Scintillation (LS) analyzer. Each sample was counted for 5 min through two cycles and the disintegrations per minute averaged. Distilled deionized water was added to the centrifuge tubes without disturbing the sediment. At specified times (0.25, 0.5, 1.0, 2.0, 3.0, 5.0, 7.0 days), 2 ml of the overlying water was removed, placed in glass centrifuge tubes, and centrifuged at 12,000 rpm (7,400 x g) for 30 min. One milliliter of the supernatant was counted by LS and 1.0 ml was discarded. Two milliliters of distilled deionized water was added to the glass centrifuge tubes to replace the water that was removed.

10. Following the last sampling, foam plugs were extracted three times with 5-ml aliquots of hexane. The extracts were combined and concentrated to 5 ml. One milliliter of the concentrate was counted, and the remainder was frozen for possible gas chromatography analysis. Controls (unspiked

sediments) were sampled concurrent with the various radiolabeled treatments using the same procedures.

Model Description

11. To make hazard assessments, the extent and magnitude of the influence of contaminated sediment on the overlying water column must be delineated. RECOVERY, a PC-based zero dimension model, was developed to assess the impact of contaminated sediment on the overlying water (Boyer and Chapra 1989). The model was modified to make it more applicable to laboratory microcosm settings and short-term scenarios (7 days), and to facilitate use by USACE field offices for assessing the potential impact of contaminated sediment on the overlying water. The analysis is limited to organic contaminants and to well-mixed surface waters.

12. RECOVERY is designed for interactive implementation via personal computer. The program allows the user to generate and analyze the expected course of events for contaminated sediments. The results are displayed as plots of contaminant concentration in the water versus time and flux of the contaminant from the sediment into the water versus time. The model will only predict desorption (DiToro and Horzempa 1982). A more detailed description of the model and a model user's guide are presented in Appendix A.

13. Means and standard errors were determined for each parameter within a treatment. To determine the statistical significance of difference between means, t-tests were conducted.

PART III: RESULTS

Sediment Physical Characteristics

14.   Louisville and Brown's Lake sediments have higher percentages of fine material than Mark Twain, Oakland Harbor, and Wayne County sediments (Table 1). Organic carbon content was higher in Wayne County, Brown's Lake, and Louisville sediments (9.0, 2.8, and 2.6 percent, respectively), than in Oakland and Mark Twain (1.8 and 1.2 percent, respectively). Partition coefficients (Table 2) normalized for organic matter content (K_{oc}) are useful to estimate K_d for other sediments with other values of f_{oc} (fraction organic carbon) (Hamaker and Thompson 1972).

Table 2
K_{oc} Values for Each Contaminant

Sediment	Fluoranthene	Naphthalene	PCB 153
Mark Twain	9.25×10^7	1.37×10^9	9.25×10^7
Louisville	1.20×10^{10}	8.53×10^9	1.28×10^{11}
Oakland Inner Harbor	1.10×10^{10}	1.88×10^9	1.25×10^{11}
Brown's Lake	1.05×10^9	3.71×10^9	3.30×10^{10}
Wayne County	1.46×10^9	9.25×10^8	7.40×10^9

Desorption Kinetics Study

15.   The desorption partition coefficients (K_d) for each sediment are shown in Table 3. K_d was mathematically determined by dividing the concentration of the contaminant sorbed to sediment solids by the concentration of contaminant in the aqueous phase. The K_d values provide estimates of organic contaminant desorption and indicate that desorption was minor.

Fluoranthene

16.   Fluoranthene desorption was biphasic, consisting of a rapid phase, followed by a slower approach to steady state (Figure 2). Desorption from Louisville and Oakland sediments was essentially complete within the first 2 days. The decrease observed in fluoranthene concentration after 2 days was

Table 3

Desorption Partition Coefficients (K_d) for Each Contaminant, ℓ/kg

Sediment	Fluoranthene	Naphthalene	PCB 151
Mark Twain	1.11×10^7	1.64×10^6	1.11×10^7
Louisville	3.13×10^7	2.22×10^7	3.33×10^8
Oakland Inner Harbor	1.14×10^7	2.04×10^6	1.42×10^8
Brown's Lake	3.13×10^6	1.04×10^7	9.10×10^7
Wayne County	1.31×10^7	8.33×10^6	6.67×10^7

not significant ($P < .01$). Analysis of Mark Twain and Brown's Lake desorption kinetics show that desorption was complete after the first 2 days. Fluoranthene desorption from the Brown's Lake sediment showed an apparent increase throughout the study (Figure 2). However, between Days 3 and 7, there was only a small increase of approximately 0.6 $\mu g/\ell$; this increase was not significant ($P < .01$). Desorption from Wayne County sediment was essentially complete after the first day.

Naphthalene

17. Kinetic trends for naphthalene were similar among sediments (Figure 3), but the percentage of naphthalene desorption varied with sediment at steady state (Table 4). Wayne County and Brown's Lake sediments displayed similar trends and magnitude of desorption. Mark Twain and Oakland Inner Harbor sediments have the lowest sediment organic carbon content and the highest naphthalene desorption (approximately 11 $\mu g/\ell$). Generally, naphthalene was rapidly desorbed after 6 hr, followed by a gradual approach to steady state. The amount of naphthalene desorbed ranged from <1 percent (Louisville sediment) to 11 percent (Oakland sediment).

Polychlorinated biphenyl

18. Brown's Lake sediment achieved steady state after 2 hr (Figure 4). The remaining sediments showed somewhat erratic desorption kinetics (Figure 4). Generally, <0.1 percent of the PCB 153 added to all sediments was desorbed with the exception of the Wayne County sediment (Table 4). Wayne County sediment, which has the highest total sediment organic carbon content, lost approximately 3.5 percent of its initial PCB content to desorption. This
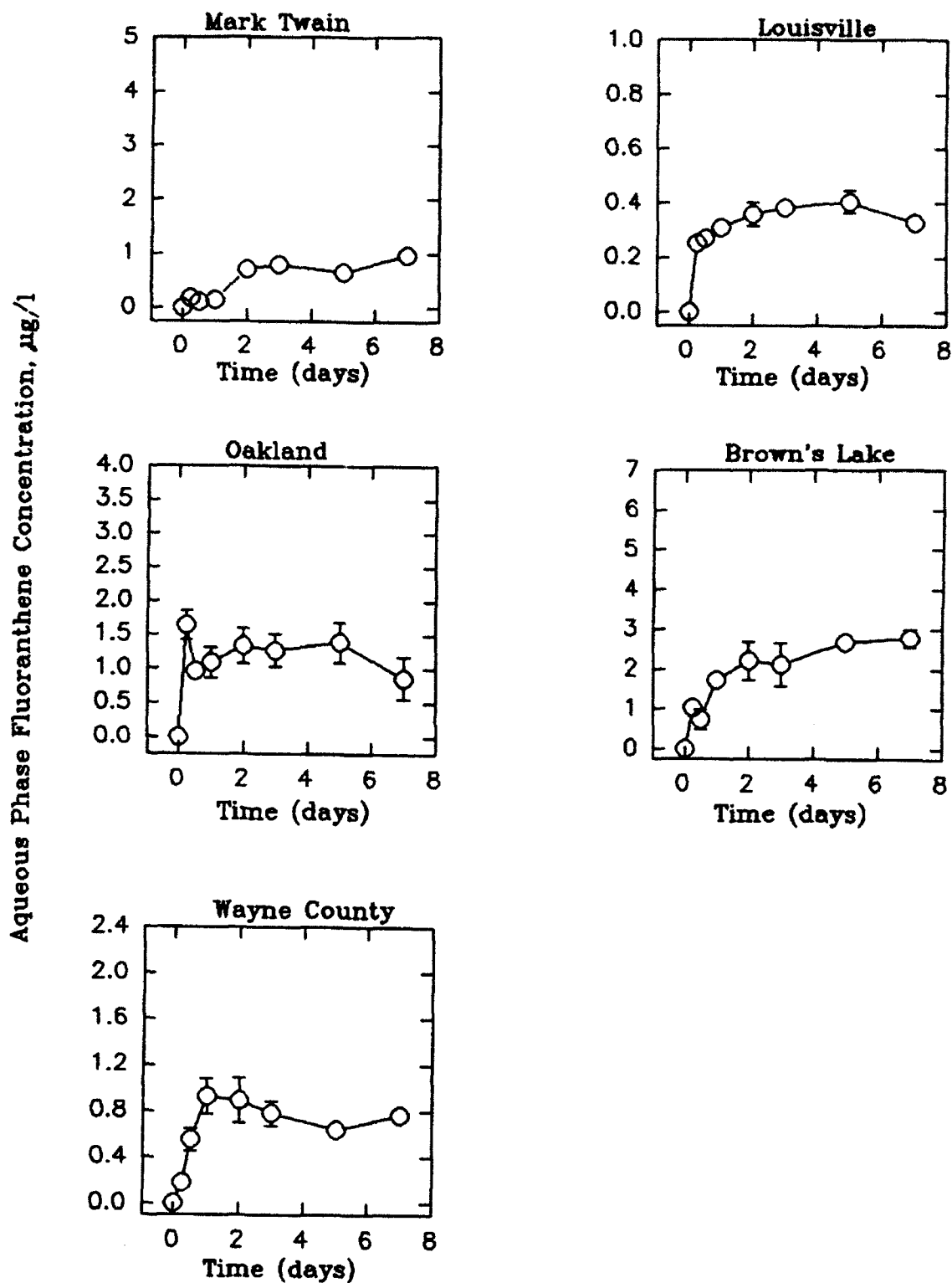
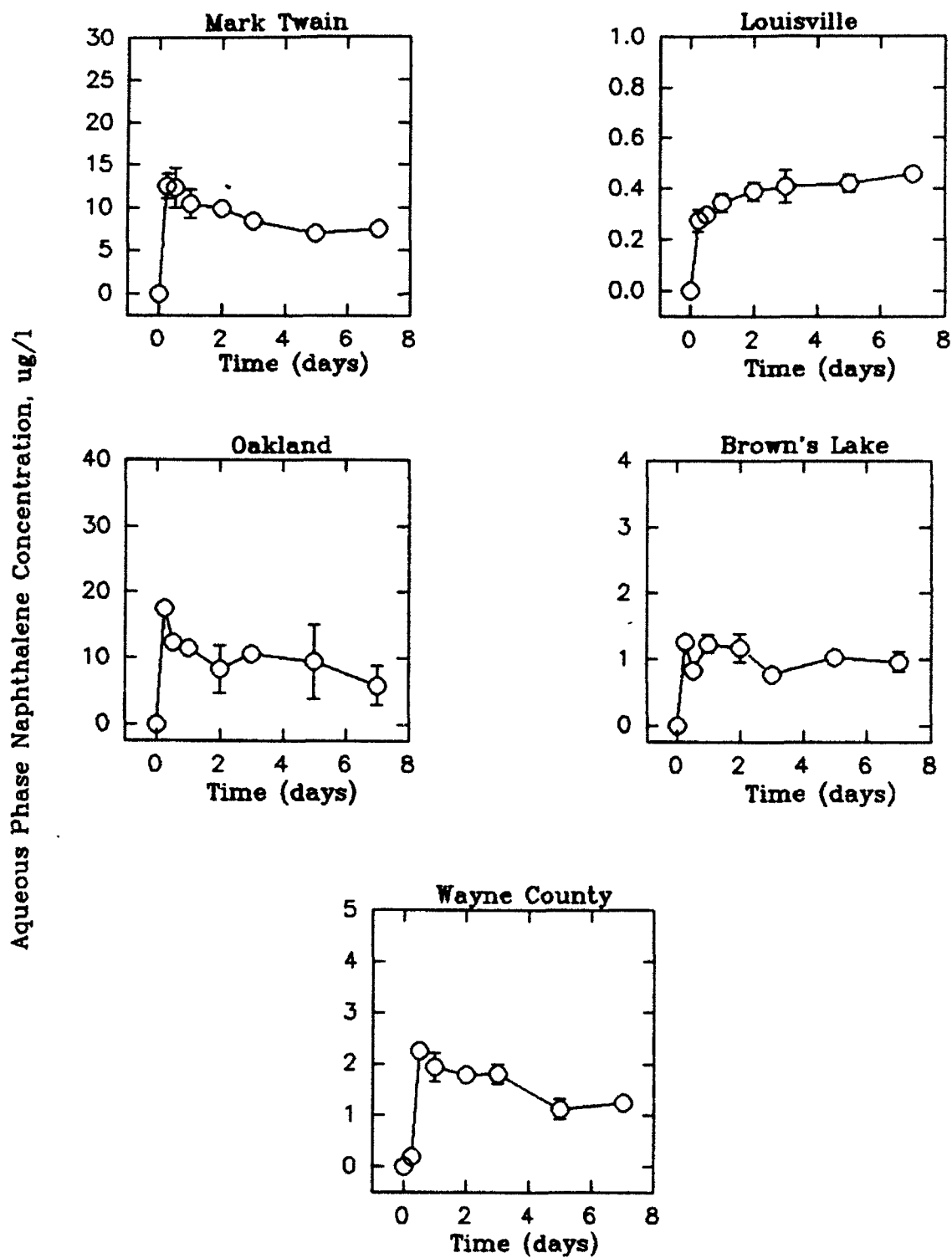Figure 2. Kinetic curves for desorption of fluoranthene

Figure 3. Kinetic curves for desorption of naphthalene

Table 4

Percentage of Contaminant Desorbed from Each Sediment

Sediment	Fluoranthene	Naphthalene	PCB 151
Mark Twain	1.0	11.0	<1.0
Louisville	<1.0	<1.0	<1.0
Oakland Inner Harbor	1.7	11.0	<1.0
Brown's Lake	3.0	1.4	<1.0
Wayne County	<1.0	1.9	3.5

probably resulted from facilitated transport of PCB into overlying water from colloidal material.

Model Application

Fluoranthene

19. Model estimates for fluoranthene desorption from Mark Twain and Oakland Inner Harbor sediments agreed with the experimental data (Figure 5). The values estimated for fluoranthene desorption from Mark Twain and Oakland Inner Harbor sediments were not significantly different from the values observed in the laboratory (P <.01). Louisville, Browns's Lake, and Wayne County fluoranthene desorption kinetics were consistently underestimated by the model, but the trends displayed were similar to those observed in the laboratory.

Naphthalene

20. Estimated naphthalene desorption did not compare favorably with experimental data, especially for Louisville, Brown's Lake, and Wayne County sediments (Figure 6). The model tended to overpredict naphthalene desorption, and kinetic trends were dissimilar to those observed in the experimental data. For example, the predicted desorption kinetics for the Brown's Lake sediment was a slow and steady increase that reached equilibrium between Days 3 and 7, at approximately 9 $\mu g/\ell$. The experimental data showed that equilibrium was reached within 24 hr at approximately 0.3 $\mu g/\ell$. The model provided a better fit to the experimental naphthalene desorption data from Mark Twain and Oakland Inner Harbor sediments. The estimated naphthalene desorption values were

Figure 4. Kinetic curves for desorption of PCB 153
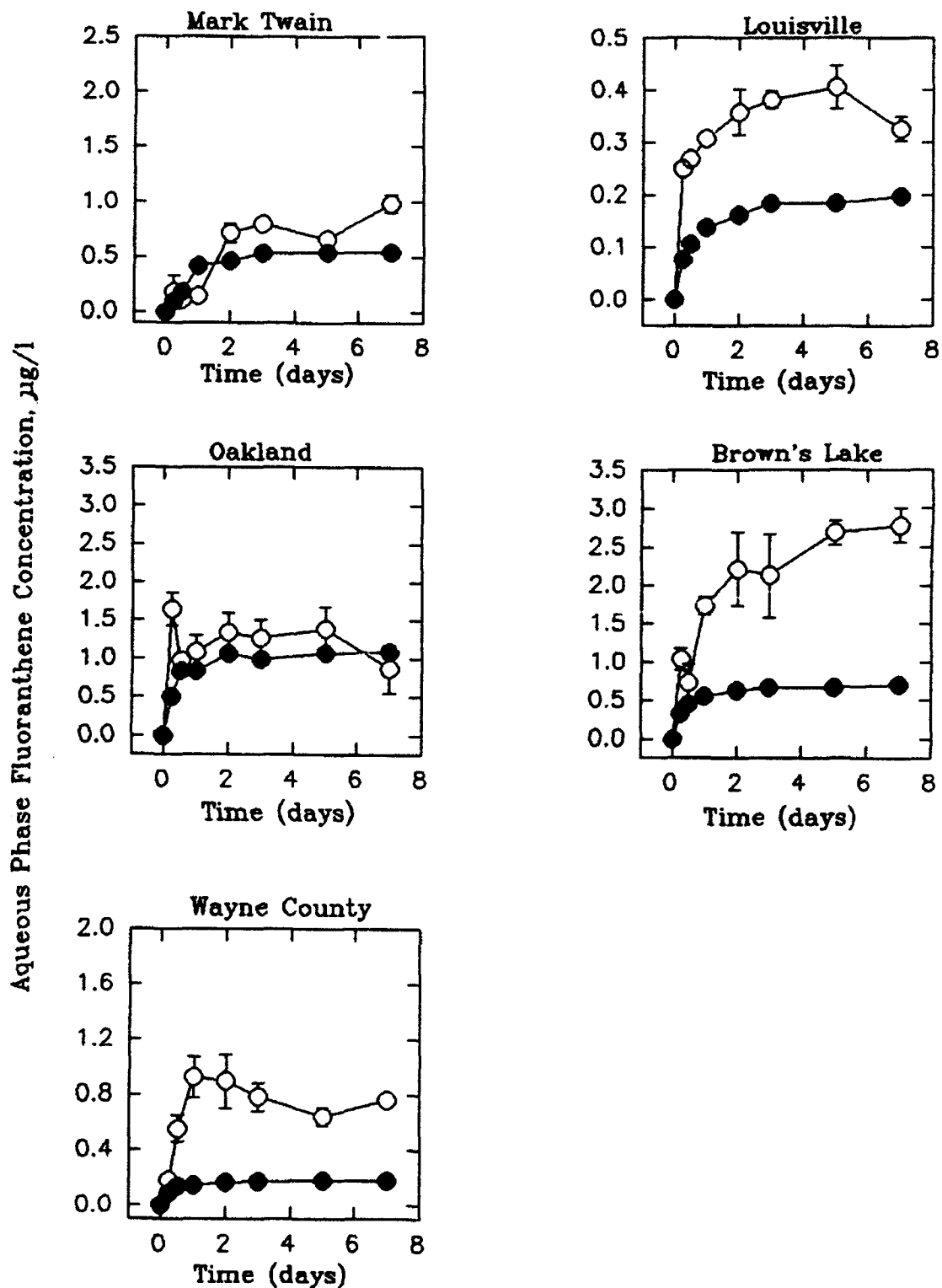
Figure 5. Experimental (hollow circle) and predicted (solid circle) kinetic curves for desorption of fluoranthene
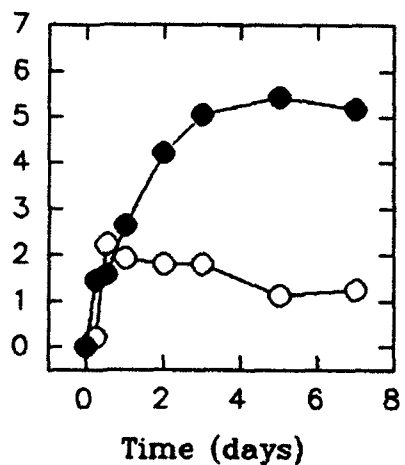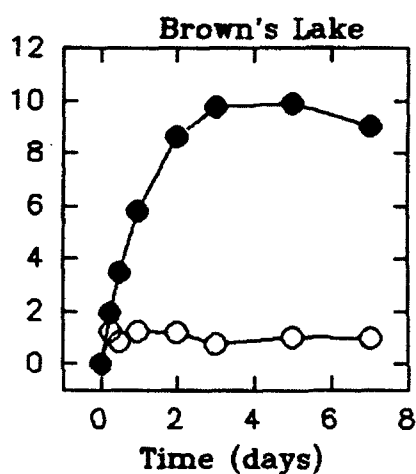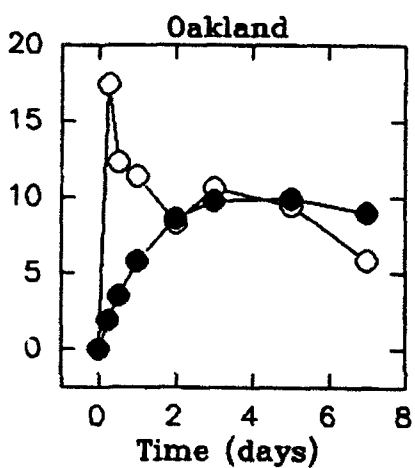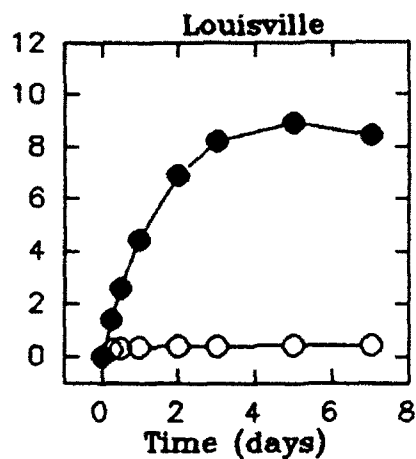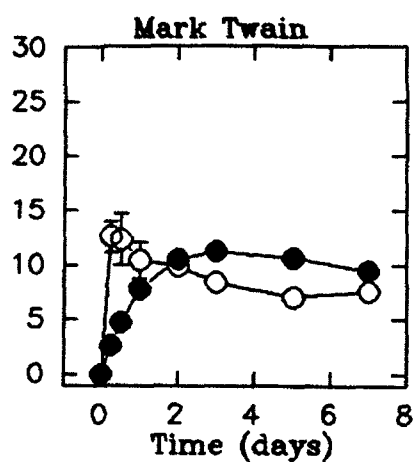
Figure 6. Experimental (hollow circle) and predicted (solid circle)
kinetic curves for desorption of naphthalene

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not significantly different from the experimental values at equilibrium for both Mark Twain and Oakland Inner Harbor sediments. The model did not predict the biphasic trend, but did predict equilibrium and a slight decrease in naphthalene desorption.

21. The predicted naphthalene desorption values were based on the highest decay coefficient of 480/hr (estimated time required for 50 percent of contaminant to degrade), which is considered moderately fast (Howard et al. 1991). However, when a lower decay coefficient (48/hr) was used, the model provided a better fit to the naphthalene experimental data (Figure 7). Estimated decay coefficients were based upon field data and range from 480/hr to 12/hr (Howard et al. 1991).
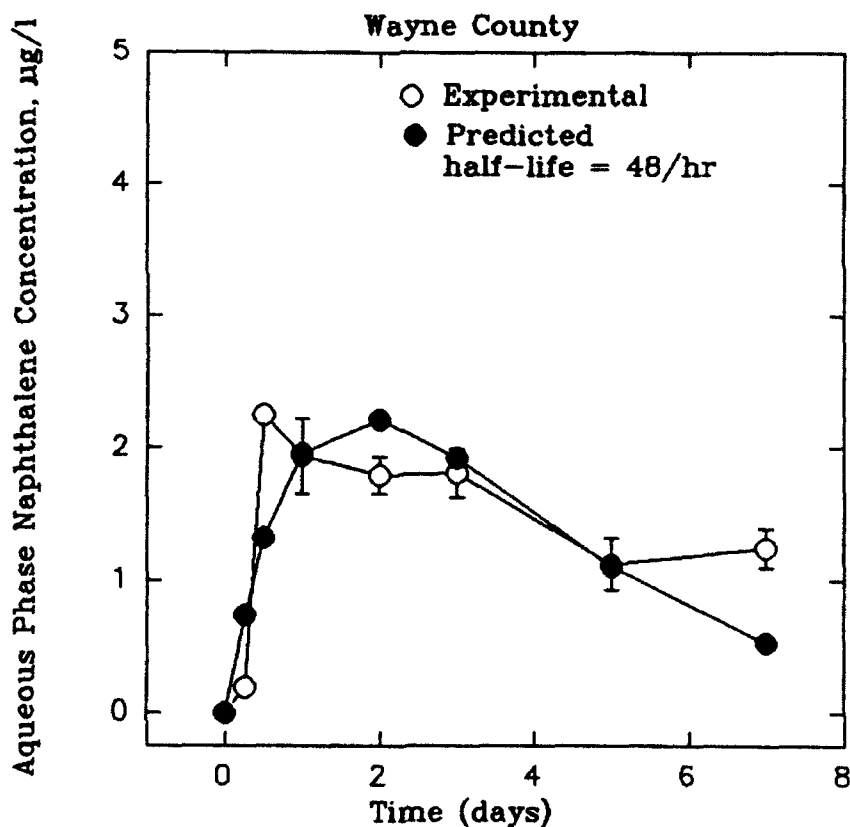
Figure 7. Kinetic curves for naphthalene desorption from Wayne County

PCB

22. The predicted PCB 153 desorption data provided a good fit with experimental data for all sediments except Wayne County (Figure 8). The problem with fitting the predicted data may be due to facilitated transport of PCB

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bound to colloidal organic matter. The model predicted the biphasic trend. Estimated values generated by the model were not significantly different from experimental values (P <.01). Wayne county PCB 153 desorption values were underestimated by the model.
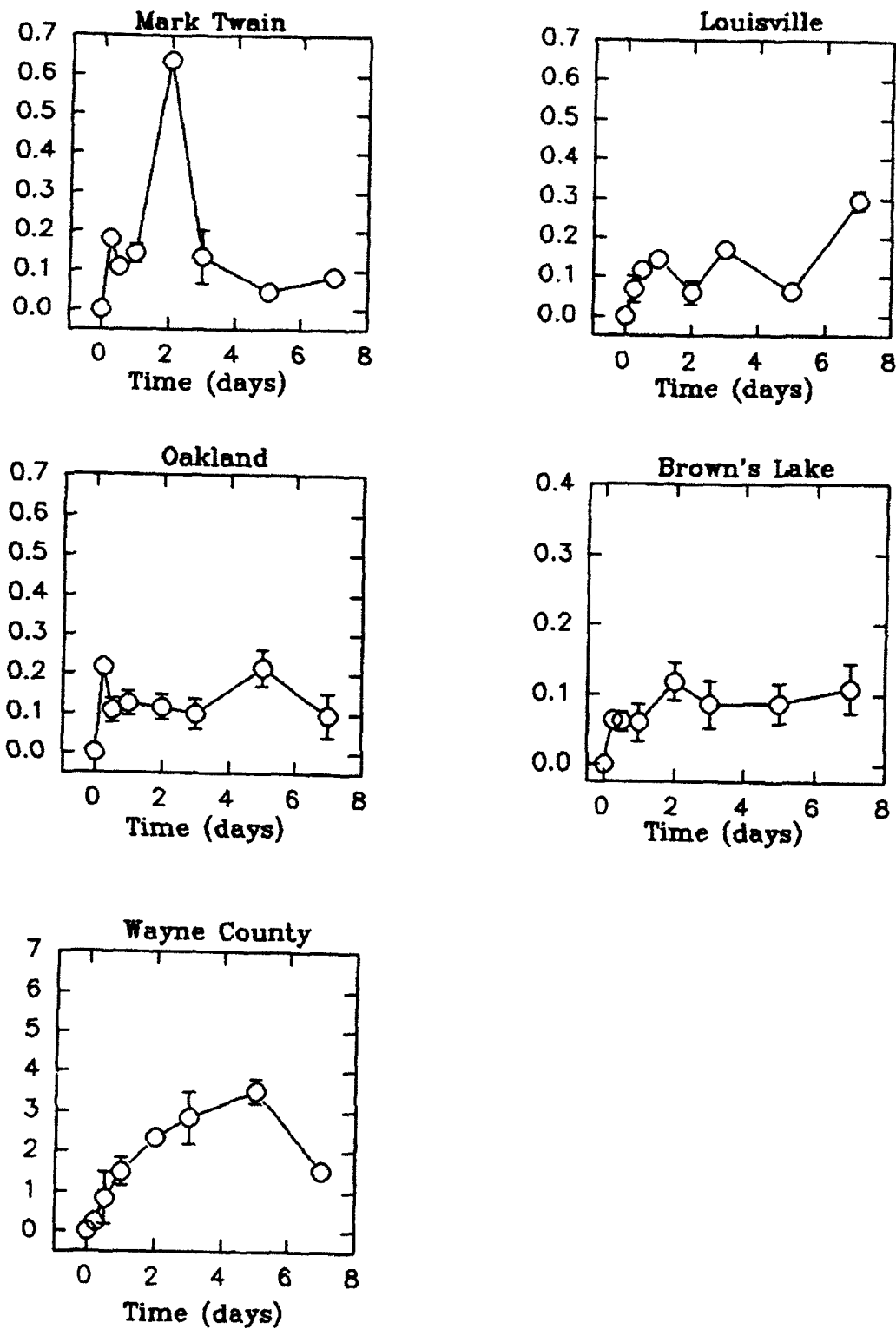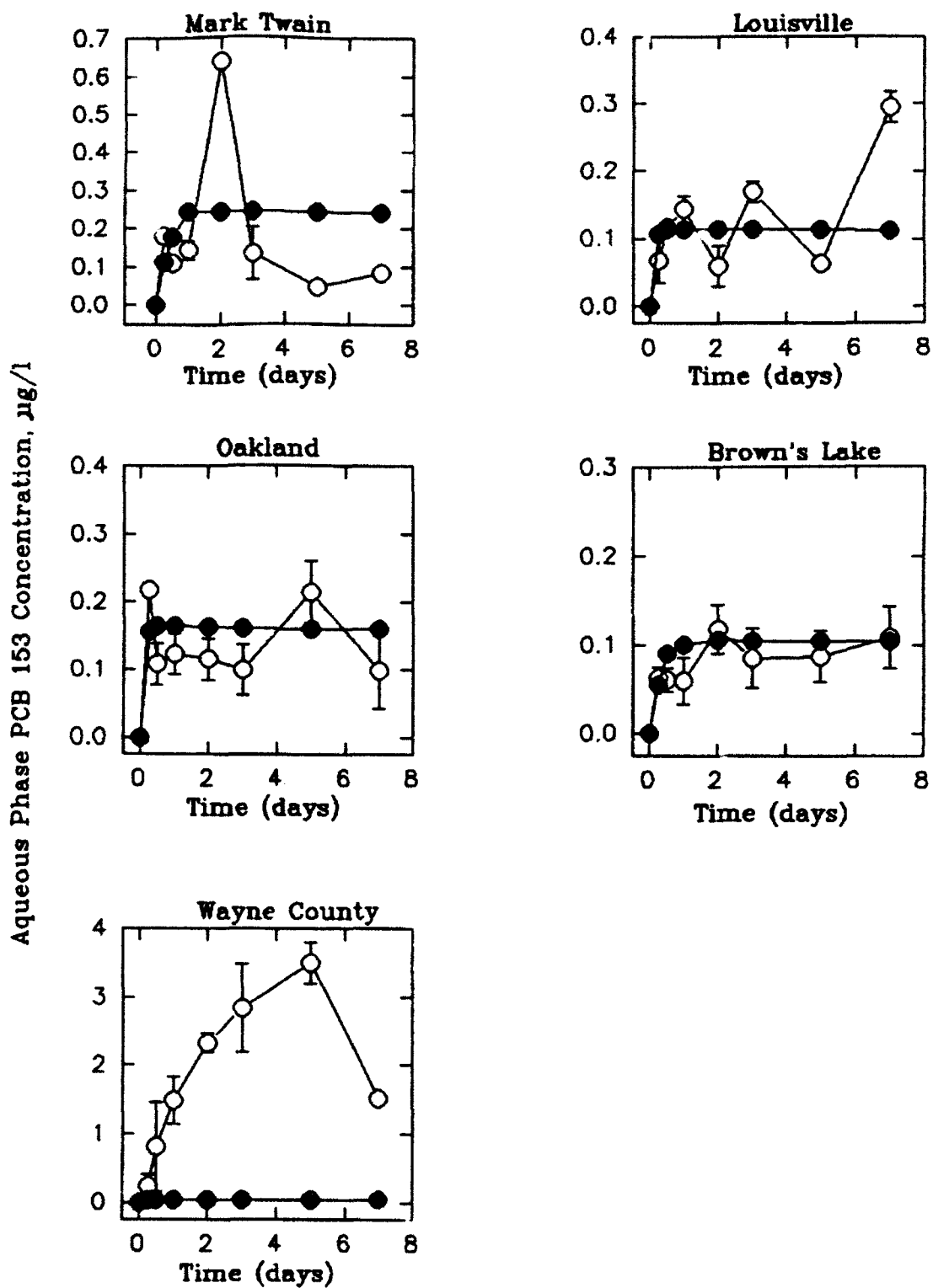
Figure 8. Experimental (hollow circle) and predicted (solid circle) kinetic curves for desorption of PCB 153

PART IV: DISCUSSION

Desorption Kinetics

23. Desorption kinetics for fluoranthene, naphthalene, and PCB 153 were generally biphasic, consisting of a rapid initial phase followed by gradual changes. Most of the changes (percent of steady-state values) occurred within the first few hours of incubation. For naphthalene desorption kinetics, unlike those for fluoranthene and PCB 153, the rapid phase was followed by a decrease. The decrease may be ascribed to several factors. Dissolved naphthalene is subject to photolysis by sunlight and artificial light and to bio-transformation or biogradation.

24. Several investigators have shown that naphthalene is easily bio-degraded (Lee and Ryan 1976; Lee and Anderson 1977; Vennberg 1977). Lee and Ryan (1976) measured microbial degradation rates as high as 4 $\mu g/\ell$ per day in the Skidway River. Lee and Anderson (1977) reported that after 1 day of expo-sure to natural river microbial populations, the amount of naphthalene was reduced to 50 percent because of adsorption and degradation. Vennberg (1977) observed that under aerobic conditions, 50 percent of naphthalene initially present was converted to CO_2 by microorganisms after 1 day. Naphthalene is highly soluble and is not adsorbed strongly to sediment. This may account for the relatively high concentration of naphthalene in the overlying water when compared with fluoranthene and PCB 153.

25. Fluoranthene and PCB 153 have log octanol/water coefficients greater than 4 and are highly insoluble. This indicates that PCB 153 and fluoranthene should strongly adsorb to particulate matter. The results of this study indicated that fluoranthene and PCB 153 are strongly bound and are not appreciably desorbed from the five sediments. The percentage of PCB 153 desorbed from the Wayne County sediment was higher than from other sediments. This result is somewhat surprising, since the total organic carbon content was higher in the Wayne county sediment. It is postulated that sediment organic matter is being mobilized into the overlying water and that PCB bound to dis-solved organic carbon may explain the elevated levels of PCB in the overlying water (Wu and Gschwend 1986).

26. Fluoranthene and PCB 153 displayed a rapid desorption component followed by a slower component. DiToro and Horzempa (1982) found that PCB 153 had two components, a rapid reversible component and a resistant desorption

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component. The rapid component observed in this study may correspond to DiToro and Horzempa's reversible phase, while the slowly released fraction may correspond to their resistant component. DiToro and Horzempa (1982) found that while adsorption was rapid, the reverse process was slow, because a significant portion of the sorbed chemical was highly resistant to release. Karickhoff and Morris (1985) distinguished between the labile or rapidly desorbing component and the nonlabile or slowly desorbing component. The nonlabile phase appears to be derived from nonsurface sorbent, accessed by highly retarded molecular diffusion, while the labile phase is a surface or external phenomenon. Oliver (1985) suggested that hydrophobic chemicals such as PCBs are present in a continuous adsorbed state that becomes increasingly less susceptible to desorption over time.

27. Reversible and nonreversible concepts proposed by DiToro and Horzempa (1982) may be important when assessing the environmental impact of contaminated sediment on the overlying water column, particularly when the quantity desorbed is much less than the amount initially adsorbed. This information will be useful in developing remedial measures. For example, if allochthonous sources of contaminants are reduced or eliminated, the existing contaminants from suspended or bedded sediments will constitute a major source of contaminants to the overlying water.

28. Results from this study and previous studies conducted by Gunnison et al. (1991) showed that organic and inorganic contaminants are strongly bound to the sediment and that desorption is minor. Therefore, the magnitude and extent of the impact of contaminant mobilization from sediment on the overlying water column may be minimal and governed by the fate of the sediment, rather than by desorption.

RECOVERY Model

29. The RECOVERY model was limited to measurable system parameters, based on known physical and chemical processes. For the most part, plots generated by the model provided a reasonable fit to the experimental data with few exceptions. In instances where the model did not estimate desorption values, trends that were similar to those observed in the experimental data were predicted.

30. The RECOVERY model can be used to predict organic contaminant desorption. Incorporating easily measured or estimated parameters in the

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model enhanced and improved the capability for predicting desorption of organic contaminants from sediments. The overestimation of naphthalene desorption by the model may be ascribed to diffusion, high aqueous solubility of naphthalene, and the high decay coefficient input data. The high decay coefficient is recommended for naphthalene to predict worst-case conditions. This information is important. When appropriate management actions are taken to deal with worst-case conditions, such actions will also address less severe conditions.

31. Use of the model, model description and user's guide, and the data required to assess the potential impact of contaminated sediments on the overlying water using the RECOVERY model is found in Appendix A (Table A3). To apply the RECOVERY model, the user must provide data (i.e., hydrology, morphometry data, and system properties and compound properties) only if the contaminant under consideration is not listed in the model database.

32. To use RECOVERY to assess a site, the user should have site-specific information such as contaminant concentration, flow, surface area, depth of water, depth of contaminated sediments, average suspended solids in the water, organic carbon content of water and sediments, sediment particle size, and sediment porosity. In addition, information that may be more difficult to obtain but necessary includes resuspension velocity, burial velocity, and settling velocity of sediment. However, only two of the values are needed; the third value will be estimated by the model from a solids mass balance. Settling velocities can be estimated by determining an average particle size (from grain size analysis data) and then using Stokes' Law to estimate settling velocity for the average particle. Burial velocities can be estimated from long-term average deposition rates or from sediment dating.

33. The last group of data needed to run RECOVERY is properties of the specific contaminant. The RECOVERY model contains some of this information for compounds in its database (See Appendix A for list of compounds in the database). Three properties, Henry's constant, octanol-water partition coefficient, and molecular weight, are in the database. Molecular diffusivity and decay coefficients must be estimated from laboratory data or from the literature. Molecular diffusivity has a default value of 10^{-5} cm^2/sec. One source for decay coefficients is the Handbook of Environmental Degradation Rates. Groundwater Chemicals Desk Reference and US Environmental Protection Agency (1979) are excellent references for obtaining compound properties needed for a RECOVERY application.

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PART V: SUMMARY AND CONCLUSIONS

34. The K_d values determined experimentally indicate that desorption
was minor for all contaminants tested. The quantity of chemical desorbed was
much less (<1 to 11 percent) than the quantity initially adsorbed to the sedi-
ment. Therefore, the environmental fate of adsorbed fluoranthene and PCB 153
will be dictated by the transport fate of the sediment rather than by desorp-
tion. These results are consistent with adsorption/desorption results of
Gunnison et al. (1991). Gunnison et al. (1991) showed that PCB 151 became
tightly bound to the sediment and that long-term effects of desorption on
mobilization of PCB 151 would be minimal. They also showed that an inverse
relationship existed between K_d and sediment concentration. Therefore,
results from present and past studies suggest that an equilibrium approach is
appropriate for describing bed sediment interactions with the overlying water
for organic contaminants.

35. Partitioning models in which equilibrium between sorbed and dis-
solved species is assumed are sufficient to provide management level estimates
of the fate of contaminants. The RECOVERY model, which assumes that contami-
nants follow linear equilibrium sorption and first-order decay kinetics, is an
effective tool that can be used to predict organic contaminant desorption.
This information can be used by the USACE to assess the potential impacts of
contaminated sediment on the overlying water column of specific reservoir
projects.

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APPENDIX A: RECOVERY MODEL DESCRIPTION, USER'S GUIDE, AND
INSTALLATION AND RUN

MODEL DESCRIPTION

1. The RECOVERY model is an application and extension of frameworks developed previously (Chapra 1982, 1986, and Chapra and Reckhow 1983).* As in Figures A1 and A2, the system is idealized as a well-mixed surface water layer, underlain by a vertically stratified sediment column. The sediment is well mixed horizontally, but segmented vertically into a well-mixed surface layer and a deep sediment. The latter, in turn, is segmented into contaminated and uncontaminated regions. The specification of a mixed surface layer is included because an unconsolidated layer is often observed at the surface of sediments because of such processes as bioturbation and mechanical mixing.
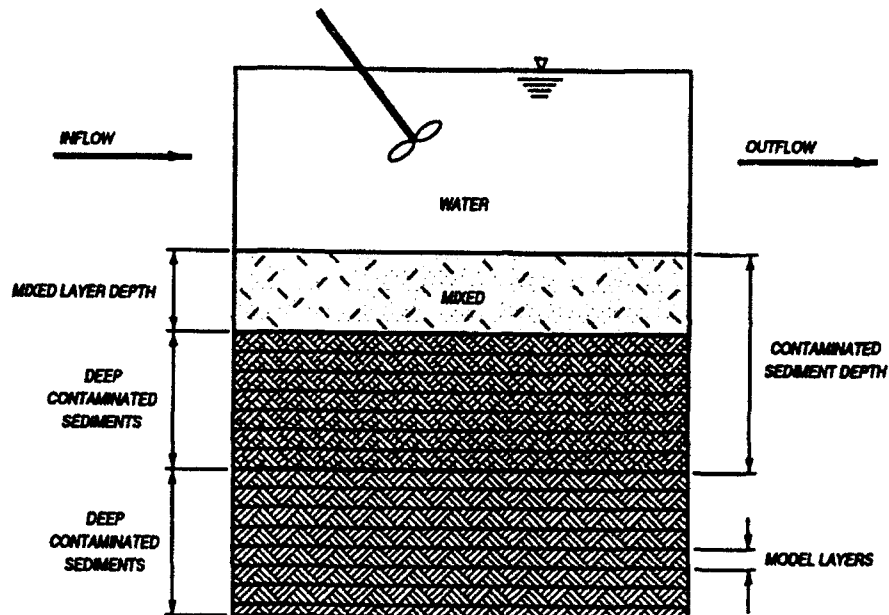
Figure A1. Physical configuration of RECOVERY

2. A list of assumptions used in the development of this model is included (Table A1).

Contaminant Mass Balances

3. A mass balance for the contaminant in the water can be written as

---

* References cited in this appendix are included in the References at the end of the main text.
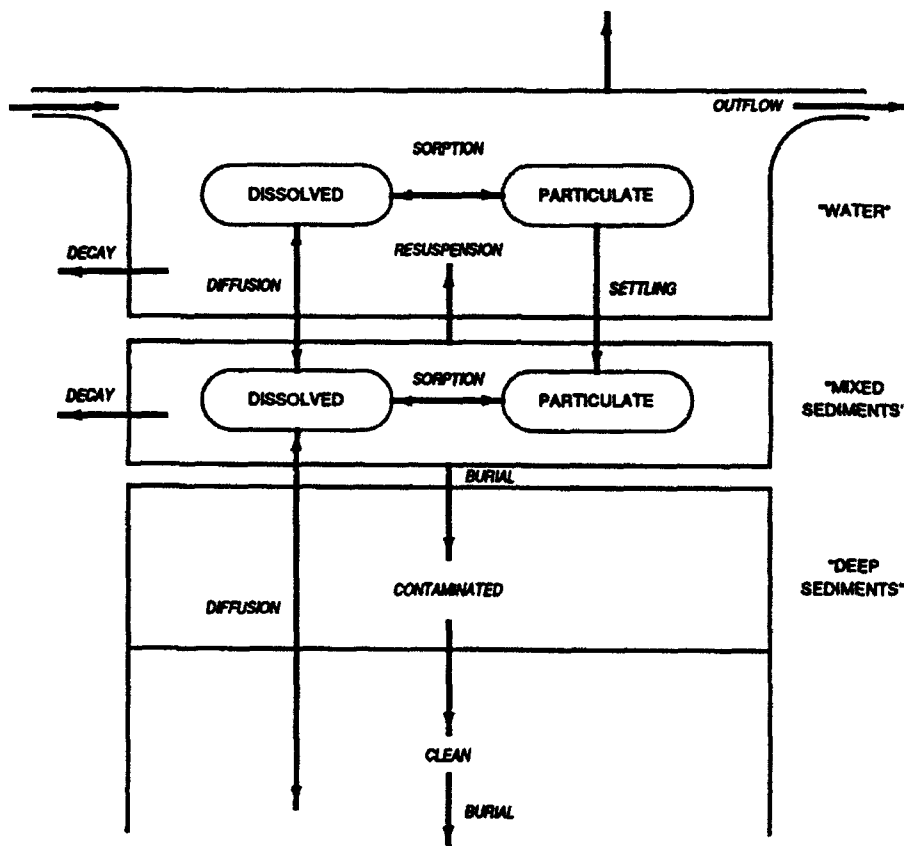
Figure A2. Schematic of RECOVERY

$$V_w \frac{dc_w}{dt} = Qc_i - Qc_w - k_w V_w c_w - k_v V_w c_w - \nu_s A_w F_{pw} c_w + \nu_r A_m c_m$$

$$+ \nu_d A_m \left(F_{dp} c_m - F_{dw} c_w \right) \tag{1}$$

where

V_w — volume of water body, m^3

c_w and c_m — concentrations of toxicant in water and mixed sediments, respectively, $\mu g/m^3$

t — time, years

Q — flushing flow rate, $m^3/year$

c_i — inflow concentration, $\mu g/m^3$, which reflects both direct and tributary loadings (in the present version of the model, this concentration is assumed to be zero)

Table A1

Assumptions Used in the Development of RECOVERY

1. Contaminant is of organic nature.

2. The water body is well mixed.

3. The "mixed" layer is well mixed.

4. In the deep sediments, contaminant concentration varies in the vertical direction only.

5. The initial concentration of the contaminant in the contaminated region is uniform throughout the region.

6. The initial concentration of the contaminant in the region below the contaminated region is zero.

7. The sediments are the only source of the contaminant to the water body.

8. The contaminant follows a linear equilibrium sorption isotherm.

9. The contaminant decays according to first order kinetics.

10. No compaction has occurred in the sediments.

11. The system is isothermal.

12. The water body is at 25 °C.

13. Only single component mass transfer is described. The movement of the contaminant is independent of the presence of other contaminants.

14. Flow-through is constant.

---

k_w = decay rate constant of the contaminant in the water, per year

k_v = volatilization rate of contaminant, per year

ν_s = settling velocity of particulate matter, m/year

A_w and A_m = surface areas of water and mixed sediment, respectively, m^2

F_{pw} = fraction of contaminant in particulate form in the water

ν_r = resuspension velocity of sediments, m/year

ν_d = diffusion mass transfer coefficient at the sediment-water interface, m/year

F_{dp} = ratio of contaminant concentration in the sediment pore water to contaminant concentration in total sediment

F_{dw} = fraction of contaminant in the dissolved form in the water

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4. The initial condition for Equation 1 is at $t = 0$, $c_w = c_{wo}$ (c_{wo} = initial concentration of contaminant in water).

5. A mass balance for the mixed-sediment layer can be written as

$$V_m \frac{dc_m}{dt} = -k_m V_m c_m + \nu_s A_w F_{pw} c_w - \nu_r A_m c_m - \nu_b A_m c_m + \nu_d A_m \left(F_{dw} c_w - F_{dp} c_m\right) \tag{2}$$

$$+ \nu_d A_m \left(F_{dp} c_s(0) - F_{dp} c_m\right)$$

where

> V_m = volume of mixed layer, m^3
>
> k_m = decay rate constant of the contaminant in the mixed layer, per year
>
> ν_b = burial velocity, m/year
>
> $c_s(0)$ = contaminant concentration at the top of the deep contaminated layer, $\mu g/m^3$

6. The initial condition for this equation is at $t = 0$, $c_m = c_{mo}$ (c_{mo} = initial concentration of contaminant in the mixed layer).

7. Both the deep contaminated and clean sediments can be modeled with one-dimensional advection-diffusion-decay equations of the form:

$$\frac{\partial c_s}{\partial t} = \phi F_{dp} D_s \frac{\partial^2 c_s}{\partial z^2} - \nu_b \frac{\partial c_s}{\partial z} - k_s c_s \tag{3}$$

where

> c_s = contaminant concentration in the deep sediments, $\mu g/m^3$
>
> ϕ = sediment porosity
>
> D_s = diffusion rate in the sediment pore water, $m^2/year$
>
> z = depth into the sediment, m, where $z = 0$ at the top of the deep sediments
>
> k_s = decay rate constant of the contaminant in the deep sediments, per year

8. The initial and boundary conditions for Equation 3 are:

> IC: at $t = 0$, $c_s = c_{so}$ ($z_m < z < L$)
>
> IC: at $t = 0$, $c_s = 0$ ($L < z < \infty$)
>
> BC 1:   at $z = z_m$, $J = J_{ms}$

$$\text{BC 2:} \quad \text{at} \quad z - \infty, \quad \frac{\partial c_s}{\partial z} - 0$$

where L - distance from the top of the mixed layer to the bottom of the contaminated layer, J - mass flux of the contaminant, $g/(m^2\text{-yr})$, J_{ms} - mass flux of the contaminant from the mixed layer to the sediment layer, $g/(m^2\text{-yr})$, and c_{so} - initial concentration of contaminant in the deep sediment layer.

9. The F's in Equations 1-3 are dimensionless ratios that reflect how the contaminant partitions between solid matter and water, assuming a linear sorption mechanism. Denoting the contaminant as A, they are defined as

$$F_{pw} = \frac{K_{dw}S_w}{1 + K_{dw}S_w}$$

$$= \left[\frac{\dfrac{\text{Mass of A (Particulate Form)}}{\text{Total Volume}}}{\dfrac{\text{Mass of A (Dissolved Form) + Mass of A (Particulate Form)}}{\text{Total Volume}}} \right]_{\text{water body}}$$

(4)

$$F_{dw} = 1 - F_{pw} = \frac{1}{1 + K_{dw}S_w}$$

$$= \left[\frac{\dfrac{\text{Mass of A (Dissolved Form)}}{\text{Total Volume}}}{\dfrac{\text{Mass of A (Dissolved Form) + Mass of A (Particulate Form)}}{\text{Total Volume}}} \right]_{\text{Water Body}}$$

(5)

$$F_{dp} = \frac{1}{\phi + K_{ds} (1 - \phi)\rho}$$

$$= \left[\frac{\dfrac{\text{Mass of A (Dissolved Form)}}{\text{Volume of Pore Water}}}{\dfrac{\text{Mass of A (Dissolved Form) + Mass of A (Particulate Form)}}{\text{Total Volume}}} \right]_{\text{Sediment}}$$

(6)

where

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K_{dw} and K_{ds} — contaminant partition coefficient in the water and sediments, respectively, m^3/g

s_w — suspended solids concentration in the water, g/m^3

ρ — density of sediment solids, g/m^3

Note that the model allows different values of this parameter to be employed in the mixed layer and the vertically segmented sediments (F_{dpm} and F_{dps}).

10. The decay rate constants k_w, k_m, and k_s, represent all mechanisms for decay except volatilization, which is accounted for separately. These mechanisms include photolysis, hydrolysis, and bacterial degradation.

11. The mass transfer coefficient for diffusive sediment-water exchange is related to more fundamental parameters by

$$\nu_d = \frac{\phi D_s}{z'} \tag{7}$$

where

ϕ — porosity

D_s — diffusion coefficient in the sediment pore water, $m^2/year$

z' — characteristic length over which the gradient exists at the sediment-water interface, m

Note that a value of 1 cm is assumed for z' after Thomann and Mueller (1987). Also, D_s is related to molecular diffusivity D_m by the relation (Berner 1980; Manheim and Waterman 1974)

$$D_s = D_m \phi^2 \tag{8}$$

Solids Budget

12. The velocity terms--ν_s, ν_r, and ν_b--in Equations 1 and 2 are computed according to a steady-state mass balance for mixed-sediment layer solids as described by Chapra and Reckhow (1983). The mass balance is

$$0 = \nu_s A_w s_w - (\nu_r + \nu_b) A_m (1 - \phi) \rho_p \tag{9}$$

13. The framework assumes that suspended solids concentration s_w is given. Therefore, if two of the three velocities are specified, Equation 9 can be employed to calculate the third.

14. In addition to these transfer velocities, the other facet of the model related to the solids budget is the sediment porosity. Different porosities are allowed for the mixed layer and the deep sediments. Within these regions, porosity is constant. This means that compaction is not included and has no impact on the accuracy of the model.

Default Parameters

15. Several parameters in the above framework are provided by the software as default values. These are suggested values that represent first estimates and can be easily modified by the user.

Volatilization rate

16. The volatilization rate is computed by

$$k_v = F_{dw} \frac{\nu_v}{z_w} \tag{10}$$

where ν_v = a volatilization transfer coefficient, m/year, which can be computed according to the Whitman two-film theory as

$$\nu_v = \frac{K_l K_g H_e}{K_g H_e + K_l} \tag{11}$$

where H_e = a dimensionless Henry's coefficient that is related to the common form, $H_{e'}$, atm m^3/mole, by

$$H_e = \frac{H_{e'}}{RT} \tag{12}$$

where

R = universal gas constant, 8.206×10^{-5} atm m^3/(mole K)

T = absolute temperature, °K

A temperature of 298 °K (25 °C) is assumed in the model.

17. The parameter K_g is a gas-film mass transfer coefficient (meters per year) that can be related to wind speed, U_w (meters per second), and molecular weight, MW (grams per gram mole), by (Mills et al. 1982)

$$K_g = 61320 \left[\frac{18}{MW}\right]^{0.25} U_w \qquad (13)$$

18. The parameter K_l is a liquid-film mass transfer coefficient (milligrams per year) that can be related to wind speed, U_w (meters per second), and molecular weight, MW (grams per gram mole), by (Mills et al. 1982; Banks 1975; Banks and Herrera 1977)

$$K_l = 365 \left[\frac{32}{MW}\right]^{0.25} (0.728U_w^{0.5} - 0.317U_w + 0.0372U_w^2) \qquad (14)$$

Partition coefficient

19. The partition coefficient for organic contaminants is computed via (Karichhoff et al. 1979)

$$K_d = 0.617 f_{oc} K_{ow} \qquad (15)$$

where

f_{oc} — weight fraction of organic carbon in the solid matter, g-orgC/g

k_{ow} — octanol-water partition coefficient, (mg/m^3-octanol)/(mg/m^3-water)

Note that the model assumes a default of 0.05 for f_{oc}.

Numerical Methods

20. The coupled set of differential equations is solved numerically. The two first-order are solved using an adaptive step size, fourth-order Runge-Kutta method (Press et al. 1986). The partial differential equation is solved using the Crank-Nicolson technique (Chapra and Canale 1988).

21. The total number of years for which the model is run is determined by approximating the time required for the contaminant concentration in the

water to decrease to 10 percent of the maximum value achieved. This is determined by using an analytical solution for the case where only the water and a single well-mixed layer are considered. This procedure has been found effective in approximating the total time.

22. Use of the RECOVERY program is described in this section. Two
files are required to run this program--RECOVERY.EXE and CORPCOMP.DAT.
CORPCOMP.DAT contains the chemical database information. The other files
included on the distribution disk are only required for specific hardware
systems and to alter the database. (See Changing the Database and Specific
System Issues below.) Source code for the model is also included (See Model
Source). Do not run RECOVERY from a write-protected disk, as this will result
in an error.

23. To start the program, move to the directory that contains the soft-
ware and type a:RECOVERY at the DOS prompt. The first screen is a title
screen. Press ENTER to view the introduction screen which follows. Press
ENTER again and choose between creating a new file and retrieving data from an
existing data file. If the second selection is made, any files ending in .REC
and the subdirectories located in the current directory are displayed. The
.REC files are the data files that are created when saving a run made by
RECOVERY. (This will be discussed later). If your file is not located in the
current directory or in one of the listed subdirectories, press BACKSPACE and
specify the path name to your file. Your .REC file should then be displayed.
After a file is chosen, you can either view and/or change the input file or
just run the model using that data file. If "create a new file" is chosen, a
list of compounds is displayed. The properties of 18 compounds are included
in the database. If the compound under consideration is not listed, choose
number 0. The selection is made by moving the cursor to the desired selection
using the arrow keys and pressing ENTER.

24. If selection 0 was made, a screen appears to enter the name of the
contaminant. As the user types, the name will appear in the highlighted area.
Corrections can be made by using the BACKSPACE or DELETE keys. After the name
has been typed in, press ENTER to enter the name. If changes are necessary at
this point, pressing F2 will allow modification of the name. If the user
starts to type without pressing F2, the first entry is lost and the new name
appears. This editing process is similar to that used by Lotus 1-2-3 (R) and
is used on all input screens. Press F10 to store the data and advance to the
next screen.

25. The next five screens are used to enter or change input values.
After typing in a cell, the user must press ENTER before proceeding to the

next cell. The first morphometry and hydrology screen should be displayed.
If a different compound is desired at this point, pressing ESCAPE will allow
this change. The user may change or leave the water concentration at the
default value of zero. Three of the next four values need to be entered.
Press F9 to calculate the fourth and its values will be displayed. When all
the data is entered, press F10 to store the values and advance to the next
screen. If invalid values are entered, a message will appear at the bottom of
the screen.

26. The next screen is for the contaminated sediments layer. If
nothing is changed, the default values will be used. Press F10 to continue.
System properties are listed on the next screen. Default values are listed
for the first eight variables. These values can be changed as described
above. Since the three velocity values are interrelated, two of the three
values need to be entered. Typical values are listed in the center column.
After entering two values, press F9 to calculate the third value. It will
appear near the bottom of the screen. Press F10 to store the data and
proceed.

27. The next two screens list contaminant properties. Default values
are listed in the far right column and will be specific to the selected
compound if it is in the database. These values will be used unless the user
changed them in the center column. The second screen also contains intermedi-
ate values calculated from the previously entered data (e.g., Fdw, Kdw).
Press F10 to store and advance.

28. If the user wants to return to a previous screen in the input pro-
cess described above, he/she can press ESCAPE until the desired screen
appears.

29. The next screen serves as a check to see if the entered data are
correct, and if not, the user can return to the input screens. Selecting the
third option starts the model. If graphics capabilities are available on the
system being used, the concentration profile in the deep sediments is dis-
played. The total number of years is calculated as the approximate time when
the water concentration decreases to 10 percent of its maximum value. Since
the numerical method uses an adaptive step size, the time between profile
displays will not be even. When the computation is finished, a message
appears in the lower right hand corner of the screen.

30. After a key is pressed, another menu appears. If one of the first
five options is chosen or number 8, this menu appears again so another

selection can be made. Options 1-4 are graphics plots. If the system being used does not have graphics capabilities, a message appears informing the user of this; a key can be pressed to return to the menu. Results on systems having graphics capabilities other than those listed in the program feature section of this report will be unpredictable. The first two plots are graphs of the contaminant concentration in the water layer and the mixed layer, respectively, versus time. The third plot shows the flux of the contaminant from the sediments to the water versus time. A graph of the volatilization rate of the contaminant will be displayed if number 4 is selected. These results can be printed by typing Shift+Print Screen. Select number 5 to print a table of results on the printer. Number 6 should be selected to make modifications to the existing run and number 7 should be used to return to the beginning of the program. Choose number 8 to save the existing run. The user will be prompted for a file name to be used to store the results. Choosing number 9 will result in exiting the program.

Changing the Chemical Database

31. Currently, data for 18 chemicals are included in the data file CORPCOMP.DATA. This file can be changed and enlarged to include a maximum of 39 compounds. Changes are made by altering the file CORPSDAT.BAS, which is included with the distribution disk. This file contains the following data for a compound:

```
Name
Molecular Weight
Octanol-Water Partition Coefficient
Henry's Constant
Molecular Diffusivity
Decay Constants - water, dissolved phase
                  water, particulate phase
                  mixed layer, dissolved phase
                  mixed layer, particulate phase
                  deep sediments, dissolved phase
                  deep sediments, particulate phase
```

Additions and changes are made by altering or adding data statements to the file CORPSDAT.BAS and running the program. Errors will occur in RECOVERY when there are more than 39 compounds, a compound name with greater than 28 letters exists, or additional parameters are added to the data statements.

Model Source

32. To access the model source code in the QuickBasic environment, type qb recovery /1 reclib when you are in a directory containing QuickBASIC Version 4.5 and the following files appear (included on the distribution disk).

RECOVERY.MAK
RECOVERY.BAS
CRANK.BAS
ADAPTEST.BAS
MODEL.BAS
RECLIB.QLB

Program Features

33. A list of data needed to run this program can be found in Table A2. Since the compound properties for several contaminants are included in the provided database, the user needs to provide compound properties only if the contaminant under consideration is not one that is in the database. The values in the database included on the distribution disk are listed in Table A3. The data file can be changed as described in the section "Changing the Chemical Database" on the previous page.

34. The data are entered on a series of input screens with editing capabilities. The user can easily page forward and backward through the screens while entering data. On-line help is also available. If any of the entered data are invalid, an error message appears instructing the user to reenter the data. For computers with graphic display capabilities, the deep-sediment concentration profile will be displayed during the model computation.

35. The final results are displayed as plots on the screen and can be printed on a printer using the Shift+Print Screen command. Numerical results can be dumped to the printer also. The plots are:

   a. Contaminant concentration in the water versus time.

   b. Contaminant concentration in the mixed layer versus time.

   c. Flux of the contaminant from the sediments into the water versus time.

   d. Volatilization losses of the contaminant from the water versus time.

36. The input data can be stored on a disk and retrieved for later use. The user can also easily return to the input screens to make modifications.

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Table A2

Input Data for the Recovery Model

Water Column Morphometry/Hydrology: (3 specified, 4th computed)

       Flow through, m^3/year
       Residence time, year
       Surface area, m^2
       Water depth, m

Water Layer:

       Initial concentration, $\mu g/m^3$

Contaminated Sediments:

       Depth of contaminated sediment layer, m
       Depth of mixed Layer, m
       Mixed layer surface area, m^2
       Initial concentrations, $\mu g/m^3$
           Mixed layer
           Deep contaminated sediments

System Properties:

       Suspended solids concentration in water, g/m^3
       Mixed layer porosity
       Deep sediment porosity
       Sediment particle density, g/m^3
       Wind speed, m/sec
       Fraction organic carbon, g-orgC/g-dry wt solids
           Water layer
           Mixed layer
           Deep contaminated sediments

       Two of the following three velocities:
           Resuspension velocity, m/sec
           Burial velocity, m/sec
           Settling velocity, m/sec

Compound Properties:

       Molecular diffusivity, cm^2/sec
       Decay coefficients, year: particulate - water
                             dissolved - water
                             particulate - mixed layer
                             dissolved - mixed layer
                             particulate - deep sediments
                             dissolved - deep sediments
       Henry's constant, atm-m^3/gmole
       Octanol-water partition coefficient
       Molecular weight, g/gmole

Table A3

Compound Properties*

Compound	Henry's Constant @ 25 °C atm m³/gmole	log(K_{ow})	Molecular Weight g/gmole
Chlordane	4.8×10^{-5}	2.78	409.6
DDT	3.9×10^{-5}	5.00	354.5
Dieldrin	2.0×10^{-7}	3.54	381.0
Lindane	4.9×10^{-7}	3.70	290.0
Arochlor 1242	8.4×10^{-3}	6.72	328.4
Arochlor 1248	3.5×10^{-3}	6.00	295.0
Arochlor 1254	2.8×10^{-3}	6.00	326.0
Arochlor 1260	7.1×10^{-3}	6.50	361.0
Benzene	5.5×10^{-3}	2.10	78.0
Chlorobenzene	3.7×10^{-3}	2.98	112.6
Ethylbenzene	8.7×10^{-3}	3.15	106.0
Pentachlorophenol	3.4×10^{-6}	5.00	266.0
Phenol	1.3×10^{-6}	1.46	94.1
Toluene	6.7×10^{-3}	2.70	92.0
Anthracene	1.7×10^{-3}	4.45	178.2
Benzo(a)pyrene	7.2×10^{-7}	5.00	252.0
Naphthalene	4.3×10^{-4}	3.36	128.0
Chloroform	4.2×10^{-3}	1.95	119.0
Fluoranthene	1.6×10^{-2}	5.33	202.3

* Values for Henry's constant, K_{ow}, and molecular weight are from Lyman et al. (1982), Schnoor et al. (1987), and Thomann and Mueller (1987). The default values for all molecular diffusivities are 5×10^{-6} cm²/s. The default values for all decay coefficients are zero.

37. This program is written in Microsoft QuickBASIC 4.5 and has been written for the following combinations of graphic adapters and displays:

> CGA and Color Display
> EGA and Monochrome Display
> EGA and Color Display
> EGA and Enhanced Color Display
> VGA and Monochrome Display
> VGA and Color Display
> Hercules Video Card and Monochrome Display

38. A math coprocessor is not required to run RECOVERY. The use of a coprocessor, however, will decrease the computation time.

System Specific Issues

39. Some procedures that are specific to particular hardware systems are described below. If you have problems running RECOVERY, please consult these.

Use of Hercules Graphics Card

40. If your system has a Hercules Graphics Card, you will need to load the Hercules driver before running the program. The driver, MSHERC.COM, ((C) Copyright Microsoft Corporation, 1987, 1988) is provided on the distribution disk. To run the program, type MSHERC. If you do not run this program, the model should run but not display any graphics.

Strange sediment profile results

41. If your system has all of the following characteristics, you may have floating-point math problems.

      a. Uses MS-DOS Version 3.20.

      b. Boots from a hard drive.

      c. Has a math coprocessor (for instance, an 8087 chip).

These problems can be avoided by booting the computer from a floppy disk drive instead of the hard drive.

WARNING: If you have floating-point math problems, the model information will not be correct. This should be evident by the graphical results.

Use of a Compaq 386 with a math coprocessor

42. If you are using a Compaq 386 that has a math coprocessor installed, RECOVERY may crash. To use the model, turn the coprocessor off by adding the line, SET NO87 = ' ', to the CONFIG.SYS file and rebooting your machine.

INSTALLATION AND RUN

Installation

43. Two BAT files are included in the RECOVERY diskette to aid in the installation and execution of RECOVERY. The RECOVERY program can be installed in the hard disk of your computer by following the steps outlined below:

   a. Turn your computer on.

   b. Insert the RECOVERY diskettes into drive A: or B:.

   c. At the DOS prompt (> or C:>), type A: and press ENTER.

   d. At the A:> prompt, type INSTALL. Press ENTER.

   e. The BAT file INSTALL will start the installation.

Note: Answer all questions and make the requested changes.

RUN

44. To run the RECOVERY program follow these steps:

   a. At the DOS prompt (> or C:>), type RECOVERY (or recovery).

   b. At the Dos prompt (> or C:>), type RECOVERY R and view with GRAPHER the water concentration and mixed sediment concentration.

NOTE: Make sure the modifications that were explained in the INSTALL are done and the RECOVERY.BAT is in a directory that must be included in the path statement.

Notes on RECOVERY.BAT

45. This file runs the RECOVERY program from anywhere in your hard disk. However, if this program is installed in a drive other than "C:," it must be modified. If the program is installed in drive "D:," edit the RECOVERY.BAT file by changing "c:" to "d:" where indicated. The changes will be indicated by "rem" before and after the statements that need modification.

46. The graphics package GRAPHER is not included with RECOVERY. If an auxiliary graphics is needed, GRAPHER is a suggested software package. However there are other graphics packages that will perform similar tasks. The use of GRAPHER does not constitute an endorsement of the product.

Files Included in the Diskette

README	1ST	This file.
ANSWER	COM	A utility that allows interactive bat files.
INSTAL	BAT	Interactive installation program. Allows the user to install RECOVERY in a selected hard disk drive from the floppy drive A:
RECOVERY	BAT	The bat file is used to run RECOVERY with or without using the GRAPHER software.
RECOVERY	<DIR>	Location of all RECOVERY files. Directory of A:\RECOVERY.

Utilities

COMPLINK	BAT	Bat files for compiling and linking RECOVERY using
RECOMLIN	BAT	QUICK BASIC 4.5.
MSHERC	COM	Utility for computers with a Hercules Graphics Monitor; use is described in the enclosed manual.
RECLIB	LIB	Libraries for recompiling RECOVERY using Microsoft
RECLIB	QLB	Quick Basic 4.5 including the graphics subroutines
RECOVERY	MAK	and other proprietary software.
RECOVERY	EXE	The executable file.
CORPCOMP	DAT	Program data set to modify, add, or delete the
CORPSDAT	BAS	RECOVERY database. Run under Quick Basic 4.5.
CRANK	BAS	The RECOVERY model RECOVERY.BAS calls the Graphic
MODEL	BAS	subroutines and runs the model (MODEL.BAS).
RECOVERY	BAS	CRANK.BAS and ADAPTEST.BAS are the numerical subrou-
ADAPTEST	BAS	tines to solve the sediment model (layers) or the water and mixed sediment compartments.
RESUL	DAT	File with the results of the last run.
ANTH	REC	Data files of different RECOVERY runs enclosed as
CHLOR	REC	examples for future runs.
PCB	REC	
DDE	REC	
DIELDRIN	REC	
LINDANE	REC	
GRAPHS	<DIR>	Location of files that interact with GRAPHER. Directory of A:\RECOVERY\GRAPHS
RESUL	DAT	File with the results of the last run.
SEDDATA	GRF	Files created for viewing the results using the
SEDDATA	PLT	software GRAPHER.
WATDATA	GRF	
WATDATA	PLT	
TITLESED	TXT	
TITLEWAT	TXT	
X-ALLDAT	AXS	
Y-SEDIM	AXS	

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```
Y-SEDIM2   AXS
Y-WATER    AXS
```

RECOVERY

A Decision Support Model for Screening the Fate of In-Place
Contaminated Sediments in Aquatic Environments

June, 1989
Beta Test Version 1.0

Written for   The U.S. Army Corps of Engineers
Waterways Experiment Station
and
New England Division

Written by   Jean M. Boyer and Steven C. Chapra
Center for Advanced Decision Suppport
in Water and Environmental Sytems
University of Colorado
Boulder, CO   80309-0428

MsHerc program (C) Copyright '87, '88 Microsoft Corp. All Rights reserved.

Press any key to continue.

SCREEN 1

This program is a tool for screening the fate of in-place contaminated
sediments in aquatic environments. It predicts the concentration of a
contaminant in the water, the mixed sediment layer and in the deep sedi-
ments over time. The flux of the contaminant from the sediments into
the water is also predicted. Note that the total number of years for which
the model is run is determined by approximating the time required for the
toxic concentration in the water to decrease to 10% of the maximum value
achieved, up to a maximum of 100 years.

Please refer to the documentation accompanying this software for de-
tailed instructions and model theory.

If you need help while entering data into an input screen, press F1.
Press Ctrl+Break to terminate the program at any time. Press
Shift+Print Screen to print a graph displayed on the screen.

Press any key to continue.

SCREEN 2

A22

Highlight your choice and press Enter or
press the number preceding your selection.

1. Create a new file.

2. Retrieve data from an existing file.

SCREEN 3

These are the .REC files and subdirectories listed in the specified
directory. Highlight one of these using the up and down arrows and
press Enter or press Backspace to specify an alternative directory.
Press escape to return to the previous screen.

Directory: C:\QB45\

CHLOR.REC   ANTH.REC

SCREEN 4a

The properties of the following contaminants are included in the database. If the contaminant you want to consider is not listed, choose 0.

Highlight your choice using the arrow keys and press ENTER.

0.	Compound Not Listed	10.	Chlorobenzene
1.	Chlordane	11.	Ethyl Benzene
2.	DDT	12.	Pentachlorophenol
3.	Dieldrin	13.	Phenol
4.	Lindane	14.	Toluene
5.	Arochlor 1242	15.	Anthracene
6.	Arochlor 1248	16.	Benzo(a)pyrene
7.	Arochlor 1254	17.	Naphthalene
8.	Arochlor 1260	18.	Chloroform
9.	Benzene		
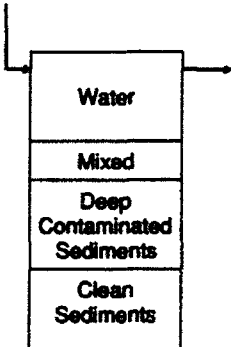
SCREEN 4b

Highlight your choice and press Enter or press the number preceding your selection.

1.   View/Change Input file.

2.   Run Using Input File.

SCREEN 5

SCREEN 6

SCREEN 7

A25

SYSTEM PROPERTIES

Suspended Solids Concentration in Water (g/m^3):	2.00
Mixed Sediment Porosity:	0.85
Deep Sediment Porosity:	0.85
Mixed Sediment Particle Density (g/m^3):	2.50E+06
Deep Sediment Particle Density (g/m^3):	2.50E+06
Wind Speed (m/sec):	5.00
Weight fraction carbon in solid - water:	5.00E-02
Weight fraction carbon in solid - mixed layer:	5.00E-02
Weight fraction carbon in solid - sediments:	5.00E-02

INPUT TWO OF THE FOLLOWING VELOCITIES AND PRESS F9:

Velocity (m/yr)	Typical Value	Value for this Run
Resuspension Velocity:	0.00E+00	0.00E+00
Burial Velocity:	5.34E-04	5.00E-04
Settling Velocity:	1.00E+02	
Calculated Settling Velocity (m/yr):		9.37E+01

Help-F1   Edit-F2   ReCalc-F9   Store Data and Advance-F10

SCREEN 8

CHLORDANE PROPERTIES

Property	Value for This Run	Default Value
Molecular Diffusivity (cm^2/sec)	5.0E-06	5.0E=06
DECAY COEFFICIENTS (1/yr)		
Dissolved Contaminant:		
In Water	0.000	0.010
In Mixed Layer	0.000	0.010
In Deep Sediments	0.000	0.010
Particulate Contaminant:		
In Water	υ.000	0.010
In Mixed Layer	0.000	0.010
In Deep Sediments	0.000	0.010

Help-F1   Edit-F2   Store Data and Advance-F10

SCREEN 9

CHLORDANE PROPERTIES

Property	Value for This Run	Default Value
Henry's Con. (atm-m^3/gmole)	4.80E-05	4.80E-05
Molecular Weight	409.60	409.60
Octanol-Water Partition Coeff.	6.03E+02	6.03E+02
(mg/m^3 octanol)/(mg/m^3 water)		
CALCULATED DATA		
Fdw	1.00E+00	1.00E+00
Fpw	3.72E-05	3.72E-05
Fdpm	1.28E-01	1.28E-01
Fdps	1.28E-01	1.28E-01
Partition Coefficients		
Kdw	1.86E-05	1.86E-05
Kdm	1.86E-0.5	1.86E-0.5
Kds	1.86E-0.5	1.86E-0.5
Volatilization rate (1/yr)	1.14E+01	1.14E+01

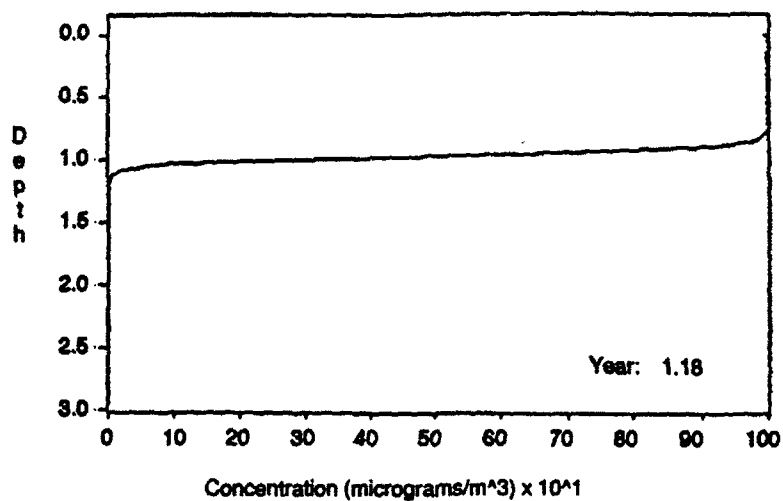Help-F1   Edit-F2   ReCalc-F9   Store Data and Advance-F10

SCREEN 10

Highlight your choice and press Enter or
press the number preceding your selection.

1. Return to input screens. Change compound.

2. Return to input screens. Same compound.

3. Entered data are ok. Continue.

SCREEN 11

Concentration Profile Below the Mixed Sediment Layer (depth in m)
Chlordane

Year: 1.18

Concentration (micrograms/m^3) x 10^1

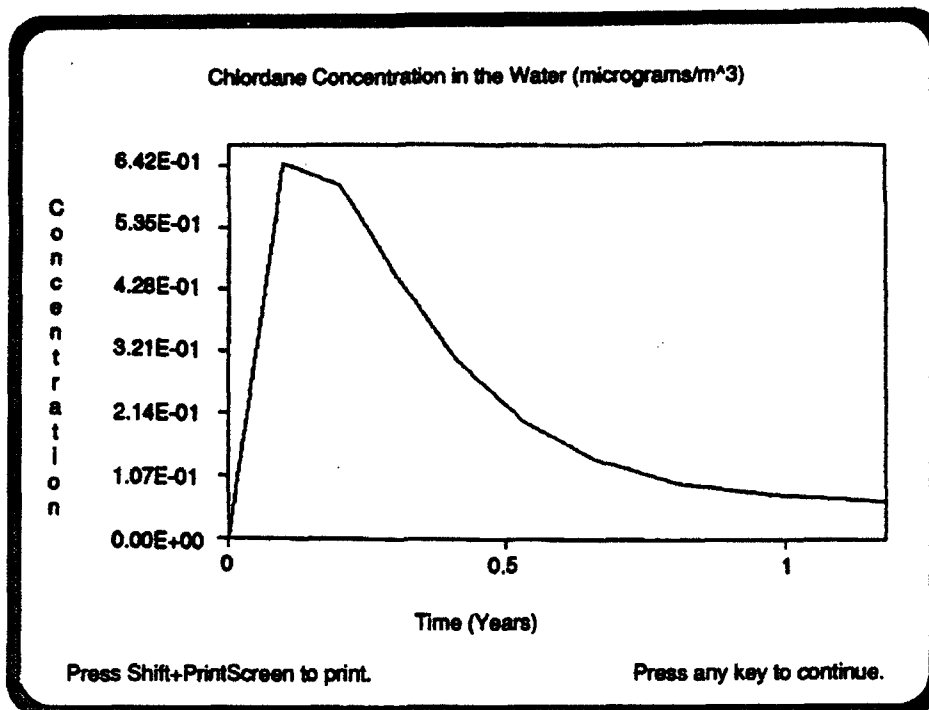Press any key for output.   Total years: 1.0
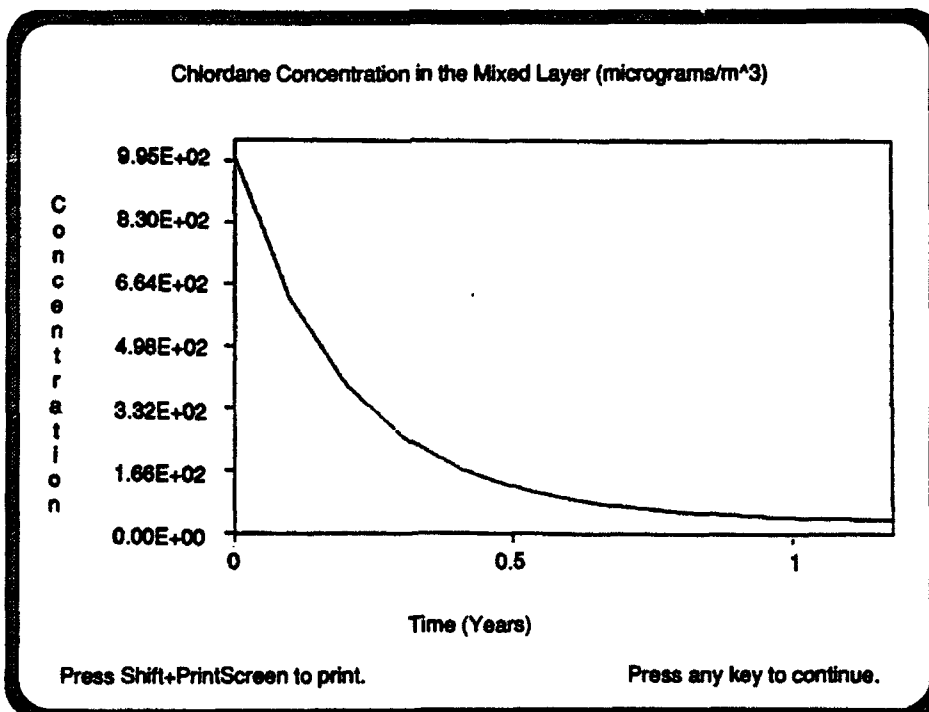
SCREEN 12

Highlight your choice and press Enter or
press the number preceding your selection.

1. Plot Contaminant Concentration in Water.

2. Plot Contaminant Concentration in Mixed Layer.

3. Plot Flux of Contaminant from Sediments into Water.

4. Plot Volatilization Rate from the Water.

5. Print Table of Results to Printer.

6. Return to Input Screens.

7. Return to Beginning of Program.
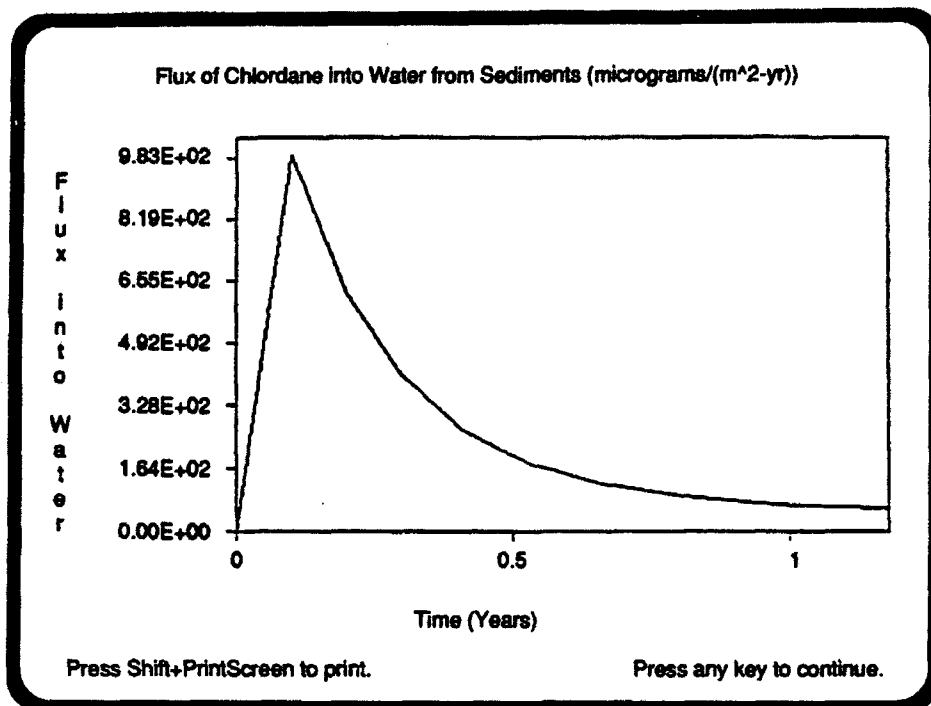
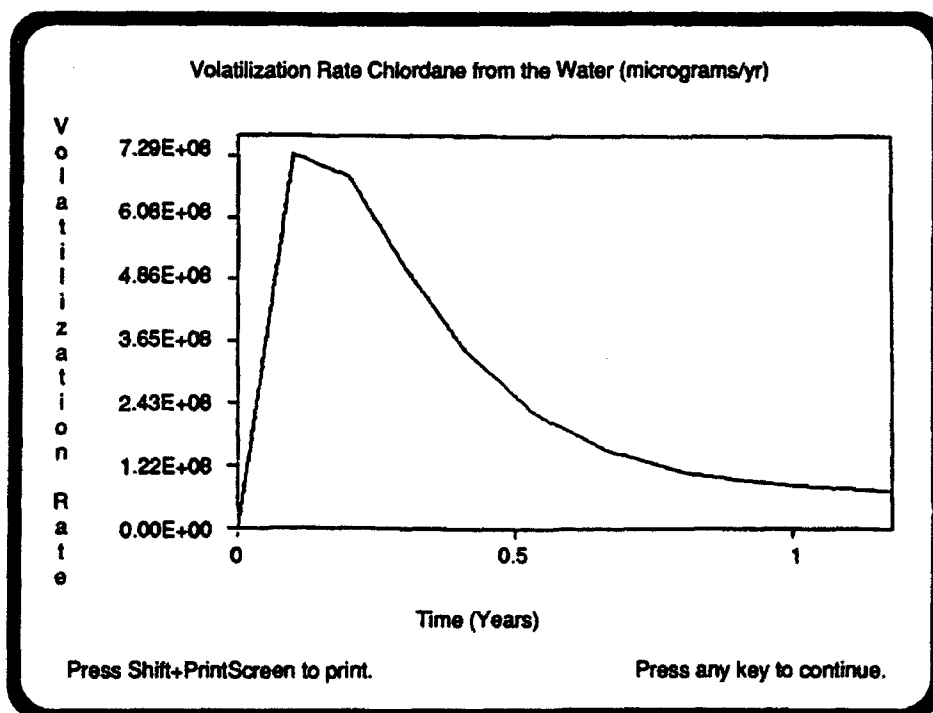8. Save the Input Data for This Run.

9. Exit Program.

SCREEN 13

A28

Chlordane Concentration in the Water (micrograms/m^3)

Press Shift+PrintScreen to print. Press any key to continue.

SCREEN 14

Chlordane Concentration in the Mixed Layer (micrograms/m^3)

Press Shift+PrintScreen to print. Press any key to continue.

SCREEN 15

A29

Flux of Chlordane into Water from Sediments (micrograms/(m^2-yr))

SCREEN 16

Volatilization Rate Chlordane from the Water (micrograms/yr)

SCREEN 17

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13. ABSTRACT (Maximum 200 words)

Laboratory studies and model simulations were conducted to investigate and predict desorption kinetics for several polycyclic aromatic hydrocarbons and polychlorinated biphenyl 153. Desorption kinetics were biphasic, consisting of a rapid phase followed by gradual changes. Most of the changes (in percent of steady-state) occurred within the first few hours of incubation. Desorption partition coefficient (K_d) values indicated that desorption was minor.

Model simulations were compared with laboratory experimental data to evaluate the accuracy and the applicability of the RECOVERY model in predicting desorption kinetics. For the most part, model simulations provided a reasonably good fit to the experimental data with few exceptions. In situations where the model did not accurately estimate desorption values, it predicted trends similar to those observed in laboratory experimental data.

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Desorption   Organic contaminant
Distribution coefficient   Polychlorinated biphenyl
Fluoranthene   RECOVERY
Naphthalene   Sediment-water