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AN EQUILIBRIUM MODEL FOR THE PARTITIONING OF SYNTHETIC ORGANIC COMPOUNDS INCORPORATING FIRST-ORDER DECOMPOSITION

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AN EQUILIBRIUM MODEL FOR THE PARTITIONING OF SYNTHETIC ORGANIC COMPOUNDS INCORPORATING FIRST-ORDER DECOMPOSITION*

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A simple equilibrium model incorporating several first-order decomposition pathways has been calibrated for DDT and PCB mixtures in a l-m^2 ecosystem with the characteristics of Lake Michigan. This exercise has revealed the weakness in currently available process-rate information. The model, as constructed, yields some valuable insights into the environmental pathways of hydrophobic organic contaminants in aquatic ecosystems.

1. INTRODUCTION

A previous report (Eadie, 1981) described a model based on the concept of fugacity, which predicted the equilibrium distribution of hydrophobic organic contaminants in aquatic ecosystems. This model did not contain decomposition and as such could only describe a static ecosystem. Although many synthetic organic compounds are designed and used because of their stability, they are subject to multiple environmental decomposition pathways, such as photolysis, biological decomposition, and chemical oxidation. These, along with physical processes, such as outflow and sediment burial, combine to remove the contaminant from an ecosystem. The obvious question to ask of a model is how long will it be before the contaminant concentration drops below a specified level.

There are several ways to address such questions; the approach basically comes down to the level of detail required and the level of information available. The latter is the constraining factor in the development of ecosystem models. This report describes a simplified approach in which all transformations are handled as first order with respect to contaminant concentration and that provides useful insight into the fates of synthetic organic compounds in well-mixed aquatic systems.

2. THE EQUILIBRIUM MODEL

The model, which is based on the fugacity concept described in detail elsewhere (Mackay, 1979; Eadie. 1981). assumes all compartments are in

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equilibrium, but allows input and transformations. Briefly, the model calculates the fugacity or escaping tendency of the contaminant within each ecosystem compartment. At equilibrium, the fugacities in all compartments are equal. At the low concentrations of contaminant encountered, fugacity (f) is proportional to concentration (C),

$$C = fZ, \qquad (1)$$

where Z is the fugacity capacity.

At equilibrium

$f1 = f_2 = \ldots f_i$, i = number of compartments, and

the total mass in the system (M) is

$$M = \Sigma C_i V_i,$$

where Vi = volume of the ith compartment. Then from (1)

$$M = \Sigma f_i Z_i V_i = f_i \Sigma V_i Z_i;$$

thus

$$fi = M/ \Sigma V_i Z_i$$

and

$$Mi = f_i V_i Z_i,$$

where Mi is the contaminant mass in the ith compartment. The concentration in the ith compartment is

$$C_i = f_i Z_i.$$

The fugacity capacity (Z) values for each compartment are calculated as follows:

- Vapor phases: PV = nRT ideal gas
  fV = nRT at low concentration
  CV = ZnRT from (1)
  z = 1/RT from CV = n
  R = 82 x 10^{-6}
  T is Kelvin temperature

  Liquid phases: H = P/C Henry's constant
  H = f/C at low concentration
  z = 1/H from (1)

  Sorbed phases: $Z = K_p/H$,

where K_p = equilibrium partition coefficient, which is estimated, in this model, from the solubility of the contaminant and the organic content of the substrate as follows:

$$\log K_{oc} = 4.75 - 0.70 \log s$$

where S = solubility in μmol/L and $K_p = K_{oc}$ x % substrate organic carbon/100.

Fish: Z = 6 x bioconcentration factor/B
log BCF = 3.5 - 0.54 log s
factor of 6 converts wet weight to dry weight.

Conceptually, the water column is divided into two parts and the equilibrium distribution is calculated twice each year, representing the stratified (no mixing) and unstratified (complete mixing) periods.

For more detail on these calculations, see Mackay (1979) and Eadie (1981).

3. INCORPORATING DECOMPOSITION

A more realistic model is constructed by including decomposition processes (photolysis, biolysis), settling, and burial in the fugacity model. All of the removal mechanisms are approximated as first-order reactions. The sum of the first-order rates for each compartment (i), period (j) is:

$$K_{ij} = \sum_{k-1}^{n} K_{i,j,k}, \qquad n = \text{number of processes.}$$

Thus the total removal rate from compartment i is

$$V_i C_{i,j} K_{i,j} \text{ mol/half year.}$$

4. DEFINING TEE ECOSYSTEM

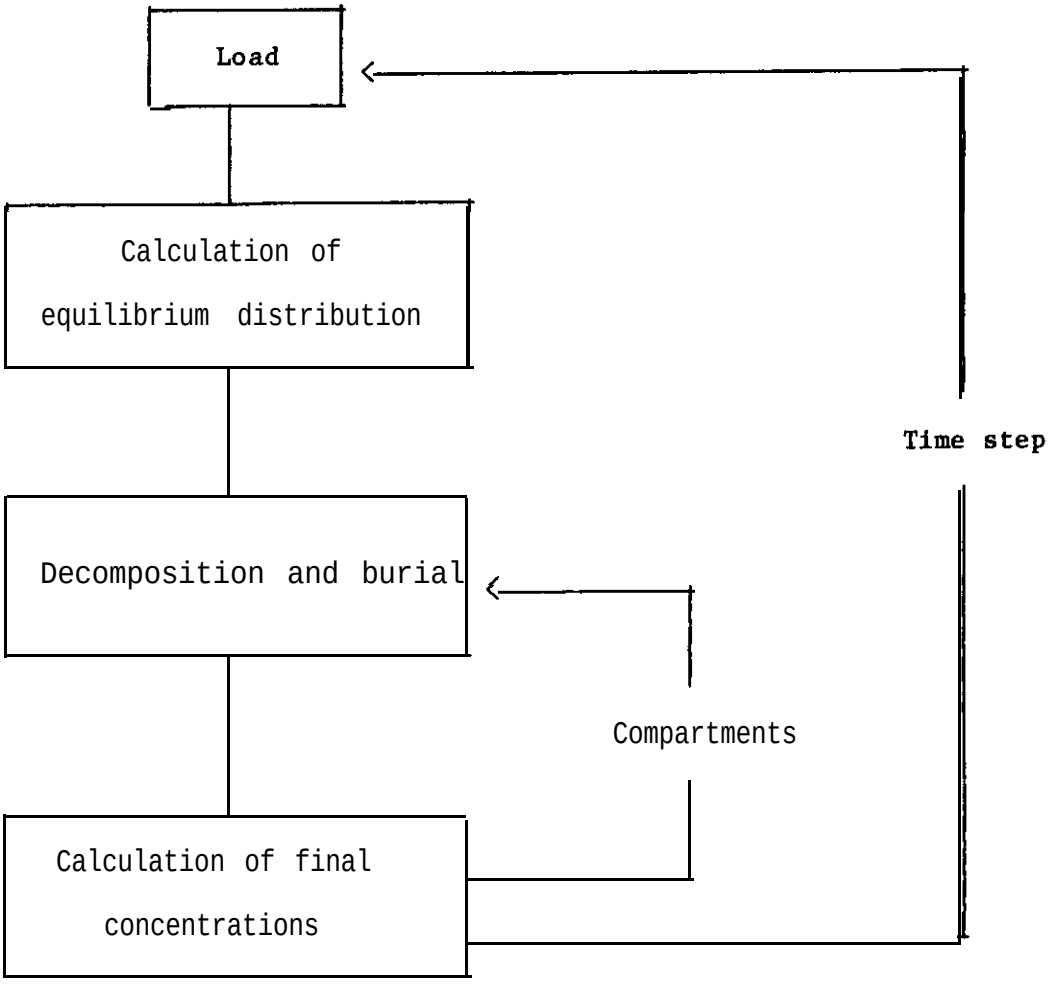
For the purposes of initial analyses and flexibility, the ecosystem will represent a 1-m^2, 100-m-deep basin with the biological and sedimentary characteristics of lake Michigan.

Ecosystem compartment	Volume (m^3)	comments
Atmosphere	10^4	10 km thick
Epilimnion	25	25 m deep
Hypolimnion	75	75 m deep
Detritus	1.5 x 10-4	1.5 ppm; 10% organic order
Biota	5 x 10^{-6}	50 mg/m^3; 40% organic order
Sediments	2 x 10-2	2 cm mixed; 2% organic order
Fish	2 x 10-7	

The semiannual time steps represent a cold, well-mixed system (temperatures = 4°C) and a stratified condition with an epilimnion temperature of 20°C and hypolimnion temperature held at 4°C. A caveat in this conceptual framework is that the sediments and hypolimnion are considered to be in equilibrium with the epilimnion and atmosphere during the stratified period when it is well known that transport through the thermocline region is small. The effect of this will be discussed later.

5. THE MODEL'S OPERATION

Graphically, the model runs as follows:



Thus, at the end of each time step, the contaminant in each compartment has been perturbed from equilibrium by decomposition (and accumulation). For example, the final mass in the sediment is:

$$MSed = MSed\ (eq) - M(Biolysis + Photolysis + Burial) + MSettling$$

Load information for trace organic contaminants is very sparse. For the model runs described in this report, loads were assumed to slowly increase for 10-15 years, level off for a period of time, and then decline rapidly. The form of this function is

$$LOAD = t^2 (c_1 - c_2 t)$$

where t = time.

By adjusting cl and c_2, the loading function can be altered to conform to the limited data available.

Detritus settling is set at ~ 0.3 m/day (Chambers and Eadie, 1981); thus, one-half of the detritus mass enters the sediment each time step and an equivalent mass of sediment is buried, leaving the mixed layer constant. For this model, the detritus mass is renewed each time step, keeping all compartment volumes constant. At the end of each time step, a mass balance calculation is made to warn of any internal inconsistencies.

5.1 Model Runs

The model was run for DDT and a mixture of PCB's as Aroclors®. The results are presented below. In the graphical output, winter conditions imply that the epilimnion was kept at 4°C for all time steps and that microbial decomposition was one-quarter and photolysis one-half of the summer case. These winter/summer scenarios were designed to approximately span the range of decomposition rates in the literature. When the time steps were alternated between winter and summer conditions, the increase in solubility and vapor pressure at the higher temperatures strongly affected the distribution as shown in figure 1.

The local maxima in the sediments and biota are the winter values. The model predicts an epilimnetic depletion of contaminant that can be tested with a relatively modest field effort, currently being planned.

5.2 The Model Applied to DDT

DDT research is almost out of vogue; however, after the large amount of money spent, some relatively basic information regarding the decomposition of the compound is on shaky ground. There is no clear information on loads; thus the model input was calibrated to concentrations reported in bloater chubs for Lake Michigan [International Joint Commission (IJC), 1979]. Information on solubility and vapor pressure as a function of temperature was not found; a difference of 50 percent was assumed between 4" and 20°C. This is less of a range than for many similar halogenated aromatic hydrocarbons. The values used in the model are listed in table 1.

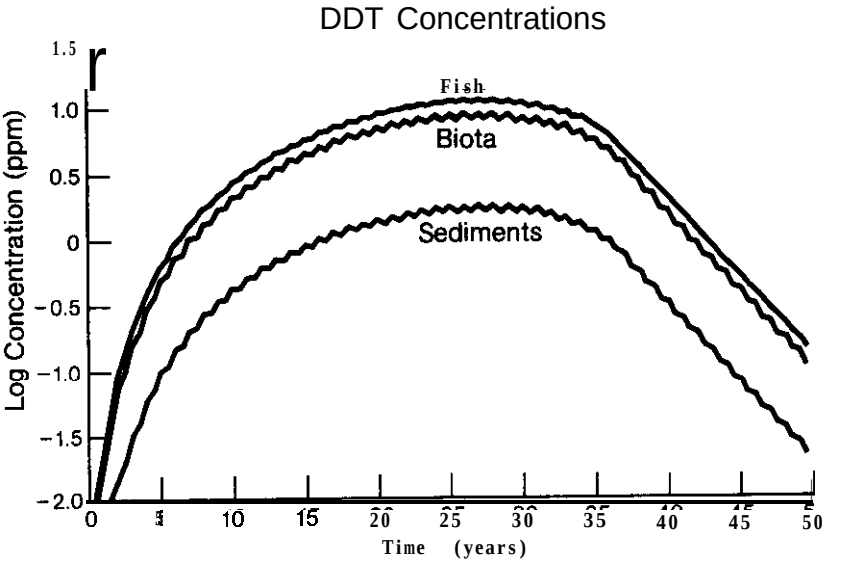


Figure 1.--*Model* ***output of DDT concentrations in*** *fish, biota,* ***and sediments. The sawtooth effect is caused by alternating winter and*** *summer* ***conditions in the model.***

Table ***l.--Input*** *parameters* ***for DDT model***

Molecular weight--356

Parameter	4°C (Winter)	20°C (Summer)	comment
Solubility (g m^{-3})	0.8 x 10-3	1.2 x 10-3	1
Vapor pressure (mm Hg)	0.8 x 10^{-7}	1.6 x 10^{-7}	1
Photolysis rate (0.5 $yr)^{-1}$	0.9 x 10-3	1.8 x 10^{-3}	2
Biolysis rate (0.5 $yr)^{-1}$	0.06	0.24	2
Burial rate (0.5 $yr)^{-1}$		0.00525	3

1) Solubilities, for 20°C, are currently accepted as best values within the ***range*** reported in the literature.

2) Rates are for the epilimnion; photolysis taken from Wolfe et al. (1977), biolysis rates from Lee and Ryan (1979; ~ 0.1 per half year) and Pafaender and Alexander (1972; 0.05-0.5 per half year).

3) Burial rate is calculated from mass flux rates of 0.7 g m^{-2} day (Chambers and Eadie, 1981), a detritus concentration of 1.5 g m^{-3}, and a constant mixed sediment thickness of 2 cm.

The DDT input ($I = 2 \times 10^{-3} \times (1.2 \times 10^{-3}(TS)^2 - 1.6 \times 10^{-5}(TS)^3)$), where I is in moles and TS is the time step, increased for approximately 30 years, then declined rapidly, with zero input for the last 15 years. (By year 33, the input was near zero, equivalent in this calibration to 1970, when production was stopped.) Figure 2 illustrates predicted concentrations in sediments, fish (by bioconcentration), and biota (sorption; 40 percent organic carbon). Only sparse data are available for comparison. Leland et al. (1973) found a mean of 18.5 ppb and a maximum of 175 ppb (dry) in the sediments of southern Lake Michigan. In the model, predicted sediment concentration peaks at approximately 120 ppb (dry), but rapidly declines. The simulated sediments are representative of the average depth of Great Lakes sediment (2 percent organic carbon) and as such would be expected to be higher than Leland's mean. The model output for 1970 is 100 ppb, which is within the reported range.

For this calibrated DDT run, the losses, in moles per half year, are illustrated in figure 3. The total of the first-order processes is primarily composed of biological decomposition in sediments and water with burial and photolysis orders of magnitude lower.

The model predicts declining concentrations in all compartments. The 1980 Great Lakes Water Quality Agreement states that DDT (and its metabolites) should not exceed 3 parts per trillion (ppt) in water and 1 part per million (ppm) in fish. Data for water are not available, but the calibrated model output gives a concentration of approximately 40 ppt in 1970, declining to less than 1 ppt by the mid-1980s. Game fish, such as lake trout and coho salmon, appear to have had a higher concentration of total DDT in 1970 (15-20 ppm). Assuming the loss rate is similar to the bloater chub prediction, it would have taken until approximately 1980 to reduce those levels to the 1 ppm.

The total mass loaded into the system in order to achieve calibration was 4.74×10^{-4} moles (170 mg) of DDT. Since the ecosystem was approximately that of Lake Michigan, the load value can be multiplied by 5.8×10^{10} m^2 to get an approximation of the total lake loading, 9,900 metric tons. This value corresponds to approximately 2 percent of the total DDT used in the United States (as estimated by Woodwell et al., 1971), a reasonable figure since the surface area is approximately 1 percent of the contiguous United States. By 1980, the model predicts that greater than 99 percent of the total load had been removed by decomposition, evaporation, or burial below the well-mixed zone.

DDT is rapidly being removed from the Great Lakes ecosystem through natural decomposition processes. The same cannot be said for the second contaminant analyzed in this report, polychlorinated biphenyls (PCB).

5.3 The Model Applied to PCB's

The environmental history of PCB's is similar in many ways to DDT. Both compounds were first developed in the 1930's and slowly leaked into ecosystems for which they were not intended. DDT values reported prior to about 1975 are very often contaminated with PCB's because analytical techniques had not been designed to separate them.

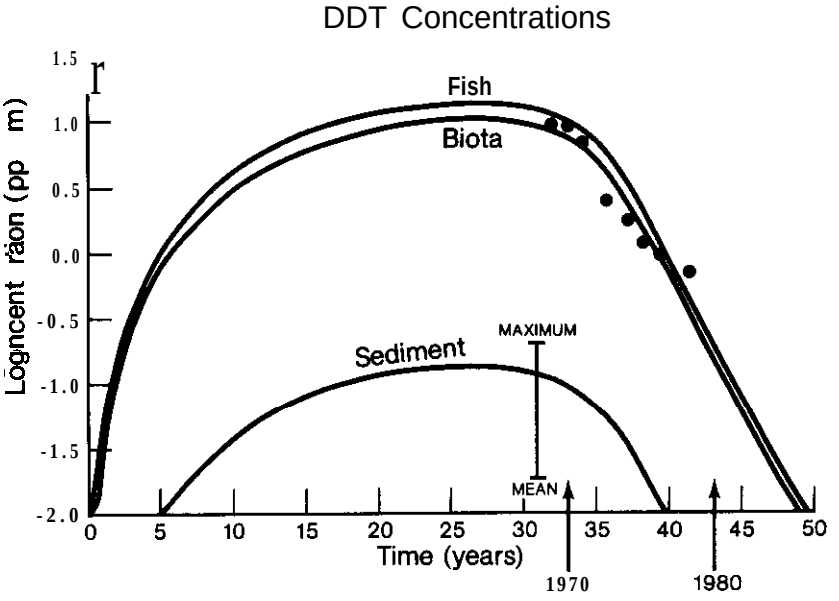


Figure 2.--*DDT concentrations. The lines are output* from a *simulation using* continuous *summer conditions; points are data* for *bloater chubs and sediments from* Lake *Michigan.*

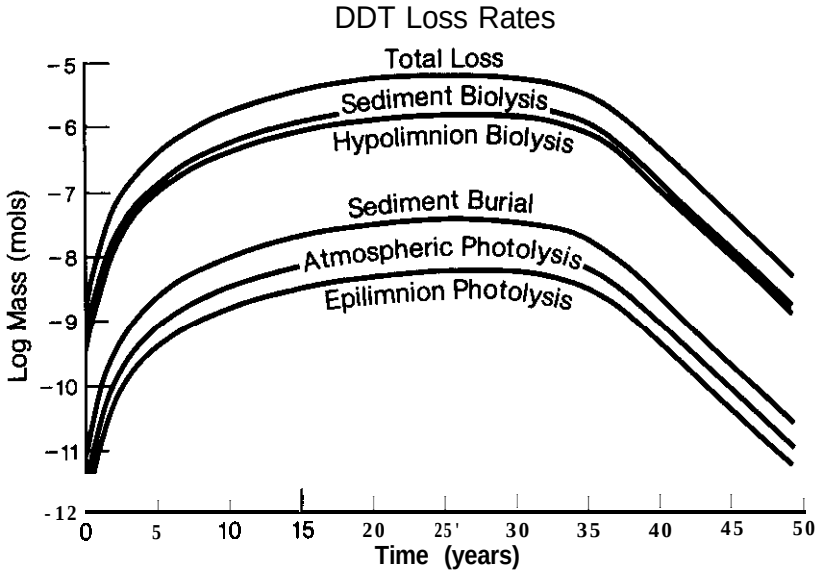


Figure 3.--*DDT lose rates (mols per half* year). *Microbial decomposition is the major loss.*

This class of compounds, consisting of more than 200 theoretical isomers (less than one-half of which are believed to be present in any quantity in the environment), is of current concern in the Great Lakes. Lake Michigan sport fish have concentrations many times higher than the 5-ppm Food and Drug Administration level considered safe for human consumption. This report applies the calibrated DDT model to the PCB's, attempting to gain insight into their rate of removal from a Lake Michigan-like ecosystem. The National Research Council (NRC) recently published a report on PCB's in the environment (NRC, 1979) that has been used as a major source of information for this report.

Unfortunately, information on PCB's is predominantly reported in terms of commercially available mixtures, called Aroclors® in the United States. These are coded such that the last two digits represent the weight percent chlorine in the mixture (e.g., 1254 contains 54 percent chlorine, an average of five chlorines per molecule). Figure 4 illustrates the approximate composition of the Aroclors®. The modeling of these mixtures is very unsatisfying because of the range of characteristics and, consequently, environmental pathways that are "smoothed over" in this averaging process. Also, it appears that a major photodecomposition reaction is dechlorination, which produces another PCB. Improvements in ecosystem simulation models can only come when sufficient information is available to model the individual isomers.

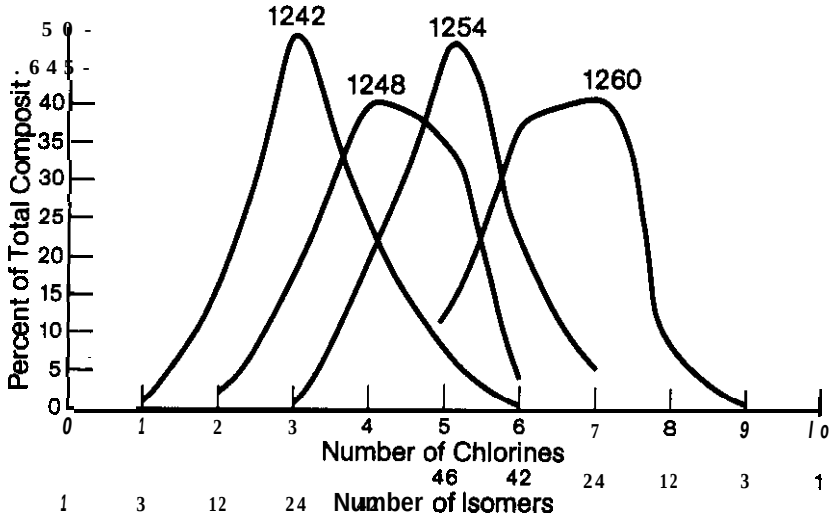


Figure 4.--*Isomeric composition of commercially available Aroclors®.* Modified from *NRC 119791.*

The version of the model discussed in this report follows the movement of PCB mixtures 1242, 1248, 1254, and 1260. The model information is listed in table 2. The two temperatures and corresponding pairs of rate numbers and physical characteristics are designed to span a range that can be obtained from the literature. The low rates (winter conditions) are combined for the first run and the high rates (summer conditions) for the second run, producing an envelope of prediction.

Table 2.--Input *parameter6 for PCB model*

	1242	1248	1254	1260	Comments
"Molecular weight"	258	290	324	375	1
Temperature (°C)	4; 20	4; 20	4; 20	4; 20	1
Solubility (g m^{-3})	0.20; 0.24	0.043; 0.054	0.010; 0.012	0.002; 0.003	2
Vapor pressure (mm Hg) x 104	1.5; 7.2	1.3; 6.3	0.28; 1.5	0.14; 0.75	3
Photolysis rate (0.5 yr)$^{-1}$	0.05; 0.1	0.03; 0.06	0.02; 0.04	0.01; 0.02	4
Burial rate (0.5 yr)$^{-1}$	0.005; 0.02	0.005; 0.02	0.005; 0.02	0.005; 0.02	5
Biolysis rate (0.5 yr)$^{-1}$	0.5; 1.	0.2; 0.4	0.05; 0.1	0.01; 0.03	

1) From NRC (1979).

2) Calculated from information in NRC (1979).

3) Estimated from Simmons (personal communication).

4) From Chambers and Eadie (1981); Robbins (personal communication).

5) Calculated from Rice (personal communication); Anderson (1980), Furukawa et al. (1978). See discussion on microbial decomposition rates for dissolved contaminant reduced by 10x (Lee and Ryan, 1979).

Individual process rates are often difficult to extrapolate from the literature. Early results from GLERL's program at The University of Michigan (Simmons, personal communication) provide the most realistic numbers for photolysis. These have been subjectively combined with the results of Safe and Hutzinger (1971), Ruzo et al. (1972), Herring et al. (1972), Hutzinger et al. (1972), and Crosby and Moilanen (1973). Variations in experimental conditions and exotic experimental procedures (from the point of view of someone trying to extrapolate to an aquatic ecosystem) make objective comparisons impossible. Thus, the photolytic rate numbers in table 2 are comparatively weak at this time.

5.4 Microbial Degradation

The basic mechanisms involved in biodegradation of PCB's are different from those found for DDT. The absence of an alkyl group between the benzene ring in PCB's rules out the separation of the rings by cleaving the unconjugated bond. The typical mechanism described for PCB degradation consists of hydroxylation, followed by ring fission, of the lesser-chlorinated ring.

One of the major drawbacks to direct application of laboratory rates to natural systems is the type of organisms used in the rate-determination experiments. The first problem is the use of pure (or axenic) rather than mixed cultures. Pure cultures do not exist in nature. The use of mixed cultures provides a better simulation of an environment where many types are present simultaneously, each representing unique intrinsic metabolic capabilities. The source of the cultures is also a weak point; most exponents employ enrichment isolation techniques that alter the population structure of the original culture.

Many researchers noted that degradation rates changed with time, increasing to a maximum as time progressed. This phenomenon, known as acclimation, is not well understood in natural populations, but the occurrence of higher degradation rates for organisms from regions of chronic contamination is fairly well documented. At the present time, acclimation (and rate changes that are due to acclimation) in natural systems is an important part of the problem pertaining to the applicability of laboratory rates to rates found in the environment. From the limited evidence provided by a few experiments with simulated natural conditions, the difference in overall rates does not seem to be too substantial.

There are four identified major variables that have an effect on degradation rates: (1) temperature, (2) type of organism, (3) cell concentration, and (4) substrate (PCB) concentration.

Each type of bacterium will have an intrinsic rate of degradation specific for that organism. (See Furukawa et al., 1978; Clark et al., 1979.) The bacteria that were tested in the experiments below had similar rates in most cases. Another factor that would presumably be specific for each bacterium is the induced rate, the rate following acclimation to the substrate. As stated above, acclimation times and their variablility are not known for natural systems at the present time.

Furukawa and his co-workers showed that overall degradation rates increase with increasing cell concentration. They measured changes in the rate of formation of a yellow compound, with a known absorption maximum, from a 4'substituted biphenyl (2,5,4'-trichlorobiphenyl) as the optical density of the culture was increased. They found similar results with both of the cultures they tested: the amount of yellow compound formed increased to a maximum as the number of bacteria (optical density) increased. Boethling and Alexander (1979) showed that degradation rates increased as substrate concentration increased. While they used p-chlorobenzoate, chloroacetate, 2,4-dichlorophenoxyacetate (2,4-D), and 1-naphthyl-N-methyl-carbamate (NMC), it is reasonable to believe that the results are generally applicable to PCB biodegradation. They found that virtually no degradation occurred below a threshold concentration of 2 to 3 ng mL^{-1} for 2,4-D and NMC. At higher concentrations, degradation (complete conversion to carbon dioxide) occurred at a rate of approximately 10 percent per day. For these experiments, microbial populations were collected from a stream in New York that drains agricultural runoff and receives treated sewage upstream from the sampling site.

Another important point raised by Boethling and Alexander (1979) was that extrapolation of rate information from high to low substrate concentrations is not an accurate prediction of rates at low levels. When measuring complete degradation of 2,4-D to carbon dioxide, they found that using laboratory rates found for 22 mg mL^{-1} and 220 ng mL^{-1} to predict the rate at 2.2 ng mL^{-1} (by assuming direct proportionality with substrate concentration) yielded predicted rates that were more than one order of magnitude greater than actual laboratory rates.

Wong and Kaiser (1975) isolated bacteria from Hamilton Harbour, Lake Ontario, and determined their ability to degrade PCB's. To isolate these organisms, they used media in which Aroclors® 1221, 1242, and 1254 were the sole carbon and energy source. All of their determinations were performed at 20°C. With 0.05-percent solutions, no growth occurred on Aroclor" 1254, but degradation could be followed on 1221 and 1242. Wong and Kaiser found that the less-chlorinated compounds were degraded at a higher rate than the more highly chlorinated compounds. Thus, in experiments with single isomers, degradation rates could be arranged as follows: biphenyl > 2-chlorobiphenyl > 4-chlorobiphenyl. They also observed that the position of chlorination, as well as the degree of chlorination, was important in determining the rate.

The bacterial population used in the Aroclor" 1221 experiment (summarized in table 3) started at approximately 10^4 cells mL^{-1} and reached an asymptotic maximum of 10^7 cells mL^{-1} within 7 days, by which time up to 55 percent of some of the gas chromatographic (GC) peaks had been degraded. This reduces to a rate of about 4 ng degraded $cell^{-1}$ day^{-1}, assuming that 55 percent of the total PCB present was degraded by 10^4 bacteria mL^{-1} in 500 mL of solution in 7 days.

In another experiment, two species of bacteria were tested for their ability to degrade specific PCB isomers. Furukawa and his co-workers (Furukawa et al., 1978) used *Alcaligenes* sp. and *Acinetobacter* sp. isolated from "aquatic sediment" by biphenyl and 4-cholorobiphenyl enrichment,

Table 3.--*Laboratory microbial decomposition* of *PCB (per day)*

Investigator	Number of chlorines 1	2	3	4	5	Comment
Anderson (1980) #7	--	0.20	0.13	0.019	0.009	1
#10	--	0.12	0.13	0.021	0.008	1
Kaiser and Wong (1974)	0.055	--	--	--	--	2
Baxter et al. (1975)	--	--	0.062	0.040		3
Furukawa et al. (1978)	--	--	0.2-3.2	--	--	4

1) Conditions: stirred, aerated, 37 gm sed L^{-1} (#7), 14.7 g L^{-1} (#10), mixture of individual isomers.

2) High concentrations.

3) Biphenyl added.

4) Pure cultures.

respectively. They found an increase in degradation with increased levels of bacteria. As expected, they noted that degradation occurred more readily if: (1) there were fewer chlorines in the compound and/or (2) all chlorines were on one ring. Also demonstrated were differential rates for isomers with ortho-substituted chlorines; the *rates* were much slower for these compounds, especially when orthochlorines occurred on both rings. Preferential ring fission was seen on the lesser-chlorinated ring.

Tucker et al. (1975) used activated sludge from a local municipal sewage treatment plant in a semi-continuous system (SCAS) to measure the disappearance of Aroclors® 1221, 1242, and 1254 from solution. An acclimation time of 5 months for each compound tested (one per activated sludge unit) was allowed before rates were measured. Suspended solids were maintained at about 2,500 mg L^{-1} and no irreversible adsorption to, or uptake by, the culture was found. It was noted that the components of 1221 that remained following degradation were the major components of 1242.

Baxter et al. (1975) performed two series of experiments on each of two species of bacteria: *Nocardia* sp. and ***Pseudomonas*** sp. (NCIB 10603 and NCIB 10643, respectively*). The first series consisted of simple systems containing one, two, or three PCB isomers (some also included biphenyl), while the second was run with commercial mixtures along with excess biphenyl. Results showed that compounds with up to six chlorines could be degraded under the proper conditions (in the presence of certain other isomers and/or biphenyl, or as part of a commercial mixture). As before, the isomers with fewer chlorines were generally degraded faster.

Clark et al. (1979) experimented with a mixed culture of bacteria obtained from polluted Hudson River sediment (the "Fort Miller disposal site"). The most numerous organisms (in order of greater numbers) were *Alcaligenes odorans* and *Alcaligenes denitrificans*. Again, lower chlorinated isomers were degraded fastest, with differential rates according to the position of chlorination.

Anderson (1980) reanalyzed the data from previous experiments and calculated first-order rate constants. Ha also calculated first-order rate constants from his own work using sediment suspensions from Saginaw Bay and mixtures of PCB's. The averaged results are summarized in table 3.

Intercomparison between investigators is difficult considering the variations in experimental procedures employed. However, it is clear that the rates seem to agree fairly well, except for those of Furukawa et al. Their use of pure bacterial cultures known to degrade PCB isomers led to predictably high rates.

In summary, several main points can be extracted from all of these experiments:

(1) degradation decreases with increasing chlorination (or decreasing water solubility);

(2) differential degradation occurs according to position of chlorination;

(3) degradation increases with increased bacterial, and substrate, concentration; and

(4) degradation rates (for some compounds) change with certain isomeric combinations and with the addition of acetate or biphenyl.

Several points must be kept in mind. First, all of the experiments described employed enrichment techniques of some sort, which obviously changed the populations. Second, most of the experiments were conducted at ambient temperatures (20° to 25°C). Third, the PCB concentrations used in

*NCIB: National Collection of Industrial Bacteria

these experiments were much higher (on the order of hundreds of parts per million) than those found in freshwater systems. Current PCB levels in the Great Lakes are on the order of 10 ppt (water) to 100 ppb (sediments).

All of these indicate that natural rates should be lower than those measured in laboratory experiments. Other arguments concerning these results also center around the cultures themselves. There is little doubt that pure cultures do not exist in nature. The use of mixed natural populations would be more appropriate to obtaining rates similar to those found in nature. It is logical to assume that rates would be different in an environment in which a number of species participated in degradation.

A microbial decomposition rate can be estimated for Aroclor® mixtures from the isomer distribution illustrated in figure 4 and the biolysis rates in table 3 as follows:

$$R1242 = 0.1 \times R2 + 0.4 \times R3 + 0.2 \times R4 + 0.2 \times R5 + 0.1 \times R6,$$

where R2 = rate for dichlorobiphenyl (table 3), etc., and R6-9 = 0. Then

$$R1422 = 0.07\ day^{-1} = 12.6\ (0.5\ yr)^{-1}$$

$$R1248 = 0.02\ day^{-1} = 3.6\ (0.5\ yr)^{-1}$$

$$R1254 = 0.009\ day^{-1} = 1.6\ (0.5\ yr)^{-1}$$

$$R1260 = 0.001\ day^{-1} = 0.25\ (0.5\ yr)^{-1},$$

which yield reasonable laboratory rates. The deep water and sediment temperatures of the Great Lakes range from near zero to 4°C. This will lead to a reduction of at least an order of magnitude in the rate numbers (Lee and Ryan, 1979). The rates are probably high for other reasons cited above.

Considering the caveats, I have set the high rates equal to approximately 10 percent of the laboratory values and the low rates at one-third the value of the high rates.

6. RESULTS

Model output for sediments and biota are shown in figures 5 (winter conditions) and 6 (summer conditions). The winter condition is the result of using the low rates in table 2 and is calibrated to yield a maximum concentration of approximately 10 ppm in the biota. At the same time, sediment concentrations peak at approximately 75 ppb, a value within the range reported for Lake Michigan (Konasewich et al., 1978). In order to obtain similar maximum concentrations, the summer condition run (figure 2) required 20 times the load of PCB used for the winter case.

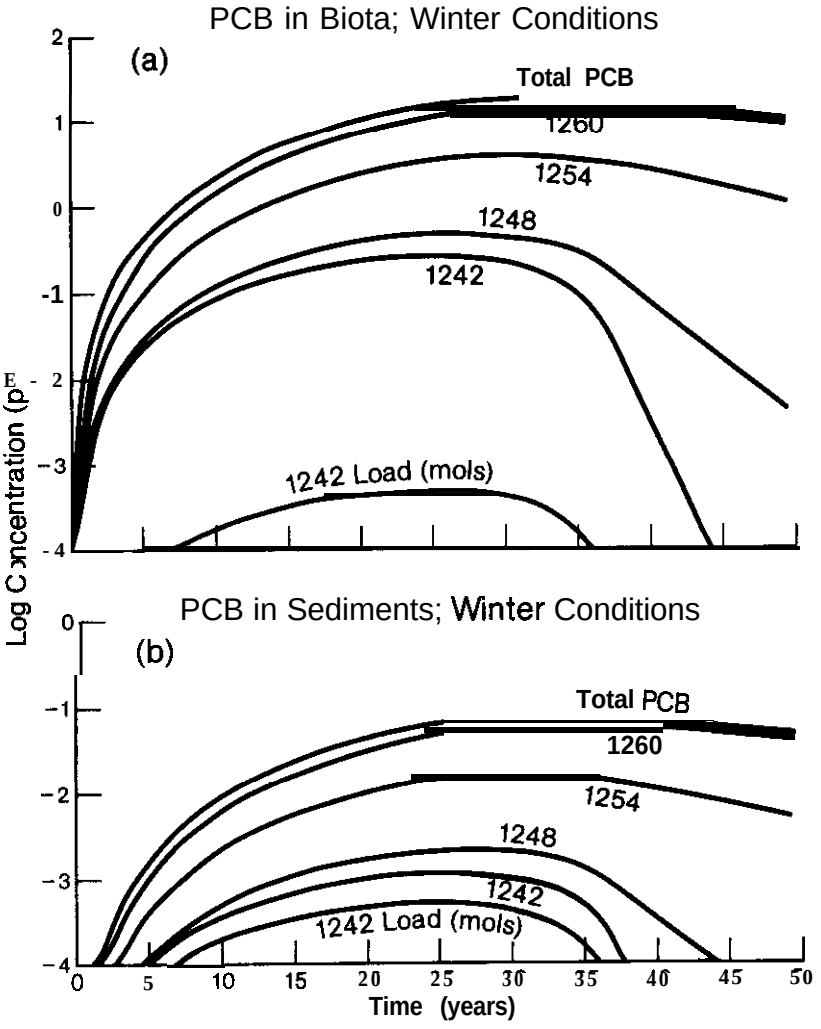


Figure 5.--*a) PCB* ***mixtures in biota using the low rates in table 2.*** The *numbers* refer *to Aroclors®* as described in figure 6. ***The 1242 load is depicted to give a feeling*** for ***the shape of the input*** function. *The* ***other Aroclors® have the same load function but a lower*** *(0.25x) magnitude.* ***b)*** *PCB* ***mixtures in sediments for the same run.***

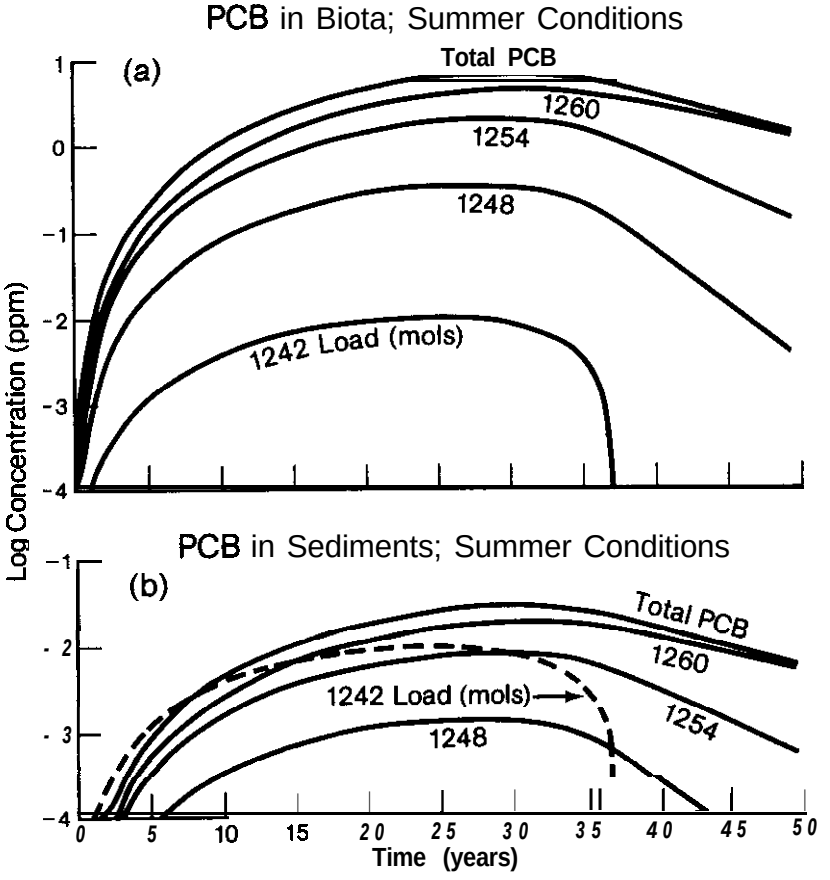


Figure 6.--*a) PCB mixtures* in ***biota using the high rates in table 2.*** *b) PCB* ***mixtures in sediments*** for ***the same run.***

As for the DDT simulation, year 35 is approximately equal to 1972. Figure 7 compares model output for the winter and summer cases with PCB data for Lake Michigan fish as summarized in Sonzogni et al. (1981). The model outputs can be moved up and down the page by altering the load, and the outputs will remain very nearly parallel. The agreement with bloaters and coho salmon is encouraging, considering the simplicity of the model. The lake trout data could not be simulated with a model as simple as this. Weininger (1978) proposed considerable food chain transfer from benthic organisms to lake trout and there is no food chain accumulation explicitly considered in this model.

The model outputs indicate that the loss we are presently observing in fish and sediments is primarily the lesser chlorinated isomers contained in 1242 and 1248, whereas the Aroclors" 1254 and 1260 decay much more slowly. This scenario predicts an exponential approach to a lower concentration of predominately hexachlorinated and higher isomers that will remain for a long time. The absolute value of this lower concentration strongly depends on the present concentration of highly chlorinated isomers because atmospheric transport of such isomers is small and future loads are predicted to be small.

The loss rates from the ecosystem are illustrated in figure 8. Aroclors" 1242, 1254, and 1260 are shown; 1248 is intermediate between 1242 and 1254, and was omitted for clarity. Atmospheric photolysis predominates, followed by microbial decomposition in the water and sediment. In the Great Lakes, burial is a slow process, which is slowed by bioturbation. The model considered a general condition of a 2-cm-mixed thickness with 0.5- to l-mm accumulation per year. Assuming desorption occurs, the sediments can act as a source of stored hydrophobic contaminants for several decades.

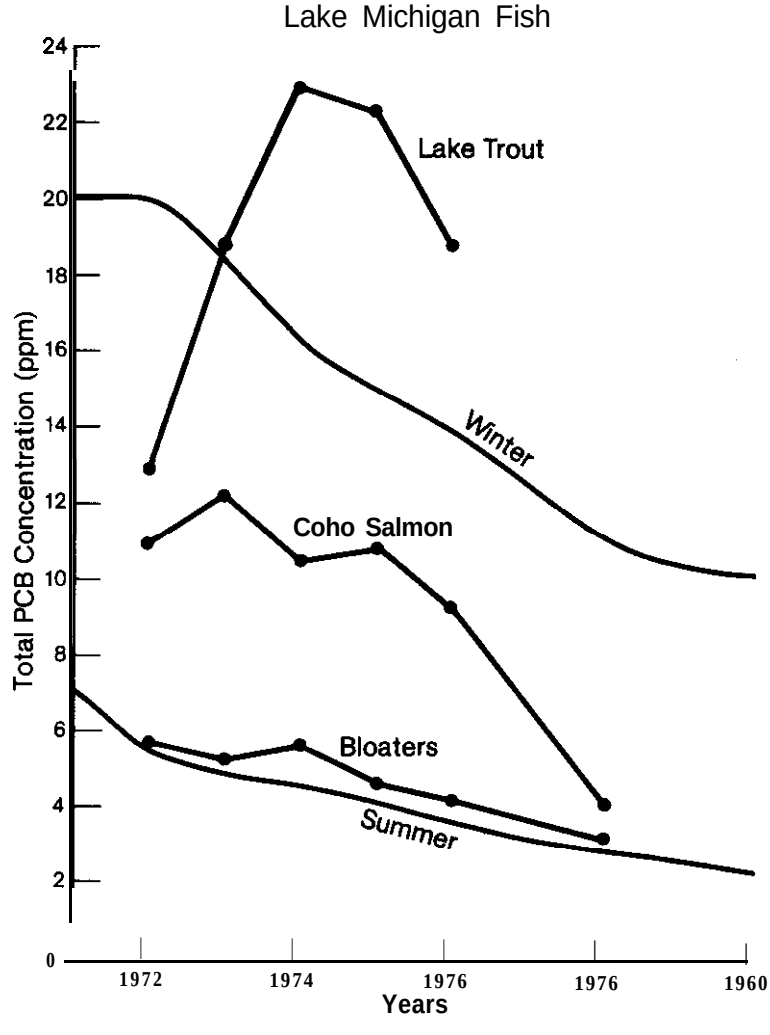


Figure 7.--*Total PCB's in Lake Michigan fish. Data are from Konasewich et al. (1978) and IJC (1979). The model outputs for biota from the runs illuetmted in figures la and 2a are shown as smooth curves.*

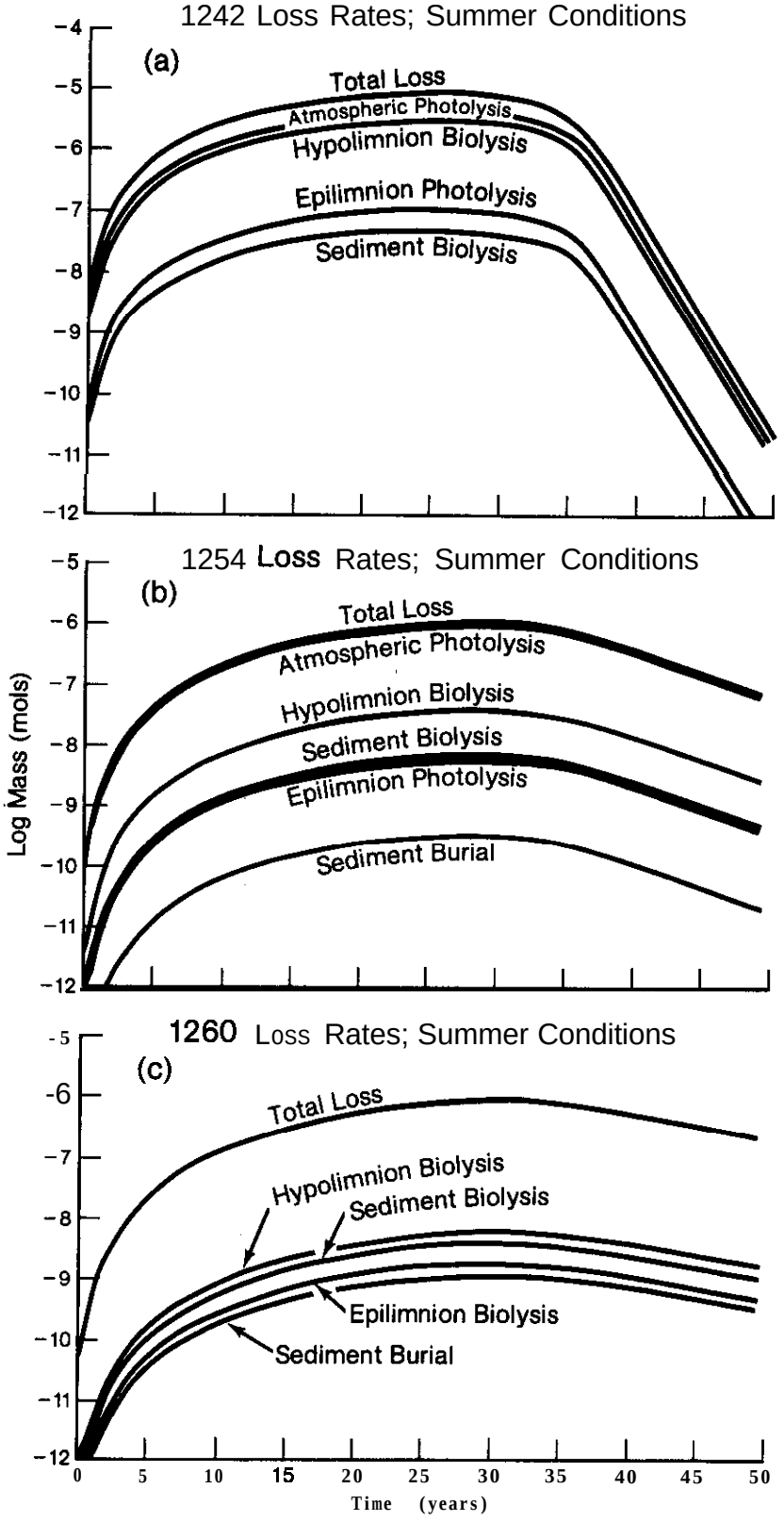


Figure 8.—*PCB toss rates (mol per half year) from the summer scenario (figure 6). a) Aroclor® 1242, b) Aroclor® 1254,* and *c) Aroclor® 1260.*

7. ACKNOWLEDGMENTS

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9. Appendix--PROGRAM OUTPUT

```
GET,FUGMOD3
/COPY,FUGMOD3
      PROGRAM MOD2 (INPUT,OUTPUT,TAPE3,TAPE5=INPUT,TAPE6)
C  DIMENSION OF A , B. A1, A2 & R ARRAYS MUST BE (NT,# OF VARIABLES1
c  THESE ARRAYS ARE FOR PLOTTING ROUTINES
      DIMENSION A1(100,10),A2(100,10),TBIO(100),TSED(100)
      DIKENSION R(100,10),ND(20),A(100,9),B(100,8)
      COMMON /INDAAT/ S(5,2),TK(2),MW(5),AA(5),BB(5)
      COMMON /INFO/ LC,Z(8),VP(5),H(5),OC(8),V(8)
      COKKON /RATE/ PK(5,8),BK(5,8)
      COKKON /INDEX/ I,J,K,JJ,NC,NT,NX
      COMMON /PARM/ TM(101,5),CM(8,100,5),PM(8,100,5),CC(8,100,5)
      COKKON /LOSS/ TLOSS(5),SD(100,5),TL(100,5),BD(8,100,5),PD(8,100,5)
      COKKON /INTO/ X(5),TINPUT(100,5),TLOAD(100,5)
C
      DATA A /900 * -999./
      DATA B /800 * -999.1
      'DATA R /1000 * -999./
      DATA A1 /1000 * -999.1
      DATA A2 /1000 * -999.1
C THE ABOVE PRESET THE PLOTTING ARRAYS ; DIMENSIONS MUST BE EXACT
C
C **** ALL INPUT DATA IS IN THIS SECTION ***
C
C  * CALIBRATION DATA FOR DDT *
      DATA TK /275.,293./
C  TK = TEMPERATURES FOR THE TYO TIME STEPS
      DATA S /5*0.8E-3,5*1.2E-3/
C  S = SOLUBILITY(G/M3) ; 5 CONTAWINENTS ; 2 TEMPS
      DATA MW/5*356/
C  KU = MOLECULAR WEIGHTS
      DATA PK /3.6E-3,7.2E-3,1.8E-3,2*3.6E-3,1.8E-3,3.6E-3,0.9E-3,
     12*1.8E-3,30*0./
C
C  PHOTOLYSIS RATE CONSTANTS (PER .5 YR)
      DATA BK /5*0.,7*(0.24,0.24,0.24,0.48,0.12)/
C  BIOLOGIGAL LOSS RATES (MOL/M3/0.5YR)
      DATA X /5*2E-3/
C  X SCALES THE LOAD FUNCTION ; X * SIN(TIME**2)
C  VAPOR PRESSURE (MM HG)
      DATA UP /5*1.6E-7/
C
C SET UP UITH TECKTRONIX TERMINAL GRAPHICS OUTPUT
C
C EQUILIBRIUM MODEL(FUGACITY) DESIGNED TO TAKE 0.5YEAR TIME STEPS
C
C
```

```
C  MODEL UNITS ARE IN MOLS ; EXCEPT CC(I,J,K) WHICH IS G/M3
C  S = SOLUBILITIES OF AROCLORS 1242-1260 AT 2 & 20 DEG C (G/M3)
C
C  INTERACTIVE INPUT
C
      PRINT*,"ENTER THE NUMBER OF TIME STEPS (100 MAX)"
      READ*,NT
      PRINT*,"ENTER THE NUMBER OF COMPOUNDS (5 MAX)"
      READ*,NX
C
C  I IS THE COMPARTMENT INDEX
C  J IS THE TIME STEP
C  K IS THE COMPOUND INDEX
C
      R = 82E-6
C  TL = TOTAL LOSS OF CONTAMINENT ; TM = TOTAL MASS
C
C  DESCRIBE THE ECOSYSTEM
C
      NC = 7
C  NC = NUMBER OF COMPARTMENTS
C  1 = ATMOSPHERE (10 Kn X 1M2)
      V(1) = 1E4
C  2 = EPILIMNION (25M)
      V(2) = 25
C  3 = HYPOLIMNION (75M)
      V(3) = 75
C  4 = DETRITUS (1.5PPM;10%ORG.C)
      V(4) = 1.5E-4
C  5 = BIOTA (50 MG/M2)
      V(5) = 5E-6
C  6 = SEDIMENTS (2CM MIXED,2% DRG C)
      V(6) = 2E-2
C  7 = FISH ; USING A BIOCONCENTRATION FACTOR
      V(7) = 2E-7
C PERCENT ORGANIC CARBON INPUT
      OC(4) = 10
      OC(5) = 40
      OC(6) = 2
C
      DO 5 K = 1,NX
      TLOSS(K) = 0.
    5 TLOAD(1,K) = 0.
      DO 100 J = 1,NT
      DO 100 K = 1,NX
C
      CALL LOAD
C
C  JJ = 1 FOR UNSTRATIFIED(WINTER; = 2 FOR SUMMER
      JJ = 2 - (J-(J/2)*2)
      JJ = 2
C  CALCULATE HENRYS CONSTANT
      H(K) = (VP(K)/760)/(S(K,JJ)/MW(K))
```

```
C  CALCULATE Z VALUES FOR EACH COMPARTMENT
      Z(1) = 1/(R*TK(JJ))
      Z(2) = 1/H(K)
      Z(3) = 1/((VP(K)/760) / (S(K,1)/MW(K)))
C  HYPOLIMNION(3) IS HELD AT 2 DEG C
      DO 20 I =4,6
   20 Z(I) = 10**(4.75-0.70*ALOG10(S(K,JJ)*1000/MW(K)))*.01*OC(I)/H(K)
C  BIOCONCENTRATION FACTOR CALCULATION
      Z(7) = 6*10**(3.5-0.54*ALOG10(S(K,JJ)*1000/MW(K)))/H(K)
      Z(6) = 0.05 * Z(6)
C  PARTITION COEFFICIENT IN SEDIMENTS LOUER BY FACTOR OF 20
C  CALCULATE THE FUGACITY
      SUMF =0.
      DO 30 I = 1,NC
   30 SUMF = SUMF + V(I) * Z(I)
      F = TM(J,K)/SUMF
C  CALCULATE THE EQUILIBRIUM DISTRIBUTION
      DO 40 I = 1,NC
      CM(I,J,K) = F*V(I)*Z(I)
C  CALCULATE COMPARTMENT CONCENTRATIONS
   40 CC(I,J,K) = CM(I,J,K)*MW(K)/V(I)
C
C
      CALL DECAY
C
  100 CONTINUE
C
C     CALL OUTPUT
C
C  FILLING ARRAYS FOR PLOT

      DO 300 K = 1,NX
C
C  FILLING A ARRAY ; COMPARTMENT CONCENTRATIONS
      DO 250 J = 1,NT
      A(J,1) =  J
      IF(TINPUT(J,K) .GT. 0.) A(J,2) = ALOG10(TINPUT(J,K))
      DO 250 I = 1, NC
  250  IF(CC(I,J,K) .GT. 0.) A(J,I+2) = ALOG10(CC(I,J,K))
C
C  FILLING R ARRAY ; CONTAKINENT LOSSES(MOLS)
      DO 280 J = 1,NT
      R(J,1) = J
      IF(SD(J,K) .GT. 0.) R(J,2) = ALOG10(SD(J,K))
      DO 260 I = 1,2
  260 IF(PD(I,J,K) .GT. 0.) R(J,I+2) = ALOG10(PD(I,J,K))
      DO 270 I = 2,6
  270  IF(BD(I,J,K) .GT. 0.) R(J,I+3) = ALOG10(BD(I,J,K))
  280  IF(TL(J,K) .GT. 0.) R(J,10) = ALOG10(TL(J,K))
C
C
C
  300 CONTINUE
C FILLING B ARRAY
C
```

```
C FILLING A1 ARRAY ; TOTAL CONC IN BIOTA
C
      DO 400 J = 1,NT
      TBIO(J) = 0.
      A1(J,1) = J
      DO 401 K = 1,NX
  401 IF(TINPUT(J,K) .GT. 0.) A1(J,K+1) = ALOG10(MW(K) * TINPUT(J,K))
      DO 400 K = 1,NX
      TBIO(J) = TBIO(J) + CC(5,J,K)
      IF(CC(5,J,K) .GT. 0.) A1(J,K+5) = ALOG10(CC(5,J,K))
  400 IF(TBIO(J) .GT. 0.) A1(J,10) = ALOG10(TBIO(J))
C
C FILLING A2 ARRAY ; SEDINENT CONCENTRATIONS
      DO 500 J = 1,NT
      TSED(J) = 0.
      A2(J,1) = J
      DO 501 K = 1,NX
  501 IF(TINPUT(J,K) .GT. 0.) A2(J,K+1) = ALOG10( MW(K) *TINPUT(J,K))
      DO 500 K = 1,NX
      TSED(J) = TSED(J) + CC(6,J,K)
      IF(CC(6,J,K) .GT. 0.) A2(J,K+5) = ALOG10(CC(6,J,K))
  500 IF(TSED(J) .GT. 0.) A2(J,10) = ALOG10(TSED(J))
C
C
C WRITE ARRAY(J,VARIABLE) FOR TECKTRONIX PLOT
C OUTPUT URITTEN ON FILE TAPE6=NOW
C TO SUBMIT , REPLACE,TAPE6=NOW , THEN CALL,SUB(F=TEKPLT)
C
      REWIND 6
      DO 600 J = 1,NT
      DO 599 I = 1,10
  599 IF(A(J,I) .LT. -2.) A(J,I) = -2.
C
  600 WRITE(6)(A(J,1),A(J,2),A(J,4),A(J,5),A(J,6),A(J,8),A(J,9))
C
      STOP
      END
```

```
      SUBROUTINE DECAY
      COMMON /RATE/ PK(5,8),BK(5,8)
      COMMON /BAL/ THERE(100,5)
      COMMON /INDAAT/ S(5,2),TK(2),MW(5),AA(5),BB(5)
      COMMON /LOSS/ TLOSS(5),SD(100,5),TL(100,5),BD(8,100,5),PD(8,100,5)
      COMMON /PARM/ TM(101,5),CM(8,100,5),PM(8,100,5),CC(8,100,5)
      COMMON /INDEX/ I,J,K,JJ,NC,NT,NX
      COMMON /INFO/ LC,Z(8),VP(5),H(5),OC(8),V(8)
C
C PK & BK ARE PHOTOLYTIC & BIOLOOICAL DECOMPOSITION RATES(CMPD,CMPT)
C
C UNITS PK(0.5YR-1) , BK(MOL/M3/0.5YR)
C ASSUMPTIONS IN BIO CALC ; MICROBIAL DENSITY = 20CELLS/ML & 1E6/ML
C IN WATER & SEDIMENTS RESPECTIVELY
C
C CALCULATE PHOTOLYTIC DECAY
      DO 20 I = 1,NC
C PR REDUCES UINTER RATES BY 1/2
      PR = 1.0
      IF(JJ.EQ.1)PR=0.5
      PD(I,J,K) = CM(I,J,K) * (PR * PK(K,I))
   20 IF(PD(I,J,K).GT.CM(I,J,K)) PD(I,J,K) = CM(I,J,K)
c NECESSARY FOR nnss BALANCE
C
C CALCULATE BIOLOGICAL DECAY
      DO 10 I = 1,NC
      CLOUT = 1.0
      IF(JJ.EQ.1) CLOUT = 0.25
C THAT REDUCES UINTER RATES BY A FACTOR OF 4
      VIABLE = 1
C FRACTION OF VIABLE BACTERIA
      BD(I,J,K) = VIABLE * CLOUT * BK(K,I) * CM(I,J,K)
   10 IF(BD(I,J,K).GT. (CM(I,J,K) - PD(I,J,K))) BD(I,J,K) = CM(I,J,K)
     1- PD(I,J,K)
C NECESSARY FOR HASS BALANCE
C
C
C CALCULATE THE NEU CONCENTRATION
      DO 30 I = 1,NC
      CM(I,J,K) = CM(I,J,K) - (BD(I,J,K) + PD(I,J,K))
      IF(CM(I,J,K) .LE. 0.) CM(I,J,K) = 0.
   30 CC(I,J,K) = CM(I,J,K) * MW(K) / V(I)
C
C  CALCULATE SEDIHENT ALTERATION ; RECEIVES 50% OF DETRITUS PER TIHE
C   STEP ; THICKNESS REMAINS CONSTANT
      SD(J,K) = 0.375 * CM(6,J,K) / 100.
      CM(6,J,K) = 99.625*CM(6,J,K)/100. + 0.5*CM(4,J,K)
      CM(4,J,K) = 0.5 * CM(4,J,K)
C SD = MASS (MOL) BURIED IN DEEP SEDIMENTS
      CC(6,J,K) = CM(6,J,K) * MW(K) / V(6)
C
```

```
C  CALCULATE NEU TOTAL MASS
      TM(J,K) = 0.
      TL(J,K) = 0.
      DO 40 I = 1,NC
      TM(J,K) = TM(J,K) + CM(I,J,K)
   40 TL(J,K) = TL(J,K) + BD(I,J,K) t PD(I,J,K)
      TL(J,K) = TL(J,K) + SD(J,K)
C TL = MASS OF REMOVED CONTAMINENT
C THERE = MASS IN SYSTEM + SYSTEM LOSSES
C
      DO 44 I = 1,NC
   44 PM(I,J,K) = 100. * CM(I,J,K)/TM(J,K)
C PM IS THE PERCENTAGE DISTRIBUTION
C
C SUMMING UP LOSSES
      TLOSS(K) = TLOSS(K) + TL(J,K)
      THERE(J,K) = TM(J,K) + TLOSS(K)
      RETURN
      END
 EOI ENCOUNTERED.
```

```
/GET,LOAD2
/COPY,LOAD2
      SUBROUTINE LOAD
      COMMON /INTO/ X(5),TINPUT(100,5),TLOAD(100,5)
      COMMON /INDEX/ I,J,K,JJ,NC,NT,NX
      COMMON /PARM/ TM(101,5),CM(8,100,5),PM(8,100,5),CC(8,100,5)
      COMMON /INDAAT/ S(5,2),TK(2),MW(5),AA(5),BB(5)
C
C ROUTINE INCREASES TOTAL COMPOUND MASS EACH TIME STEP
      TINPUT(J,K) = (X(K) / MW(K) * (1.2E-3*J*J - 1.6E-5*J*J*J))
      IF(TINPUT(J,K) .LE. 0.)TINPUT(J,K) = 0.
      IF(J.EQ.1)6,7
    6 TM(1,K) = TINPUT(1,K)
      GO TO 8
    7 TM(J,K) = TM(J-1,K) + TINPUT(J,K)
    8 CONTINUE
C
      IF(J.EQ.1) TLOAD(J,K) = TINPUT(1,K) + TM(1,K)
      IF(J.GT.1) TLOAD(J,K) = TLOAD(J-1,K) t TINPUT(J,K)
C
      RETURN
      END
 EOI ENCOUNTERED.
```

```
/GET,OUTPUT2
/COPY,OUTPUT2
      SUBROUTINE OUTPUT
      COMMON /LOSS/ TLOSS(5),SD(100,5),TL(100,5),BD(8,100,5),PD(8,100,5)
      COMMON /BAL/ THERE(100,5)
      COMMON /PARM/ TM(101,5),CM(8,100,5),PM(8,100,5),CC(8,100,5)
      COMMON /INDEX/ I,J,K,JJ,NC,NT,NX
      COMMON /INTO/ X(5),TINPUT(100,5),TLOAD(100,5)
      COMMON /INFO/ LC,Z(8),VP(5),H(5),OC(8),V(8)
C
C CONTROLS PROGRAM OUTPUT FOR FUGMOD2
C
      JSKIP = (NT - 2)/2
      DO 100 J = 1,NT,JSKIP
      PRINT 1,J
    1 FORMAT(///,"TIME STEP =",I4,/)
      DO 100 K = 1,NX
      PRINT 7
    7 FORMAT(/,20X,"SYSTEM MASS BALANCE (MOLS)")
      PRINT 2,TINPUT(J,K),TM(J,K),TL(J,K)
    2 FORMAT(/,"T STEP LOAD =",E8.3,"     TOTAL MASS IN SYSTEM =",E8.3,
     1"     STEP LOSS =",E8.3)
      PRINT 15,TLOAD(J,K),THERE(J,K)
   15 FORMAT("TO DATE:INPUT=",E12.4,4X,"AMT TRACED=",E12.4,/)
      PRINT 8
    8 FORMAT("INDICES   CONTANINENT DISTRIBUTION",6X,"LOSS RATES(MOL/"
     1"0.5YR)")
      PRINT 3
    3 FORMAT("  I  K",4X,"CM(MOL)",3X,"PM(%)",5X,"CC(PPM)",3X,"BIO",7X,
     1"PHOTO",5X,"SED",8X,"Z",/)
      DO 91 I = 1,NC
      SED = 0.
      IF(I.EQ.NC) SED = SD(J,K)
      PRINT 4,I,K,CM(I,J,K),PM(I,J,K),CC(I,J,K),BD(I,J,K),PD(I,J,K)
     1,SED,Z(I)
    4 FORMAT(2I3,7E10.2)
   91 CONTINUE
  100 CONTINUE
      RETURN
      END
 EOI ENCOUNTERED.
```

```
/GET,TEKPLT
/COPY,TEKPLT
/JOB
/NOSEQ
PCBPLOT,T170.                                BJE.
ACCOUNT,GL14,VERDA,GERL.
CHARGE,RJ,1766212.
FTN,R=2.
GET,TAPE5=NOW.
CALL,BEPLOT.
REPLACE,TAPE2=PLOT.
GOTO,1.
EXIT.
1,GET,SAVRSLT/UN=GLERL.
DAYFILE,DAY.
REPLACE,DAY.
CALL.SAVRSLT(RESULT=BJESAV)
/EOR
      PROGRAM PCB(INPUT,OUTPUT,TAPE5,TAPE2)
      DIMENSION A(100,10),T(100)
C READ DATA 1ST VARIABLE IS INDEPENDENT
      REUIND 5
C
C NPLT = NUMBER OF PLOTS
C
C NP = NUMBER OF DEPENDENT VARIABLES ON SINGLE GRAPH
      NP = 7
C
C
      DO 1 J = 1,100
    1 READ(5) (A(J,I),I=1,NP)
C I LOOP IS THE NUMBER OF PARNS BEING PLOTTED
C  RESTRUCTURING  ARRAYS
      T(1) = 0.
      DO 10 J = 1,99
   10 T(J+1) = FLOAT(J) / 2.
C
```

```
C  TECKTRDNIX  PLOTTING  GARBAGE
       CALL  ID(" BJE$",100)
       CALL TEKTRN("AUTOHC=YES,BAUD=2400,CENTER,BATCH,TERM=4014,END$",
      1100)
       CALL BGNPL(1)
       CALL NOCHEK
       CALL TITLE(1H ,-1,"TIME(YEARS)$",100,"LOG CONCENTRATION(PPM)$",
      1100.10..7.)
       CALL GRAF(0.,5.,50.,-2.,.5,2.)
       CALL MESSAG("DDT CONCENTRATIONS;WINTER CONDITIONS",38,2.,6.5)
C
       DO 20 I = 1,NP
       IF(I.EQ.2) CALL DOT
       IF(I.EQ.3) CALL CHNDOT
       IF(I.EQ.4) CALL DASH
       IF(I.EQ.5) CALL CHNDSN
       IF(I.EQ.6) CALL RESET("CHNDSH")
   20  CALL CURVE(T,A(1,I),100,0)
       CALL ENDPL(-1)
       CALL DONEPL
       STOP
       END
 EOI ENCOUNTERED.
```

```
/GET,SUBS2
/COPY,SUBS2
B
READP  LOAD2  DECAY2  OUTPUT2
E
 EOI  ENCOUNTERED.
/
```

```
/GET,RUN3
/COPY,RUN3
GET,FUGMOD3.
GET,SUBS2.
XEDIT,FUGMOD3,I=SUBS2.
REWIND,LGO.
FTN,I=FUGMOD3,L=0,PMD.
GET,FUGMOD3.
LGO.OP=T.
COPY,OUTPUT
 EOI  ENCOUNTERED.
```