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# Predicting the Future Fate of PCBs in Lake Hartwell

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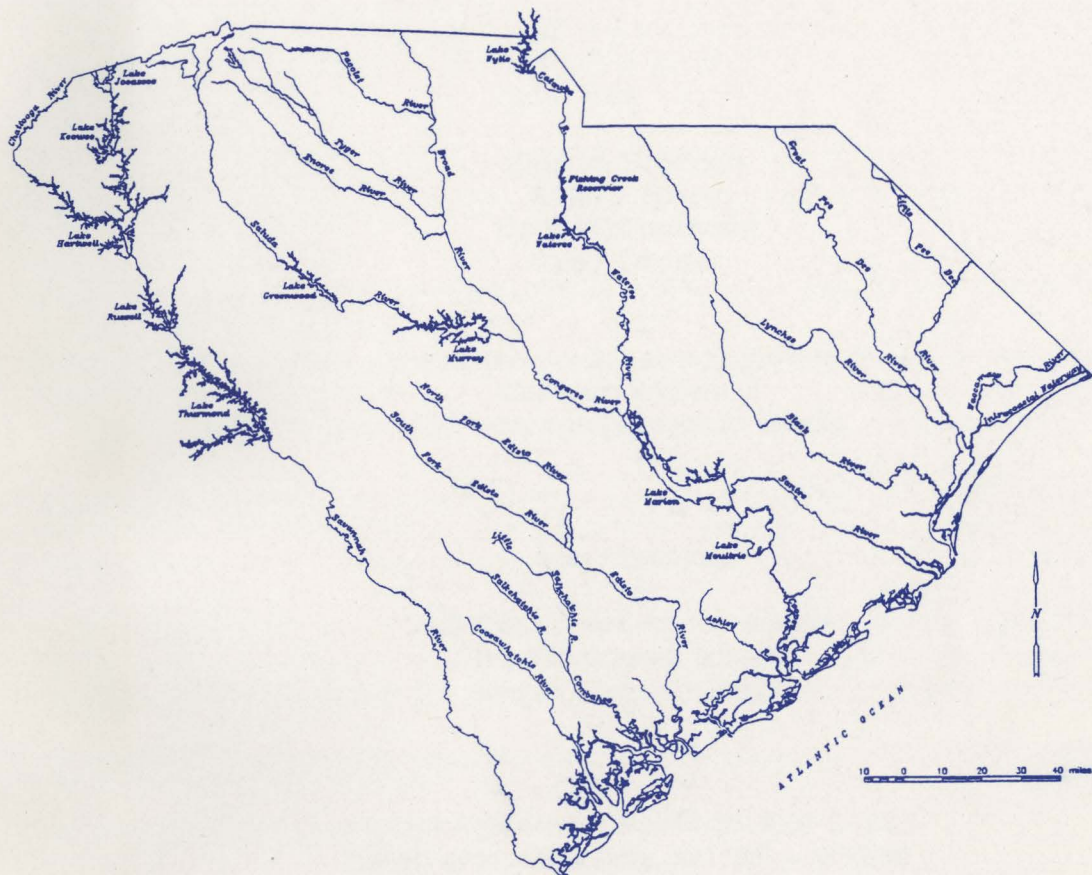
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**SOUTH CAROLINA WATER RESOURCES RESEARCH INSTITUTE  
CLEMSON UNIVERSITY**



**PREDICTING THE FUTURE FATE OF PCBs IN  
LAKE HARTWELL**

**Alan W. Elzerman, Kevin J. Farley, Frank M. Dunnivant  
and Craig Cooper**

**Report No. 139**

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## **PREDICTING THE FUTURE FATE OF PCBs IN LAKE HARTWELL**

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### **ABSTRACT**

Evidence for reductive dechlorination and aerobic decomposition was obtained. A simplified one-dimensional analytical model was developed and tested for predicting pollutant fate in river type systems, and it was applied to the source area of PCBs for Lake Hartwell. Modeling the fate and distribution of specific congeners indicated volatilization and sediment burial can be significant sinks for the Lake Hartwell system, and the characteristics of Lake Hartwell that might affect PCB distributions, and (3) collection and analysis of sediment samples for information on the sources and current inventory and distribution of PCBs. The work reported here (1) extended the determination of physicochemical parameter values using structure property relationships, (2) investigated several modeling approaches for predicting the future fate of PCBs in Lake Hartwell and evaluating remedial actions, and (3) compared results from the various models and field data on a congener specific basis.

Values for solubility, Henry's Law constants and vapor pressures were determined in the lab for selected congeners and predicted for all 209 congeners using quantitative structure-property relationships (QSPRs). Extensive lab and modeling investigations of adsorption/desorption of PCBs on sediments, including equilibrium distributions and kinetic coefficients, were also completed and indicated slow desorption rates may influence the fate and effects of PCBs. Lab results and calculated estimates of

differential weathering as predicted by sequences of equilibrations of water, sediment and air generally agreed well.

#### PREFACE AND ACKNOWLEDGMENTS

A major emphasis of the project was to accomplish congener specific analyses and assessments, since each congener has its own physicochemical and toxicological properties. The congener specific data indicated weathering of PCBs by physical, chemical, and biological processes resulted in significant fractionation of different congeners as a function of depth in sediment and distance from the main source. Evidence for reductive dechlorination and aerobic decomposition was obtained. A simplified one-dimensional analytical model was developed and tested for predicting pollutant fate in river type systems, and it was applied to the source area of PCBs for Lake Hartwell. Modeling the fate and distribution of specific congeners indicated volatilization and sediment burial can be significant sinks for the Lake Hartwell system.

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The reports summarize a large amount of information that has been collected, data that have been generated, and evaluations that have been made. It is impossible to include all of the information in this report, or even in all of the papers, theses, and dissertations that have resulted from this project. Consequently, the complete information set is maintained at the Department of Environmental Systems Engineering, Clemson University, Clemson, SC 29634; by Dr. Alan W. Eizeman. Data, discussions and conclusions for most purposes are included in the scientific papers, student theses and dissertations that have been generated. A complete listing to date is included in Appendix A of this report. Copies are available by contacting Dr. Eizeman at the address above.

Our understanding of the inputs, current distribution and likely fate of PCBs in Lake Hartwell has increased significantly. However, it should not be concluded that our understanding is now sufficient. Information needs still require more field, laboratory and modeling studies.

## PREFACE AND ACKNOWLEDGMENTS

This report is the second to the South Carolina Water Resources Research Institute based on our long term investigation of PCBs and related compounds in Lake Hartwell (between South Carolina and Georgia). The first report, "PCBs and Related Compounds in Lake Hartwell (Elzerman *et al.*, 1991), emphasized (a) field data obtained on the current distribution of PCBs in the sediments of Lake Hartwell and, (b) determinations of values for physicochemical parameters required for modeling the fate of PCBs in environmental systems. This second report (a) extends the determination of physicochemical parameter values using structure property relationships, (b) investigates the fate of PCBs in Lake Hartwell through laboratory and mathematical modeling, and (c) compares results from the various models and field data on a congener specific basis. Information from the first report is repeated here only when necessary, therefore, the first report may need to be consulted in reading this second report. This project was supported in part by a grant from the National Science Foundation (Grant # ISP-8808088).

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Our understanding of the inputs, current distribution and likely fate of PCBs in Lake Hartwell has increased significantly. However, it should not be concluded that our understanding is now sufficient. Information needs still require more field, laboratory and modeling efforts. The Environmental Protection Agency has conducted more field sampling of sediments during the summer of 1991 related to the designation of parts of Lake Hartwell as a Superfund site on February 15, 1990. The South Carolina Department of Health and Environmental Control continues to periodically monitor PCB concentrations in fish because of the continuing advisory against eating fish from parts of the lake. Although not currently funded beyond this report, we are continuing research on modeling PCBs in Lake Hartwell when possible to make use of new information and advance capabilities. Larger scale and more integrated efforts, especially in relation to toxicity and risk analysis, will probably be required before research on PCBs in Lake Hartwell is accepted as sufficient.

A project of this magnitude requires input of substantial funding and the efforts of many people. We would like to acknowledge the seed funding that allowed initiation of this project through a grant from the National Science Foundation (Grant # ISP-8011451) and the continuing funding that we have received through the South Carolina Water Resources Research Institute. The current authors would also like to thank the other students who have contributed to this project, particularly those whose thesis or dissertation is listed in Appendix A.

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The location of the reservoir (see Figure 1.1) makes it a regional resource of particular interest to South Carolina and Georgia. The importance of the Lake Hartwell resource and general concern about PCBs have led to numerous studies of PCBs in Lake Hartwell (see Etzerman *et al.*, 1991). Almost all of the attention has been focused on PCBs in the sediments, where PCBs tend to concentrate, and on PCBs in fish, which probably represent the major pathway of PCBs from Lake Hartwell to humans. The declaration of PCB contaminated areas as a Superfund site has increased interest in PCBs in Lake Hartwell in general, and on potential remedial actions in particular.

Ambient concentrations of PCBs in the various compartments of Lake Hartwell are fairly well, although not completely, known (see Etzerman *et al.*, 1991 for review). Unfortunately, however, most of the major questions still remain, such as, "How long will the PCBs remain, how will they change, and where will they go?", and "What can be done about the PCBs in Lake Hartwell without causing more problems, and is it

## CHAPTER I INTRODUCTION

PCB contamination in Lake Hartwell from one major source on Twelve Mile Creek has been recognized since the early 1970's (see Elzerman *et al.*, 1991 for a review of current knowledge). An advisory against eating fish caught from the upper portion of Lake Hartwell remains in effect due to PCB levels above FDA recommended values (see Gaymon, 1982, 1888 and 1990 for reviews of data). Recreational enjoyment of the lake and lakeside real estate values have potentially been affected. PCB contaminated areas of Pickens County, South Carolina, and Lake Hartwell were placed on the "Superfund" National Priority List on February 15, 1990 with the name "Sangamo Weston, Inc./Twelve-Mile Creek/Lake Hartwell Superfund site".

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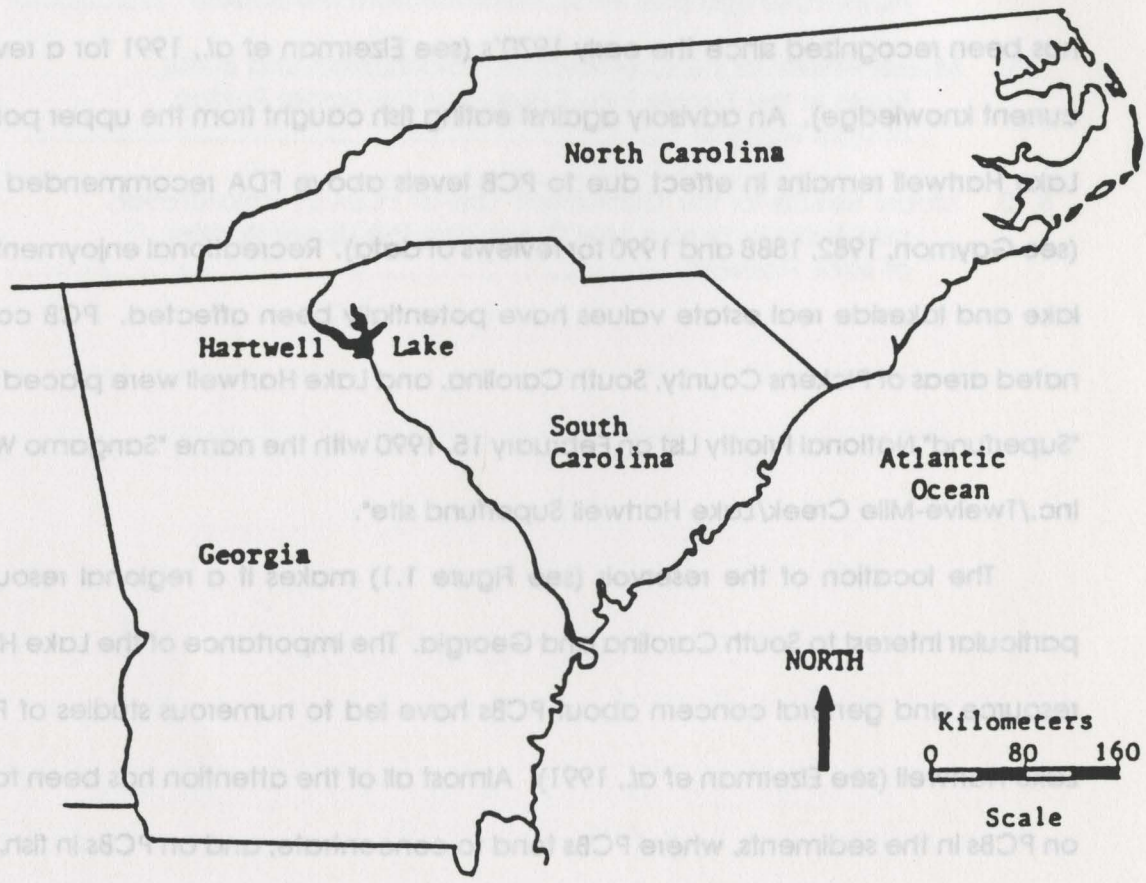


Figure 1.1. General location of Lake Hartwell.

practical?." Of course, the ultimate question for most people, "What are the risks associated with PCBs in Lake Hartwell?", also remains incompletely answered. Despite many years of research on PCBs, and intense debate on the dangers associated with PCBs, many significant questions remain.

The research reported here did not attempt to address all of the remaining questions about PCBs, but rather one of the central questions. At the center of all of the remaining concerns about PCBs in Lake Hartwell is the need to be able to predict what will happen to the PCBs in the future. The future fate of the PCBs will determine their effects as well as their longevity in the system. All risk assessments will require input information on exposure pathways and amounts. Additionally, choice of the most effective remedial actions which also avoid creating secondary problems will necessarily consider how PCBs are expected to behave and be distributed. Future concentrations in the various components of the system, differences in behavior between congeners (each congener is one of the 209 possible different individual PCB compounds, see Appendix B) and processes affecting fate and distribution must all be considered.

The future fate and distribution of PCBs in Lake Hartwell can be estimated by a combination of extrapolations from their past behavior in the system and assessments of how they should behave based on the characteristics of PCBs and the system. Both of these approaches are predicated on sufficient understanding of the inputs of PCBs to the system and their current distribution, which was the purpose of an earlier work discussed in the first report of this project (Elzerman *et al.*, 1991). Required knowledge of the characteristics of PCBs and the Lake Hartwell system was partially reported in the first report and continues in this report.

The ultimate objective is to be able to predict what will happen to the PCBs in the future under various scenarios involving either no remedial actions or specific stated

remedial actions. Such information is paramount for making informed choices between options that appropriately include technical, economic, social, and risk reduction factors. Generally, these assessments rely on some type of model, or simplification, of the system that permits obtaining intelligible and valid output results for stated assumptions and input data. The emphasis on intelligible and valid output results recognizes that it is not possible to have a perfect model of complicated systems; simplifications are required to make the model manageable and to produce results that can be interpreted. Of course, the model must also produce results that are technically correct and valid. The art of making and using models is to ask the right questions and have the model produce proper results, since it is impossible to make a totally comprehensive model of a system like Lake Hartwell. Then, the model can be used to answer questions about the future based on different sets of assumptions. Ultimate decisions will still require evaluations and judgements and will still inherently embody some risk.

A variety of modeling approaches are available. In this investigation, pictorial, physical, and both empirical and theoretical mathematical models were utilized. In some cases one model provided results not attainable with the others. However, different models were also used in some cases for the same purpose to evaluate whether they yielded similar or consistent results. Since no model is perfect, consistency between different approaches increases confidence in the end products.

Similarly, model results presented in this report are also compared to field results presented in the first report (Elzerman *et al.*, 1991) to evaluate performance. In this case, a useful model generally should be able to start with historical information and predict the current situation. Although not proving anything, consistency between model results and field observations increases confidence in both.

Figure 1.1. General location of Lake Hartwell.



Models were utilized in this investigation primarily for three purposes: (a) estimating physicochemical parameter values for PCB congeners, (b) determining the limnological characteristics of Lake Hartwell, and (c) predicting the future fate and distribution of PCBs in the Lake.

Presented first, in Chapter III, are results from quantitative structure property relationship (QSPR) models used for estimating values of physicochemical parameters required as inputs to the fate and distribution models. To completely assess the fate and effects of PCBs, each individual congener that is identifiable in the system must be considered separately, since each is a separate compound with its own characteristics. In practice, as a practical matter, they are often considered in groups with similar characteristics, but even this approach requires knowledge of or assumptions about individual congener characteristics. The purpose of the QSPR models is to provide physicochemical parameter values for the multitude of congeners potentially present (a total of 209 possible congeners) without having to perform costly and time consuming measurements of each one. By utilizing theoretical and empirical relationships between the congeners and measured values for ten to 20 congeners, values for the other congeners can be predicted. In turn, the parameter values obtained for the congeners in combination with knowledge of the lake system characteristics allow quantification of the various processes that affect the fate of PCBs (primarily degradation, volatilization, sorption, settling, burial in the sediments and advective transport).

The second major use of models in this investigation was determining the limnological characteristics of Lake Hartwell to quantify hydrologic characteristics and transport by advective and settling mechanisms. Hydrologic modeling relied primarily on using natural and anthropogenic radionuclides in Lake Hartwell as tracers. The presence of both PCB and radionuclide inputs to Lake Hartwell presents an unusual

opportunity for combined studies which our investigations have begun to exploit. The results of the radionuclide studies, some of which were also funded by the South Carolina Water Resources Research Institute, are presented in Vandeven *et al.* (1984), Fjeld *et al.* (1986), Horn (1987), and Reboul (1987). The radionuclide studies were responsible for the central conceptual model underlying all of the fate and distribution modeling. The radionuclide investigations indicated for a first approximation that the lake could be treated as a series of completely mixed reactors, an assumption that greatly simplifies the model structure required.

From this central conceptual model, several productive paths were followed. In the laboratory, a physical model of a series of reactors was approximated by doing sequential batch equilibrations of sediment, water and PCBs to follow fractionation of congeners (results presented in Chapter IV). Computer models based on empirical and theoretical relationships were also constructed to mimic the laboratory batch equilibrations (also see Chapter IV). Finally, a mathematical model describing physical transport, solids deposition, PCB adsorption, and volatilization was developed to examine the fate and distribution of PCB congeners in the Lake Hartwell system (see Chapter V).

Although this report presents the state of our project at the end of the grant funding, it should not be assumed it represents all we need to know about PCBs in Lake Hartwell. Indeed, significant questions remain unanswered, and new questions have arisen. The purpose of this phase of the project was to develop modeling approaches and to evaluate them for ease of use and usefulness of results. Considerable work on model validation for specific uses should precede any conclusive studies. Important questions, such as the effects of PCBs in the lake, risks to humans and the efficacy of remedial actions, can benefit from the results presented here, but are not directly addressed. Considerable work and evaluation remains to be done.

## CHAPTER II

### PROJECT OBJECTIVES

The research involved field, laboratory, and theoretical investigations. The ultimate goal is to characterize the inputs and current distribution, understand the processes controlling the fate, and be able to predict the future fate and distribution of PCBs and related compounds in Lake Hartwell and its tributaries. This information is required for proper evaluation of the potential effects of PCBs in the Lake Hartwell system and for assessment of proposed remedial actions. A previous report (Elzerman *et al.*, 1991) emphasized the inputs and current distribution of PCBs in Lake Hartwell, representing the earlier phases of the project which developed analytical techniques, laboratory procedures and an extensive field survey of PCBs in the sediments of Lake Hartwell. This report presents additional information on the characteristics of PCBs and Lake Hartwell and models developed to evaluate the future fate and distribution of PCBs in the lake.

Specific objectives of the research presented in this report were:

1. application of structure/property models for parameter estimation from our experimentally derived data to quantify the characteristics of all PCB congeners, which is required to quantitatively model and understand controlling processes in Lake Hartwell,
2. predictions of the extent, rate, and importance of "burial" of PCBs in the sediments as a removal mechanism,
3. evaluation of competing sinks, such as volatilization to the atmosphere,
4. investigation of potential spreading of PCBs on sediment resuspended from the bottom or input from the watershed and release of PCBs from sediment to the water column, and
5. utilization of all available information on Lake Hartwell and PCB characteristics in available generic models (e.g. EPA's WASP4) and specifically tailored models to predict the future fate of PCBs and develop approaches to evaluating proposed remedial actions.

### CHAPTER III

## QUANTITATIVE STRUCTURE PROPERTY RELATIONSHIPS FOR PCB PHYSICOCHEMICAL PARAMETERS

### Introduction

Quantitative structure-activity relationships (QSARs) are a well established tool in pharmacology and drug development, and are used to predict the biological effects (bioaccumulation, enzyme induction, biodegradation, toxicity) resulting from exposure of organisms to specific compounds under controlled conditions. However, for the estimation of chemical parameters, such as the aqueous solubility or Henry's law Constant, it is more correct to refer to the descriptor(s) as quantitative structure-property relationships (QSPRs) since evaluation of biological response or activity is not included or implied. QSPRs have recently been applied to predicting chemical and physical parameters of hydrophobic compounds and are rapidly becoming a useful tool in environmental chemistry.

Several QSPR-based models are available for predicting aqueous solubilities (S), Henry's Law constants (HLCs), and environmental partition coefficients of organic contaminants (Burkhard, 1984; Arbuckle, 1986; Sabljic, 1987; Doucette and Andren, 1988; Opperhuizen *et al.*, 1988; Nirmalakhandan and Speece, 1988a, 1988b; Kamlet *et al.*, 1988; Banerjee and Howard, 1988; Nirmalakhandan and Speece, 1989; Hawker, 1989; Brunner *et al.*, 1990), with some of these approaches allowing the predictive modeling of each chemical parameter (e.g. S, HLC, etc.) directly from structural information. However, many of these QSPR-based models are unable to account for slight structural changes between isomers and homologues or this aspect of the models has not been adequately evaluated.

The importance of highly specific QSPRs becomes obvious when the fate and transport of structurally similar compounds are considered, especially in the case of PCBs (Bopp *et al.*, 1981; Burkhard, 1984; Bush *et al.*, 1987; Dunnivant, 1988). PCBs were released into the environment in the form of multi-congener mixtures referred to as Aroclors. Each Aroclor (e.g. 1016, 1254, 1260, etc.) contains a general mixture of congeners and this "fingerprint of contamination" (based on relative amounts of major congener composition) has been used to estimate the type of Aroclor(s) present in environmental samples (Albro and Parker, 1979; Albro *et al.*, 1981). However, numerous field investigations have shown that Aroclors extracted from environmental samples contain significantly different congener compositions than those present in the original Aroclor(s) (Bopp *et al.*, 1981; Bush *et al.*, 1987; Germann, 1988). This change in congener composition has been attributed to selective microbial degradation/dechlorination (Brown *et al.*, 1984; Brown *et al.*, 1987a,b; Quensen *et al.*, 1988; Brown and Wagner, 1990) and chemical/physical partitioning processes (Bopp *et al.*, 1981; Bush *et al.*, 1987; Dunnivant, 1988; Germann, 1988). Thus, in order to effectively evaluate the relative importance of congener-specific partitioning processes accurate values of aqueous solubilities, HLCs, and solid/aqueous partition coefficients must be measured or predicted for each congener.

The purpose of this investigation was to utilize experimentally determined S and HLC data from previous investigations (Dunnivant, 1988; Dunnivant and Elzerman, 1988; Dunnivant *et al.*, 1988) in the development of QSPR models sensitive to slight changes in molecular structure such as those occurring in the homologous series of PCBs (e.g. dichlorobiphenyl, trichlorobiphenyl, etc.). A comparison of literature data reveals considerable scatter among solubilities and HLCs for identical PCB congeners. Therefore, use of an internally consistent data set, obtained under similar conditions, is necessary in order to develop a QSPR model which does not contain errors resulting

from inter-laboratory sources or use of different analytical procedures (Kaiser, 1984). The data utilized here were generated for a previous, but unsuccessful, attempt to develop predictive models based solely on already published QSPR parameters. Recent collaborations between Clemson University and Pennsylvania State University have allowed the successful prediction of aqueous solubilities and HLCs for PCBs and evaluation of other recently published QSPR models.

## Experimental Procedures

### Overview of Modeling Approach

QSPRs were obtained using the Automated Data Analysis and Pattern Recognition Toolkit (ADAPT) (Stuper *et al.*, 1979). A detailed routine-specific description of this software is beyond the scope of this paper and only a specific description of the QSPRs used will be given here. Basically, ADAPT consists of a modular set of software routines designed for the computer-assisted study of structure-property relations. The procedures used in this study consist of three stages: (a) entry and storage of molecular structures and aqueous S or HLC data, (b) generation of molecular structure descriptors, and (c) regression analysis to obtain predictive model equations.

The molecular structures of the PCBs were entered into computer disk files by sketching them on a graphics terminal under software control and storing them as connection tables. Three-dimensional models were generated with molecular mechanics calculations which minimized molecular strain energies. The dihedral angles between the two phenyl rings were fixed at the following three values: 44° for congeners with no ortho substitution (Almenningen *et al.*, 1985), 57° for congeners with ortho substitution on one ring (McKinney *et al.*, 1983), and 74° for congeners with ortho substitution on both rings (Romming *et al.*, 1974). We believe the use of these three dihedral angles provides a more accurate three-dimensional representation of the

biphenyl molecule than calculations based on single, fixed-angle approaches (discussed later).

#### Calculation of Descriptors

The ADAPT software system contains many routines for the calculation of descriptors solely from molecular structure. Total surface areas (TSA) were calculated with Pearlman's algorithm (Pearlman, 1980). The molecular conformations were generated by molecular mechanics modeling utilizing the three fixed dihedral angles between the two phenyl rings described above, thus allowing strain-energies between adjacent atoms to be minimized. Each atom in the molecule was considered to be a sphere with a characteristic van der Waals radius. A solvent radius of 1.5 Å (for H<sub>2</sub>O) was used to give the solvent-accessible surface area of each PCB molecule.

The shadow areas (SA) of each molecule were calculated from three-dimensional conformations, thus SAs are the cross-sectional areas of the molecule projected onto three orthogonal planes. This is analogous to measuring the front, top, and side of the molecule represented as a set of opaque spheres. The calculated shadow areas are dependent on the orientation of the molecule in the coordinate system. Here, the molecules were oriented such that the ring with the most substituents was imbedded in the XY plane and the single bond connecting the two phenyl rings was collinear with the YZ plane. The value of the third shadow area is related to the torsional angle between the two phenyl rings and also to the degree of substitution of the molecule. The second principal moment of inertia (SMI) was derived from three dimensional representations of the molecules. Melting point values were taken from published data summaries (Erickson, 1986).

Path four molecular connectivity indices ( $^4X_p$ ) were developed based on a graphical treatment of the molecular topology of the compounds (Randic, 1975; Kier and Hall, 1976). The path three Kappa index ( $^3K$ ) was developed using a similar

graphical approach (Kier and Hall, 1976). Polarizability descriptors, the second ( $\alpha^2$ ) and third ( $\alpha^3$ ) molecular polarizability, were calculated using the atom dipole interaction model developed by Applequist *et al.* (1972). The method has been modified to enable calculation of molecular polarizability of aromatic compounds (McKinney *et al.*, 1983).

#### Development of Calculation Models

QSPRs were developed as linear additive multivariant models: one for calculation of solubilities, and another for calculating HLCs. The ADAPT program was used to perform statistical analysis (type III residual and principle of conditional error) to determine the descriptors most important in reducing the error associated with each model. Descriptors determined to be of least importance or containing collinear relationships with other descriptors were removed from the model until a model was obtained which accurately described the experimental data and contained the least number of parameters possible. Both simple and multiple regressions were performed.

Goodness of fit for each model was evaluated based on residual sum of squares, type III residuals,  $r$ , and mean squared error (standard error of the model), as well as visual observation of plots containing experimental versus calculated aqueous solubilities or HLCs.

### Results and Discussion

#### Experimental Data

Experimentally determined  $S$  and HLC data used in this investigation were taken from previous investigations (Dunnivant, 1988; Dunnivant and Elzerman, 1988; Dunnivant *et al.*, 1988) where they were compared, in detail, to data in the literature obtained using similar analytical techniques. Comparisons between these solubility data and other literature data showed them to agree within approximately one log solubility unit



(one order of magnitude). Comparisons between the HLCs and other literature data also showed similar agreement. None of the experimental data sets appear to consistently over- or under-estimate solubilities when compared with one another; thus, the variability between different data sets probably results from uncertainties related to the difficulty in measuring aqueous solubilities of hydrophobic compounds. Such variability also inhibits development of accurate QSPR models. The data set of Dunnivant (Dunnivant and Elzerman, 1988; Dunnivant *et al.*, 1988) was selected because it has been shown to be internally consistent and consistent with solubility theory. This data set was used, in conjunction with previously unpublished data obtained under identical conditions (Dunnivant, 1988), to develop S and HLC QSPR models for polychlorinated biphenyls. As noted earlier, the use of an internally consistent data set should allow a more valid evaluation of QSPR modeling techniques by removing error sources common between inter-laboratory data sets.

#### Calculation of Solubilities for PCBs

All PCB congener solubilities described earlier (Dunnivant, 1988; Dunnivant and Elzerman, 1988; Dunnivant *et al.*, 1988) were used with the exception of IUPAC numbers 12, 104 and 129. Melting point data, a necessary parameter in the solubility model, are not available for IUPAC numbers 104 and 129. Preliminary model development indicated that solubility data available for IUPAC number 12 (3,4-dichlorobiphenyl) was in error. Review of the chromatograms from both the calibration standard and the water extracts show several peaks adjacent to the 3,4-dichlorobiphenyl peak, indicating the presence of breakdown products or impurities in the primary standard (10%-20%); thus, the data for this congener were not used.

The best QSPR solubility calculation model developed using the ADAPT program can be described by

$$\log S = - 0.0352 (\text{TSA}) - 0.0103 (\text{MP}) + 0.0389 (\text{SA}) + 8.62 \quad (3.1)$$

$$n = 22 \quad r = 0.992 \quad F(3,18) = 329.4 \quad s = 0.165$$

where  $S$  = molar solubility as solid (moles/L),  $\text{TSA}$  = total molecular surface area (Angstroms<sup>2</sup>),  $\text{MP}$  = melting point (°C),  $\text{SA}$  = third shadow area (Angstroms<sup>2</sup>). The significance of each of these parameters will be discussed later.

The 22 calculated and experimental solubilities are shown in Table 3.1 and Figure 3.1. The model resulted in a high correlation ( $r = 0.992$ ) and a low standard error ( $s = 0.165$  or 2.2% of the mean value). Additional analysis showed that Eq. 3.1 possessed (a) a stable residual error structure, (b) residuals which were not correlated with any given chlorination pattern (number of chlorines or chlorination patterns), and (c) no collinearity between descriptors. Subsequently, Eq. 3.1 was used to predict  $S$  for the remaining PCB congeners (limited to congeners with known melting points) which are also included in Table 3.1. Predicted data in Table 3.1 are in good agreement with other data obtained using similar flow-through experimental techniques (Weil *et al.*, 1974; Miller *et al.*, 1980; Dickhut *et al.*, 1986) and indicate that no systematic bias, based on chlorination pattern, exists in Eq. 3.1. Thus, the model appears to accurately predict PCB solubility ( $S$  as solids).

Prior to comparing Eq. 3.1 to other solubility prediction models, several features of the current modeling effort should be discussed. One of the most important factors limiting the effectiveness of previous prediction models appears to be the angle of conformation used in calculating descriptor values. For example, calculated surface areas and molecular volumes for specific PCB congeners were found to be highly dependent on the torsional angle selected for the phenyl rings. Previous investigations report the use of a single fixed torsion angle or, when not stated by the author, review of the data indicate that such an approach was used (Yalkowsky and Valvani, 1979;

TABLE 3.1

OBSERVED VS. CALCULATED SOLUBILITY  
(S in  $-\log$  [mol/L] at 25°C)

IUPAC Number	compd	Observed $-\log S$	Calculated $-\log S$	Error
1	2-MCB	--	4.515	--
2	3-MCB	--	4.597	--
3	4-MCB	--	5.392	--
4	2,2'-DCB	5.267	5.237	-0.030
5	2,3-DCB	--	5.215	--
7	2,4-DCB	5.281	5.318	0.037
8	2,4'-DCB	--	5.540	--
9	2,5-DCB	5.260	5.169	-0.091
10	2,6-DCB	4.967	4.940	-0.027
11	3,3'-DCB	5.799	5.496	-0.303
12	3,4-DCB	--	5.746	--
14	3,5-DCB	--	5.537	--
15	4,4'-DCB	6.788	6.965	0.177
16	2,2',3-TCB	--	5.637	--
18	2,2',5-TCB	5.703	5.760	0.057
21	2,3,4-TCB	--	6.727	--
22	2,3,4'-TCB	--	6.568	--
23	2,3,5'-TCB	--	6.062	--
26	2,3',5-TCB	6.008	6.008	0.000
28	2,4,4'-TCB	6.344	6.463	0.119
29	2,4,5-TCB	--	6.490	--
30	2,4,6-TCB	6.009	6.107	0.098
31	2,4',5-TCB	--	6.431	--
33	2',3,4-TCB	--	6.228	--
34	2',3,5-TCB	--	6.099	--
37	3,4,4'-TCB	--	6.953	--

Table 3.1 (Continued)

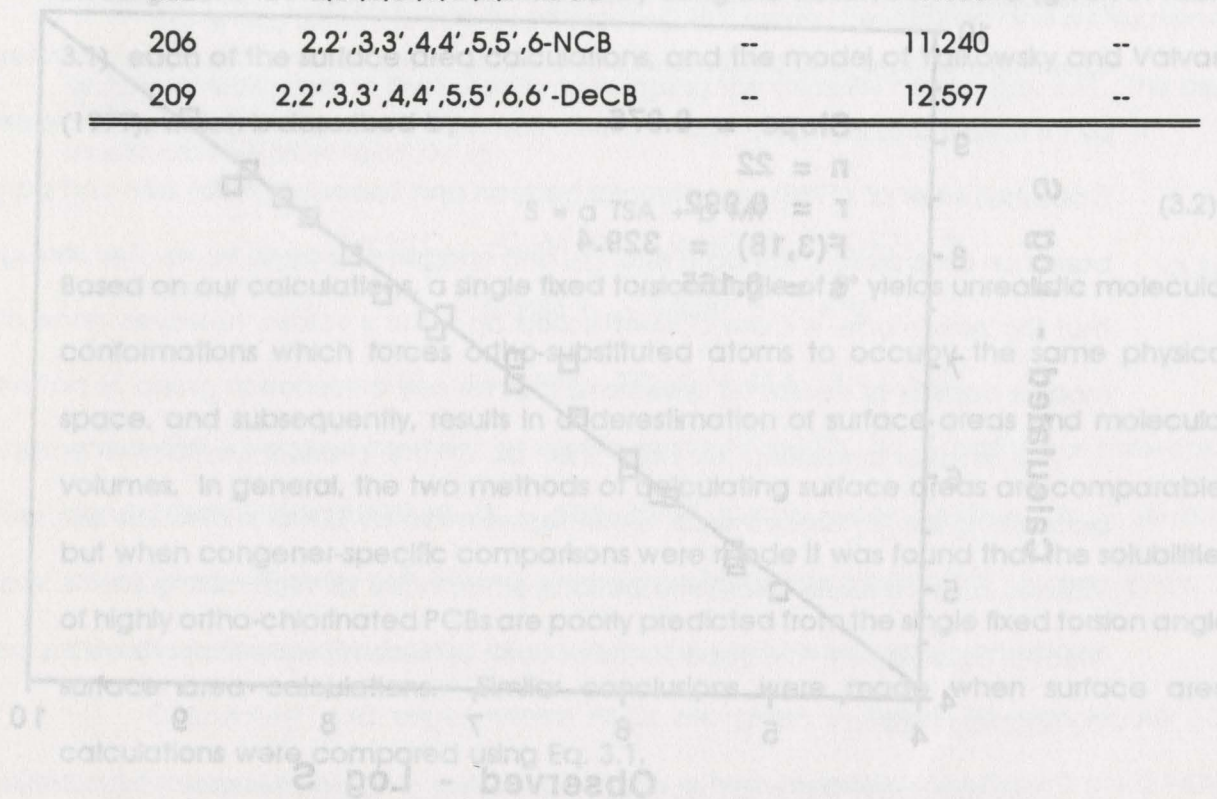
IUPAC Number	cmpd	Observed -log S	Calculated -log S	Error
39	3,4,4'-TCB	--	6.953	--
40	2,2',3,3'-TCB	7.273	7.355	0.082
42	2,2',3,4'-TCB	--	6.942	--
44	2,2',3,5'-TCB	--	6.583	--
46	2,2',3,6'-TCB	--	7.019	--
47	2,2',4,4'-TCB	--	6.769	--
49	2,2',4,5'-TCB	--	6.854	--
52	2,2',5,5'-TCB	6.426	6.942	0.516
53	2,2',5,6'-TCB	6.788	6.749	0.039
54	2,2',6,6'-TCB	7.390	7.306	-0.084
56	2,3,3',4'-TCB	--	7.405	--
58	2,3,3',5'-TCB	--	7.719	--
60	2,3,4,4'-TCB	--	8.028	--
61	2,3,4,5'-TCB	7.321	7.209	-0.112
63	2,3,4',5-TCB	--	7.604	--
65	2,3,4,5,6-TCB	--	6.831	--
66	2,3',4,4'-TCB	--	7.814	--
70	2,3',4',5-TCB	--	7.420	--
72	2,3',5,5'-TCB	--	7.436	--
74	2,4,4',5-TCB	--	7.809	--
77	3,3',4,4'-TCB	8.726	8.475	-0.251
79	3,3',4,5'-TCB	--	7.909	--
80	3,3',5,5'-TCB	8.374	8.383	0.009
82	2,2',3,3',4-PCB	--	8.067	--
87	2,2',3,4,5'-PCB	--	7.967	--
95	2,2',3,5',6-PCB	--	7.474	--
97	2,2',3',4,5-PCB	--	7.586	--

Table 3.1 (Continued)

IUPAC Number	cmpd	Observed -log S	Calculated -log S	Error
101	2,2',4,5,5'-PCB	7.684	7.540	0.144
105	2,3,3',4,4'-TCB	--	8.235	--
114	2,3,4,4',5-PCB	--	8.123	--
116	2,3,4,5,6-PCB	7.910	7.875	-0.035
118	2,3',4,4',5-PCB	--	8.215	--
128	2,2',3,3',4,4'-HeCB	9.014	9.091	0.077
133	2,2',3,3',5,5'-HeCB	--	8.917	--
136	2,2',3,3',6,6'-HeCB	--	7.980	--
137	2,2',3,4,4',5-HeCB	--	8.324	--
138	2,2',3,4,4',5'-HeCB	--	8.377	--
140	2,2',3,4,4',6'-HeCB	--	8.046	--
142	2,2',3,4,5,6-HeCB	--	8.419	--
151	2,2',3,5,5',6-HeCB	--	8.209	--
153	2,2',4,4',5,5'-HeCB	8.622	8.611	-0.011
155	2,2',4,4',6,6'-HeCB	8.202	8.201	-0.001
160	2,3,3',4,5,6-HeCB	--	8.360	--
166	2,3,4,4',5,6-HeCB	--	9.167	--
168	2,3',4,4',5,6-HeCB	--	8.568	--
169	3,3',4,4',5,5'-HeCB	--	9.934	--
170	2,2',3,3',4,4',5-HCB	--	9.523	--
174	2,2',3,3',4,5,6'-HCB	--	9.093	--
180	2,2',3,4,4',5,5'-HCB	--	9.244	--
182	2,2',3,4,4',5,6'-HCB	--	9.462	--
185	2,2',3,4,5,5',6-HCB	--	9.311	--
189	2,3,3',4,4',5,5'-HCB	--	9.947	--
190	2,3,3',4,4',5,6-HCB	--	9.254	--
194	2,2',3,3',4,4',5,5'-OCB	--	10.310	--

Table 3.1 (Continued)

IUPAC Number	cmpd	Observed -log S	Calculated -log S	Error
197	2,2',3,3',4,4',6,6'-OCB	--	9.619	--
202	2,2',3,3',5,5',6,6'-OCB	--	9.973	--
206	2,2',3,3',4,4',5,5',6-NCB	--	11.240	--
209	2,2',3,3',4,4',5,5',6,6'-DeCB	--	12.597	--



Another feature of Eq. 3.1 is the presence of the third shadow area (SA). This feature of the model was found to be particularly important for the prediction of the solubility of individual PCB congeners and may account for solute-solute interactions and effects of crystallinity of the solute which are not fully accounted for in melting point data. In any event, inclusion of SA was found to significantly reduce the calculation error of Eq. 3.1, especially for congeners containing high degrees of ortho-chlorination.

Several models are currently available for predicting the solubility of hydrophobic compounds and for comparison to Eq. 3.1. Opperhuizen *et al.* (1988) developed a model specifically for predicting PCB solubility (aqueous solubility as solids) as a function

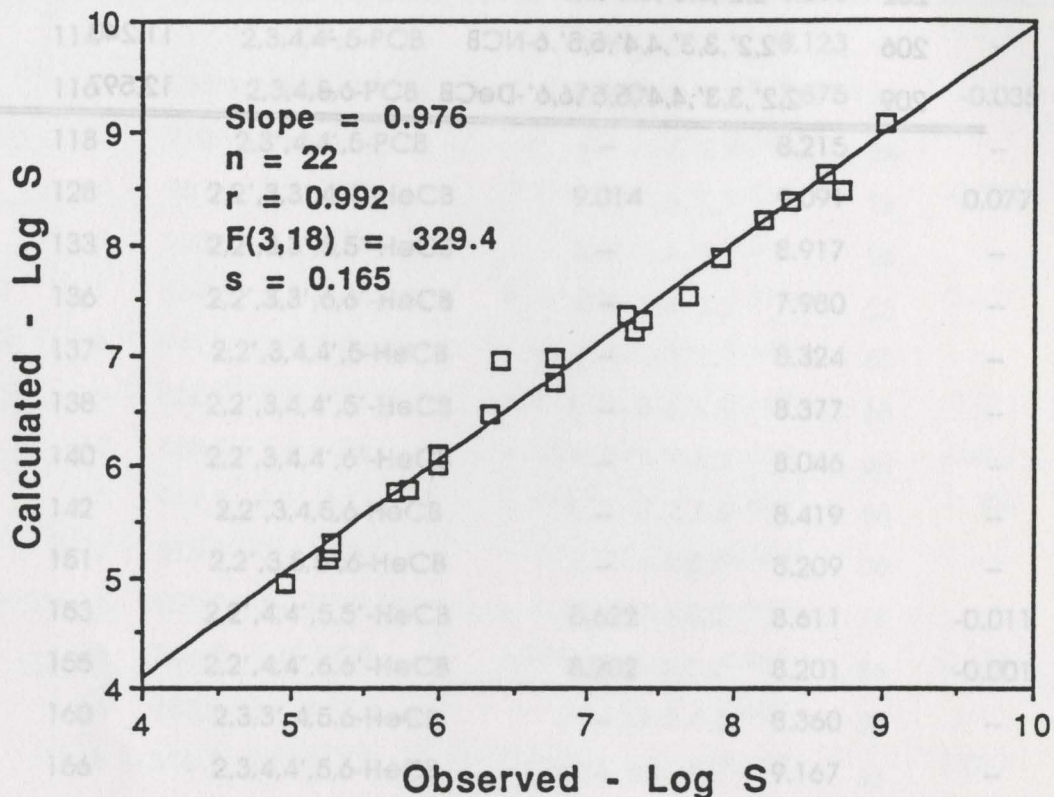


Figure 3.1. Calculated vs. observed aqueous solubility. Calculated values were obtained from Eq. 3.1. Values shown are in  $-\log$  [mol/L] at 25°C.

Burkhard, 1984; Opperhulzen *et al.*, 1988; Nirmalakhandan and Speece, 1988b; Hawker, 1989). The effectiveness of using single fixed torsion angles was evaluated by comparing surface areas calculated using (a) fixed, single torsion angles between the phenyl rings and (b) the three torsion angles, described earlier, and used in this investigation. Comparisons were made by using the observed *S* data (given in Table 3.1), each of the surface area calculations, and the model of Yalkowsky and Valvani (1979), which is described by

$$S = a \text{ TSA} + b \text{ MT} \quad (3.2)$$

Based on our calculations, a single fixed torsion angle of 0° yields unrealistic molecular conformations which forces ortho-substituted atoms to occupy the same physical space, and subsequently, results in underestimation of surface areas and molecular volumes. In general, the two methods of calculating surface areas are comparable, but when congener-specific comparisons were made it was found that the solubilities of highly ortho-chlorinated PCBs are poorly predicted from the single fixed torsion angle surface area calculations. Similar conclusions were made when surface area calculations were compared using Eq. 3.1.

Another feature of Eq. 3.1 is the presence of the third shadow area (SA). This model parameter was determined to be significant in reducing the residual error of Eq. 3.1. We interpret this parameter as codifying nonplanar features of individual PCB congeners and may account for solute-solute interactions and effects of crystallinity of the solute which are not fully accounted for in melting point data. In any event, inclusion of SA was found to significantly reduce the calculation error of Eq. 3.1, especially for congeners containing high degrees of ortho-chlorination.

Several models are currently available for predicting the solubility of hydrophobic compounds and for comparison to Eq. 3.1. Opperhulzen *et al.* (1988) developed a model specifically for predicting PCB solubility (aqueous solubility as solids) as a function



of total surface area and melting point. The model was based on TSA calculations resulting from a single fixed torsion angle ( $120^\circ$ ) and resulted in an adequate fit ( $r = 0.967$  for the best fit, no standard error was given). Nirmalakhandan and Speece (1988b) have developed a broad spectrum prediction model based on a modified polarizability parameter and two molecular connectivity indexes. Data fits between experimental data and predictions of this model were reasonable and characterized by  $r = 0.9266$  and standard error = 0.348. Equation 1 was compared to the models of Opperhulzen *et al.* (1988) and Nirmalakhandan and Speece (1988b) with comparisons based on data plots,  $r$ , standard error ( $s$ ), and congener-specific errors. Results suggest that the new model is more correct based on  $r$  and  $s$  values, however, none of the models appear to contain a systematic bias for any chlorination group or pattern.

It is also interesting to note that all of the models contain a parameter accounting for (a) surface area, either represented by TSA or molecular connectivity indexes, and (b) solute-solute interactions, either in the form of melting points, shadow area, or polarizability. The importance of each of these model parameters is supported by solubility theory.

In summary, the most accurate estimates of congener-specific solubilities (as solids) from the models tested can be obtained by using Eq. 3.1, however, melting point data are required. Unfortunately, these data are not available for all 209 PCB congeners and in such situations the model of Nirmalakhandan and Speece (1988b) is recommended. Their model appears to also accurately predict the solubility of structurally similar hydrophobic compounds based solely on molecular structure. Recently, the modeling approach of Nirmalakhandan and Speece (1988b) has been criticized due to its use of group contribution terms and connectivity terms which are highly dependent on the training data set used to calibrate the model (Yalkowsky and Mishra, 1990). However, until more fundamental, quantum-mechanical based

approaches are available, the model of Nirmalakhandan and Speece (1988b) appears to be an accurate "first-cut" tool to predict the solubility of organic compounds based solely on chemical structure.

#### Calculation of HLCs for PCBs

Numerous QSPR models for calculating HLCs were developed and evaluated in an identical manner to that used in developing the solubility model (Eq. 3.1). The best model can be described by

$$\log \text{HLC} = -0.336 \text{ SMI} + 0.240 \text{ } ^4\text{X}_p + 0.831 \text{ } ^3\text{K} - 0.0536 \text{ } a_2 - 0.0381 \text{ } a_3 - 4.96 \quad (3.3)$$

$$n = 31 \quad r = 0.948 \quad F(5,25) = 44.1 \quad s = 0.662$$

where SMI = second moment of inertia ( $\text{amu } A^2 \times 10^{-3}$ ),  $^4\text{X}_p$  = path four molecular connectivity index (unitless),  $^3\text{K}$  = path three kappa index (unitless),  $a_2$  = second principal polarizability ( $A^3$ ), and  $a_3$  = third principal polarizability ( $A^3$ ). A description of the calculation methods used for each model parameter was given above.

Calculated and experimental HLCs are given in Table 3.2 and Figure 3.2. Statistical analysis of the log HLC data show a high regression coefficient ( $r = 0.9476$ ) and a low standard error ( $s = 0.662$  or 1.9% of the mean value), which are indicative of good model predictions. Accordingly, Eq. 3.3 was used to calculate HLCs for the remainder of the 209 PCB congeners, which are given in Table 3.3 as log HLCs. Note that values for congeners 74, 80, and 128 were not included in the model development. Preliminary analysis indicated that these data were outliers. Review of the raw data from the gaseous purge technique used to measure HLCs (Dunnivant *et al.*, 1988) indicated that recoveries for PCB congeners 80 and 128 were low. Dunnivant *et al.* (1988) note that low recoveries do not allow observation of the plateau region of the depletion curve, and subsequently can result in less accurate HLC measurements.

TABLE 3.2  
EXPERIMENTAL VS. CALCULATED HLC DATA SUMMARY (25°C)

IUPAC Number	HLCx10 <sup>4</sup> (atm-m <sup>3</sup> /mol)		IUPAC Number	HLCx10 <sup>4</sup> (atm-m <sup>3</sup> /mol)	
	Exp. Data	Calculated (Eq. 3.3)		Exp. Data	Calculated (Eq. 3.3)
4	3.19	3.29	40	1.95	1.83
6	3.27	3.27	41	2.24	2.44
7	3.48	3.77	44	2.35	2.30
8	3.17	3.03	45	3.41	3.55
9	3.85	3.24	52	3.25	3.19
10	3.08	4.23	53	4.06	4.31
11	2.41	2.90	54	5.26	5.73
12	1.96	2.34	61	2.64	2.38
15	1.87	2.24	74	4.92	2.15
18	3.76	3.20	77	0.83	1.03
22	2.47	1.91	80	2.51	3.74
25	3.50	3.16	101	2.70	2.45
26	3.34	2.98	104	8.78	7.41
27	3.61	4.05	116	3.08	2.96
28	3.16	2.86	128	0.30	1.04
30	6.63	5.73	153	1.31	1.65
37	2.05	1.52	155	7.55	8.41

NOTE: Experimental data for congeners 74, 80, and 128 were not used in model development but are shown here for comparison purposes. See text for explanation.

SUMMARY OF CALCULATED HLC DATA (FOR HLC)

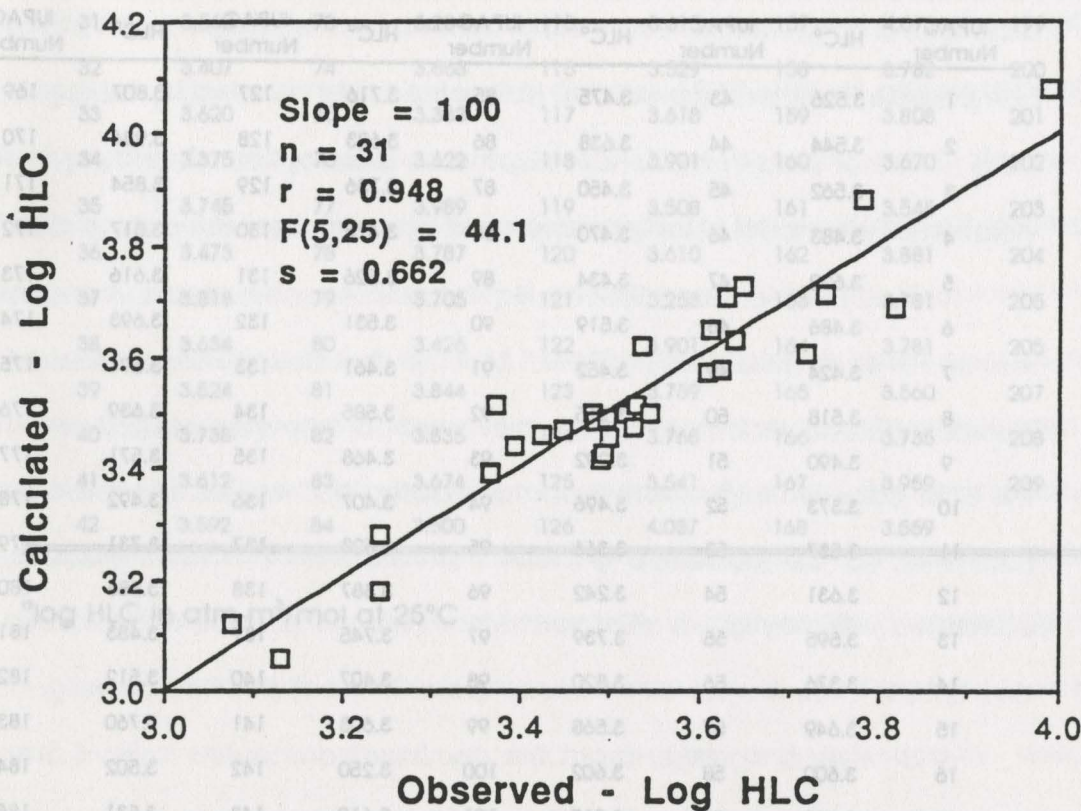


Figure 3.2 Calculated vs. observed log HLCs. Calculated HLC values were obtained from Eq. 3.1. Values shown are in  $-\log$  [atm-m<sup>3</sup>/mol] at 25°C.

TABLE 3.3

SUMMARY OF CALCULATED HLC DATA (-log HLC)<sup>a</sup>

IUPAC Number	HLC <sup>a</sup>	IUPAC Number	HLC <sup>a</sup>	IUPAC Number	HLC <sup>a</sup>	IUPAC Number	HLC <sup>a</sup>	IUPAC Number	HLC <sup>a</sup>
1	3.526	43	3.475	85	3.716	127	3.807	169	4.186
2	3.544	44	3.638	86	3.623	128	3.984	170	4.059
3	3.562	45	3.450	87	3.736	129	3.854	171	3.763
4	3.483	46	3.470	88	3.415	130	3.817	172	3.924
5	3.622	47	3.434	89	3.526	131	3.616	173	3.739
6	3.486	48	3.519	90	3.531	132	3.693	174	3.772
7	3.424	49	3.452	91	3.461	133	3.691	175	3.651
8	3.518	50	3.215	92	3.585	134	3.639	176	3.527
9	3.490	51	3.292	93	3.468	135	3.571	177	3.787
10	3.373	52	3.496	94	3.407	136	3.492	178	3.671
11	3.537	53	3.366	95	3.523	137	3.731	179	3.560
12	3.631	54	3.242	96	3.387	138	3.886	180	3.969
13	3.595	55	3.739	97	3.745	139	3.483	181	3.638
14	3.376	56	3.820	98	3.407	140	3.512	182	3.590
15	3.649	57	3.568	99	3.603	141	3.760	183	3.696
16	3.600	58	3.602	100	3.250	142	3.502	184	3.339
17	3.428	59	3.517	101	3.610	143	3.531	185	3.669
18	3.495	60	3.816	102	3.431	144	3.529	186	3.434
19	3.355	61	3.623	103	3.298	145	3.328	187	3.693
20	3.663	62	3.432	104	3.130	146	3.727	188	3.353
21	3.644	63	3.615	105	4.003	147	3.501	189	4.177
22	3.719	64	3.565	106	3.783	148	3.367	190	3.950
23	3.497	65	3.473	107	3.798	149	3.625	191	3.876
24	3.507	66	3.693	108	3.755	150	3.296	192	3.718
25	3.500	67	3.631	109	3.550	151	3.548	193	3.872
26	3.526	68	3.424	110	3.707	152	3.369	194	4.174
27	3.393	69	3.296	111	3.574	153	3.783	195	3.926
28	3.544	70	3.694	112	3.574	154	3.418	196	3.884
29	3.529	71	3.503	113	3.487	155	3.075	197	3.596
30	3.242	72	3.441	114	3.845	156	4.053	198	3.812

Table 3.3 (Continued)

IUPAC Number	HLC <sup>a</sup>	IUPAC Number	HLC <sup>a</sup>	IUPAC Number	HLC <sup>a</sup>	IUPAC Number	HLC <sup>a</sup>	IUPAC Number	HLC <sup>a</sup>
31	3.562	73	3.284	115	3.610	157	4.073	199	3.644
32	3.407	74	3.668	116	3.529	158	3.782	200	3.619
33	3.620	75	3.333	117	3.618	159	3.808	201	3.884
34	3.375	76	3.622	118	3.901	160	3.670	202	3.651
35	3.745	77	3.989	119	3.508	161	3.545	203	3.853
36	3.473	78	3.787	120	3.610	162	3.881	204	3.463
37	3.818	79	3.705	121	3.253	163	3.781	205	4.059
38	3.634	80	3.426	122	3.901	164	3.781	205	4.059
39	3.524	81	3.844	123	3.759	165	3.560	207	3.772
40	3.738	82	3.835	124	3.768	166	3.735	208	3.777
41	3.612	83	3.674	125	3.541	167	3.959	209	3.948
42	3.592	84	3.600	126	4.087	168	3.559		

<sup>a</sup>log HLC in atm·m<sup>3</sup>/mol at 25°C

Thus, the reported data for congeners 80 and 128 appear to be in error and were not used in model development. In contrast, no recovery problem was observed for congener number 74, however, model predictions are 50% higher than experimental data for this congener. Because experimental data for congener number 74 was not comparable to either the predicted HLC or the value reported by Burkhard (1984), the data were not used in model development. Examination of residuals indicated no violation of the model assumptions resulted from deletion of the three data points.

The purpose of each QSPR in Eq. 3.3 is to encode unique, congener-specific features of each molecular structure. Although five descriptors are required in Eq. 3.3, statistical analysis indicated that each of these parameters was significant in reducing the error between experimental and calculated HLC values. Also, it is important to note that Eq. 3.3 possessed a stable residual error structure, residuals were not correlated with any given chlorination pattern, and no collinearity existed between descriptors. Thus, the use of five model parameters appears to be valid.

The physical significance of the combined descriptors in Eq. 3.3 is difficult to interpret, but individual components of Eq. 3.3 can be used to provide insight into the parameters governing volatilization of hydrophobic compounds from aqueous solutions. For example, values of SMI and molecular connectivity are loosely related to the size and general shape of the molecules. Similarly, the path four kappa index encoded information about the degree of branching and size of the molecules. Values of polarizability are sensitive to structural differences between geometric isomers, and therefore, are affected by the chlorine substitution pattern on the phenyl rings. It is clear from this analysis that the molecular size and molecular shape are major factors controlling the magnitude of HLCs. Although some of the descriptors actually describe similar or identical molecular features (e.g. size, shape, etc.), it is important to note that none of the descriptors were collinearly related.

Four other prediction models, developed specifically for PCBs, were found in the literature. Burkhard (1984) calculated HLCs from the ratio of predicted PCB solubilities and vapor pressures. Although Burkhard's model utilized properties similar to those given in this investigation, calculated HLCs were overestimated for ortho-chlorinated congeners (Burkhard, 1984; Brown and Wagner, 1990). Direct attempts by Hawker (1989) to model congener-specific HLCs for PCBs were unsuccessful. Brunner *et al.* (1990) developed two equations for predicting HLCs. However, one equation utilized surface areas calculated based on a co-planar conformation (problems with this approach were discussed earlier) and the other equation was based on a model with two molecular connectivity indices which were reported to be collinearly related. Thus, the validity of Brunner's *et al.* (1990) models is questionable. Nirmalakhandan and Speece (1988b) have developed a structure-based model for predicting HLCs for a variety of compounds. Unfortunately, the ability of their model to accurately predict congener specific HLCs for PCBs has not been evaluated. It is important to note that their model utilizes a shape or size parameter and polarizability descriptors (Nirmalakhandan and Speece, 1988b). Thus, in principle, the modeling approach of Nirmalakhandan and Speece (1988b) is in agreement with the one used here (Eq. 3.3).

### Conclusions

Quantitative Structure-Property Relationships (QSPRs) have been used effectively to calculate congener-specific aqueous solubilities and HLCs for polychlorinated biphenyls (PCBs). Solubility and HLC data from previous investigations (Dunnivant, 1988; Dunnivant and Elzerman, 1988; Dunnivant *et al.*, 1988) were used in conjunction with the Automated Data Analysis and Pattern Recognition Toolkit (ADAPT) software package to develop two QSPR calculation models. One model was found to accurately calculate solubilities for PCB congeners containing similar chlorine substitution patterns. The most accurate model for calculating solubility was a function



of total molecular surface area, melting point, and third shadow area. Unfortunately, the model is dependent on melting point, a value not available for all PCB congeners, thus, not all PCB solubilities (as solids) can be predicted. The model predicting HLCs was dependent on the second moment of inertia, path four molecular connectivity index, path three kappa index and molecular polarizability. The model was shown to be effective in calculating experimentally determined HLCs, and was subsequently used to calculate HLCs for the remainder of the 209 PCB congeners. Both calculated S and HLC values are in good agreement with values from the literature. This list of S and HLC values can be used in future QSPR models and in development of fate and distribution models.

### Conclusions

Quantitative Structure-Property Relationships (QSPRs) have been used effectively to study, predict, and estimate the behavior of organic compounds. The model used to calculate congener-specific aqueous solubilities and HLCs for polychlorinated biphenyls (PCBs), solubility and HLC data from previous investigators (Dunnivant, 1988; Dunnivant and Ezerman, 1988; Dunnivant et al., 1988) were used in conjunction with the Automated Data Analysis and Pattern Recognition Toolkit (ADAPT) software package to develop two QSPR calculation models. One model was found to accurately calculate solubilities for PCB congeners containing similar chlorine substitution patterns. The most accurate model for calculating solubility was a function

## CHAPTER IV

### LABORATORY AND COMPUTER MODELS OF FRACTIONATION OF INDIVIDUAL CONGENERS DURING WEATHERING

#### Introduction

PCBs are persistent and ubiquitous pollutants in the natural environment, and the extent of environmental contamination has been well documented (Hutzinger *et al.*, 1974; Erickson, 1986). During the past three decades, the fate and distribution of PCBs has been the topic of numerous investigations (Bopp *et al.*, 1981, 1985; Bush *et al.*, 1985, 1987; Eisenreich, 1987; Dunnivant *et al.*, 1988), with each investigation reporting changes in the composition of PCB contamination relative to the PCBs originally released into the system. This change in PCB composition has been termed environmental weathering and is the result of complicated chemical, physical, and biological processes. The complexity and relative contribution of each of these processes to environmental weathering of PCBs is the basis for the following discussion.

The Hudson River is a system highly contaminated with PCBs resulting from discharges from two manufacturing facilities. Bopp *et al.* (1981) were the first to document the extent of contamination in the Hudson River by analyzing over 100 sediment samples from the Hudson River. Although packed column gas chromatography, which has low resolution for PCBs, was used, environmental weathering was noted by Bopp *et al.* (1981). Also, the level of contamination was found to decrease regularly with distance from the point sources, a trend common for a river system receiving a point source input.

The congener composition of PCBs found in the Hudson River has been the topic of investigation because of the connection between environmental weathering mechanisms and the fate of individual congeners. Information on selective

differentiation among congeners may provide clues to important mechanisms operating in the river system. Bopp *et al.* (1981, 1985) reported that some samples contained proportionately higher quantities of less-chlorinated congeners while other samples appeared to contain proportionately more highly-chlorinated congeners. Higher concentrations of less-chlorinated congeners were present only in samples taken near the point sources, while different compositional changes were noted in samples further from the sources. Bopp *et al.* (1981, 1985) attributed these changes to temporal variations in PCBs released to the system (different Aroclors utilized over time) and physical and chemical congener specific processes (solubilities, Henry's law constants, partition coefficients, etc.). Results from a series of hypothetical mixing events suggested that compositional changes could be explained by chemical/physical processes; however, due to the poor resolution inherent in the packed column gas chromatography analysis, congener specific evaluations could not be accomplished.

A later investigation of the Hudson River sediments (Bush *et al.*, 1985) noted the need for congener-specific data and utilized capillary column GC techniques to improve the resolution of PCBs in the analysis. Based on these results, Bush *et al.* (1985) postulated that the lower chlorine homologues diffuse into the water phase faster and are preferentially dissolved according to their higher water solubilities and lower affinity for the sediment particles. Further, Bush *et al.* (1985) suggested that the higher chlorinated congeners did not change significantly in the sediments due to their lower volatilization from the system and lower solubility. In a later investigation, Bush *et al.* (1987) reported that a greater percentage of the lower chlorinated congeners, relative to the total PCBs, are transported down the system and, thereby, preferentially removed from the system.

A unique feature of the investigation of Bush *et al.* (1987), the use of an Apiezon L stationary phase in the GC analysis, allowed quantitation of 2,2'-DCB independently

of 2,6-DCB. This was not possible in the investigations of Bopp *et al.* (1981, 1985). Although unable to selectively differentiate these congeners with their analytical techniques, Brown *et al.* (1984) proposed a microbial degradation scheme to explain enhanced concentrations of lower chlorinated congeners near the source which resulted in 2,2'-DCB, but not 2,6-DCB as a major end product. Bush *et al.* (1987) took issue with the proposed mechanism of Brown *et al.* (1984) noting that the superior quantitation technique used in their investigations (Bush *et al.*, 1985, 1987) showed increases in both 2,2'-DCB and 2,6-DCB, thus giving support to the physical/chemical weathering process in preference to the biological scheme proposed by Brown as the mechanism responsible for enrichment of dichlorobiphenyls in Hudson River sediments.

In summary, Bush *et al.* (1987) proposed that qualitatively observed environmental weathering of PCBs mixtures can be explained by physical/chemical processes.

Additional insights into chemical/physical weathering processes were gained by the work of Burkhard (1984). Burkhard (1984) estimated aqueous solubilities, Henry's law constants, vapor pressures, and water-sediment partition coefficients for all 209 PCB congeners, and used these estimates to develop a three-phase partition model for air, water, and sediment. Results showed the congener-specific behavior of all 209 PCB congeners, and indicated the preferential association of a PCB congener with a specific phase is dependent on the specific chlorination pattern. Since the models used by Burkhard *et al.* (1985) were based on predicted parameter values, the results must be experimentally verified.

An alternate explanation of environmental weathering has been postulated by Brown *et al.* (1984), who analyzed sediment samples from the Hudson River basin and noted increases in lower chlorinated congeners near point sources. Brown *et al.* (1984, 1987a, 1987b) attributed all environmental weathering of PCBs to selective anaerobic microbial dechlorination of highly chlorinated congeners to lower chlorinated

congeners. They suggested that the lower chlorinated PCBs produced in the dechlorination scheme could be degraded to non-toxic by-products. The mechanism proposed by Brown *et al.* (1984, 1987a, 1987b) has received substantial criticism, as summarized below.

First, the GC separation column utilized by Brown *et al.* (1984, 1987a, 1987b) did not allow for independent quantitation of 2,2'-DCB and 2,6-DCB. The proposed microbiological dechlorination pathway results in production of 2,2'-DCB, but not 2,6-DCB. As noted above, Bush *et al.* (1987) studied PCB contamination in the Hudson River system and noted changes in both 2,2'-DCB and 2,6-DCB. Consequently, it appears that selective dechlorination logically is not the major factor involved in the environmental weathering of PCBs.

The second criticism is that no detailed laboratory investigations have evaluated the existence of microorganisms in the Hudson River sediments capable of selective dechlorination of PCBs. Brown *et al.* (1987a) reported qualitative laboratory results showing relative changes in PCB composition, yet, no mass balance was conducted on either the input PCBs or the degradation products. As discussed earlier, several investigations have shown, qualitatively (Bopp *et al.*, 1981, 1985; Bush *et al.*, 1985, 1987) and theoretically (Burkhard, 1984), that physical/chemical processes can explain environmental weathering patterns without having to invoke the selective dechlorination argument. Based on an extensive literature review, it is apparent that neither physical/chemical processes nor selective dechlorination can solely explain environmental weathering of PCB mixtures in aquatic systems (Burkhard, 1984; Bush *et al.*, 1985, 1987; Bopp *et al.*, 1981, 1985; Brown *et al.*, 1984, 1987a, 1987b).

The purpose of this investigation was to provide detailed experimental data to evaluate the significance of physical/chemical processes in determining environmental weathering of PCBs in Lake Hartwell. Lake Hartwell is a reservoir located on the

Savannah River in upper South Carolina. In the mid-1970s Lake Hartwell was found to contain unusually high levels of PCBs. Subsequent investigations by the S.C. Department of Health and Environmental Control (DHEC) and the U.S. EPA traced the PCB contamination to a single point source, a transformer refurbishing plant, located in Pickens, SC. Although conditions at the plant have changed, recent data (Polansky, 1984; Dunnivant, 1985; Germann, 1988) have shown that Lake Hartwell sediments still contain high levels of PCBs (5 to 150 mg/kg). Furthermore, each of these investigations have noted changes in the composition of PCBs recovered from the sediments relative to original Aroclors discharged. Consequently, it appears clear that environmental weathering of PCBs is occurring in Lake Hartwell.

### Materials and Methods

#### Chemicals

All water used in the extractions described below was double distilled with the last distillation being in an all-glass still. Water used in the water/sediment partition experiments was Lake Hartwell water which had been filtered through a 0.45 m glass-fiber filter (Gelman Scientific, Inc.). Organic solvents (acetone, isooctane, and hexane) were Baker-ResiR analyzed grade or higher quality. Blank extractions of the solvents were analyzed by gas chromatography and were found to be free of interfering peaks in the GC analysis of PCBs. Mercuric chloride used for inhibiting microbial degradation of PCBs was ACS reagent grade. All other inorganic chemicals (NaCl, KNO<sub>3</sub>, K<sub>2</sub>HPO<sub>4</sub>, and KH<sub>2</sub>PO<sub>4</sub>) were ACS reagent grade. PCBs used in the experiments were Aroclor mixtures 1016 and 1254 (purity 99%; Supelco, Inc. and U.S. EPA). Sediment used in the water/sediment partition experiments was obtained from Lake Issaqueena, a non-contaminated tributary lake discharging into Lake Hartwell. Analysis of extracts from these sediments confirmed the absence of PCB contamination.

## GC Equipment

A Hewlett-Packard gas chromatography system equipped with a Ni electron-capture detector was used for PCB quantitation. Congener separation was accomplished with a 30-meter DB-5 capillary column (0.25 mm i.d. and 0.25  $\mu$ m film thickness) available from J&W Scientific (Sunnyvale, CA). Injections were made in the splitless mode, but after 30 sec the system was switched to a split mode (split flow rate equal to 50 mL/min; refer to Dunnivant (1988) for a description of the gasses used). Temperature settings are listed below:

Injector temperature = 275°C  
Detector temperature = 300°C  
Initial oven temperature = 100°C for 2.0 min  
Program rate 1 = 10°C/min to 150°C and hold for 0.5 min  
Program rate 2 = 1.1°C/min to 225°C and hold for 3 min  
Program rate 3 = 10 C/min to 260 C and hold for 15 min

## GC-ECD Quantitation of Peaks

Peak and/or congener-specific quantification of 64 peaks was completed using internal and external standard calibration. An internal standard, Aldrin, allowed peak (PCB congener) identification by comparing retention times with published data (Dunnivant, 1985; Dunnivant and Elzerman, 1988; Mullin *et al.*, 1984). Internal standards also allowed correction for injection errors and detector fluctuations. External standards consisted of a mixture of Aroclors 1016 and 1254 (4:1 respectively), which were known to be the primary Aroclors discharged to Lake Hartwell (Billings, 1976). Peak (congener) concentrations in each Aroclor reference standard were calculated utilizing mole-percent data from Albro and Parker (1979) and Albro *et al.* (1981). Using the mole-percent composition of Aroclors, and given the total mass of Aroclor, the mass contribution in each peak was estimated. A summary, relating Hewlett-Packard GC peak number to IUPAC number and peak composition is given in Appendix C. For a detailed description of the quantitation scheme refer to Dunnivant (1985). Because

some peaks contained more than one PCB congener, 100% peak resolution was not obtained. However, use of this separation and quantification scheme is superior to packed column GC because congener specific data are obtained or reliably estimated in many cases.

#### Measurement of Water/Sediment Partition Coefficients

Partition coefficient experiments were designed to mimic the behavior individual PCB congeners in a series of short-term sediment resuspension events, allowing evaluation of physical/chemical processes as environmental weathering agents. Apparent partition coefficients ( $K_d'$ ) were experimentally determined by taking the ratio of sorbed PCB concentration to dissolved phase concentration for all PCB congeners present at concentrations above detection limits. The term apparent partition coefficient is utilized because equilibrium was probably not attained in the resuspension experiments. Two experimental approaches were used to simulate resuspension scenarios in Lake Hartwell, each using the sediment suspension described below.

#### Model Sediment Suspension

Two types of sediment suspensions were tested. In one set of experiments contaminated lake sediment was used, while a model sediment similar to Lake Hartwell sediment containing no PCBs was contacted with PCB spiked water in the other. This allowed separate investigation of the effects of desorption and adsorption. The model sediment suspension was prepared by first mixing a predetermined mass of PCB-free sediment with filtered Lake Hartwell water for three days prior to starting the experiments. Thereafter, the sediment suspension was sieved through a number 30 mesh sieve (600  $\mu\text{m}$ ) and the suspended solids level adjusted to approximately 1000 mg/L (measured to be 850 mg/L).  $\text{HgCl}_2$  was then added at a concentration of 100 mg/L as was a phosphate buffer to give a final pH of 6.7 (Hassett and Milicic, 1985). PCBs



used in these experiments were a mixture of Aroclors 1016 and 1254 (4:1 respectively). This composition closely matches the original mixture of Aroclors released into the Lake Hartwell system (Billings, 1976). The resuspension experiments, referred to as  $K_{d1}'$  and  $K_{d2}'$ , are described below.

#### $K_{d1}'$ Determinations

The  $K_{d1}'$  experiments were designed to evaluate the effect of resuspending previously-contaminated sediment with water containing no detectable level of PCBs. PCBs were added to the sediment suspension (described above) utilizing the plating technique described in Dunnivant (1988). A predetermined volume of isooctane containing PCBs was added to a clean 3 L glass flask so as to transfer approximately 1250 g of total PCBs to the flask. The isooctane was allowed to evaporate, which resulted in plating the PCBs on the bottom and sides of the flask. The sediment solution (2.5 L) was added to the flask, the solution was capped, and mixed on a stir plate for approximately three days. After mixing, the solution was aliquoted in 20, 40 mL vials and sealed with screw caps containing Teflon-lined septa. No head space (air) remained in any of the vials.

Initial apparent water/sediment partition coefficients ( $K_d'$ ) were determined for two vials using the extraction procedures described below. The remaining vials were placed in a centrifuge and centrifuged for ten minutes at 1200 rpm (246 G). The water phase of each vial was carefully removed with a pipet in a manner that would not disturb or remove any of the sediment phase. PCB-free Lake Hartwell water, containing an identical concentration of buffers and  $HgCl_2$  as above, then was added to the vials. The vials were resealed, shaken to resuspend the sediment and placed in a padded box which was constantly inverted (on a roller mixer) to allow mixing of the suspension. The vials were mixed for two complete days, removed on the third day, and centrifuged. Apparent partition coefficients were determined on the contents of two

of the vials, the water replaced as before in the remaining vials, the vials sealed, and mixed for another two days. This cycle was repeated (each cycle called a resuspension event) and partition coefficients determined in duplicate for resuspension event numbers 0, 1, 3, 5, 7, 9, and 11.

#### $K_{d2}'$ Determinations

The next set of experiments was designed to evaluate contacting an initially uncontaminated sediment similar to Lake Hartwell sediment with water containing PCBs. These experiments are referred to as  $K_{d2}'$  equilibrations. The experimental design was similar to the  $K_{d1}'$  experiments except that the resuspension water contained a consistent initial level of PCB contamination (see below). Preparation of the sediment suspensions is described below.

The uncontaminated sediment suspension, described earlier, was placed into 25, 40 mL vials and sealed using Teflon-lined screw caps. Two vials were taken for initial  $K_d'$  determinations (blank determination since no PCBs were added to these vials) using the extraction procedure described later. The remaining vials were centrifuged, the water phase removed and discarded, water added, and the vials resealed in a manner identical to that used in the  $K_{d1}'$  experiments except that PCB contaminated water was used as the resuspension water. The resuspension water contained buffers and  $HgCl_2$  as described before, and also contained approximately 100 mg/L total PCB (4:1 Aroclors 1016:1254 respectively). The vials were mixed for two days, centrifuged, the water removed, and the sediments resuspended using the PCB-contaminated water. After each cycle, two vials were taken for measurement of apparent partition coefficients (procedure described below). The cycle was repeated and partition coefficients determined until no vials remained. The resuspension events are referred to by numbers 1-10.

### Partition Coefficient Determination

Apparent partition coefficients ( $K_d'$ ) were determined by measuring the concentration of PCBs associated with the water and sediment phases. A partition coefficient was calculated by taking the ratio of the sediment concentration ( $\mu\text{g/g}$ ) and the water concentration ( $\mu\text{g/mL}$ ). Phase separation was achieved by centrifuging the sediment suspension as described earlier. The water phase was pipetted into a volumetric flask containing isooctane (volume varied depending on expected PCB concentrations), internal standard, and NaCl (0.5 g NaCl/40 mL of water to be extracted). The flask was shaken for three minutes, the phases allowed to separate, and the isooctane transferred to a screw-capped vial. The extraction procedure was repeated, the extracts composited, appropriate dilutions made, and analyzed by GC-ECD.

The sediment fraction, remaining in the vial, was extracted using a sonication extraction technique developed and described by Dunnivant (1985) and Dunnivant and Elzerman (1988). Briefly, five mL of acetone was added to the vial, the solution mixed with a pipet, and quantitatively transferred to a 50 mL beaker. The transfer step was repeated twice more and the solutions composited in the 50 mL beaker. The beaker was placed in an ice-water bath and sonicated for 5 min with a 300 Watt Fisher Ultrasonic probe (standard tip; 80 percent relative output). After the sonication, the tip was washed with approximately 5 mL of acetone into the beaker. The acetone and extracted sediment then were placed into a 25 mL glass syringe attached to a 25 mm stainless-steel filter holder which contained a glass fiber filter (0.2  $\mu\text{m}$  pore size). The solution was forced through the filter and placed in a 250 mL separatory funnel containing 10 mL isooctane. The 50 mL beaker, syringe, and filter holder were rinsed with three, 3 mL portions of acetone. All transfers and rinses were performed in a quantitative manner. Subsequently, 125 mL of pre-extracted double-distilled water and

0.5 g NaCl were added to the separatory funnel. The mixture was shaken for three minutes, the phases allowed to separate, and the isooctane layer eluted through a glass column containing  $\text{Na}_2\text{SO}_4$ , which was effective in removing water that would interfere with the GC analysis. The isooctane extraction was repeated twice more using 5 mL aliquots of isooctane. All extracts were composited in a 50 mL volumetric flask. Appropriate concentrations or dilutions were made prior to GC-ECD analysis.

### Data Handling

Data manipulations and transformations were performed using a microcomputer and a spreadsheet software program (SuperCalc 4, Computer Associates). Due to the large volume of data collected for each resuspension equilibration, the data had to be transformed in a manner which would characterize each resuspension event relative to the others. Weight percents were chosen as a means of comparison and were calculated by dividing the mass of PCB in each peak by the total mass of PCBs in the sample; i.e., an observed weight percent. This type of comparison was useful since it normalized the data and provided a means of comparing the composition of samples containing different total initial concentrations of PCBs. Although PCB concentrations were measured for both the water and sediment phases, only weight percents for the sediments were calculated since the concentration of PCBs in Lake Hartwell water is not well documented and, therefore, is not available for comparison. An extensive data base of PCB contamination in Lake Hartwell sediments is available (Polansky, 1984; Dunnivant, 1985; Germann, 1988). Selected sediment data from the most recent investigation (Germann, 1988) will be used for comparisons with the partition coefficient experiment results.

## Results and Discussion

### $K_{d1}'$ and $K_{d2}'$ Results

Weight-percent data were calculated for each sediment as described above.

The purpose of this experiment was to show the effect of resuspending a previously contaminated sediment with PCB-free water, thus, causing desorption. This experiment should mimic the transport of contaminated sediment down a riverine system similar to Lake Hartwell. The data are summarized in Table 4.1, with each tabulated value representing the average of two determinations. Data in Table 4.1 are arranged by Hewlett-Packard GC peak numbers and are correlated to specific PCB congener(s) in Appendix D. The general trend is for lower peak numbers to correspond to fewer numbers of chlorines.

Data in Table 4.1 indicate that for the compounds associated with low Hewlett-Packard (HP) peak numbers, the fractional compositions decrease with subsequent resuspensions. As the peak number approaches 20, compositions do not appear to change with equilibration, and for peak numbers greater than 30, compositions slightly increase with subsequent equilibrations. Due to the large volume and complexity of the data in Table 4.1, the data were transformed and are presented in Figure 4.1. The trends, noted above, are more evident in Figure 4.1.

Figure 4.1 shows the pronounced effect of selectively "washing out" PCB congeners from resuspended sediments and is a result of congener specific apparent partition coefficients and aqueous solubilities. The less-chlorinated PCBs (lower peak numbers) are preferentially removed from the sediment, while the higher-chlorinated PCBs (higher peak numbers) appear to remain and increase in weight percent with increasing resuspension. The slower removal of higher chlorinated congeners with respect to resuspension event is a result of their lower solubility and higher  $K_d$ 's as compared to the less chlorinated congeners. They increase in weight percents due to

Table 4.1 (Continued)

TABLE 4.1

Table 4.1 (Continued)

SUMMARY OF OBSERVED PCB FRACTIONAL COMPOSITION  
IN  $K_{d1}$  EXPERIMENTS

Peak Number	Initial	Resuspension Event Number						
		1	3	5	7	9	11	
1	0.011	0.003	0.000	0.000	0.000	0.000	0.000	0.000
2	0.006	0.003	0.001	0.001	0.000	0.001	0.001	0.001
3	0.006	0.003	0.001	0.001	0.000	0.001	0.001	0.003
4	0.044	0.025	0.011	0.007	0.005	0.007	0.007	0.002
5	0.007	0.004	0.002	0.001	0.001	0.001	0.001	0.001
6	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.000
7	0.073	0.054	0.032	0.030	0.017	0.017	0.014	0.014
8	0.028	0.022	0.013	0.011	0.007	0.007	0.005	0.005
9	0.004	0.003	0.002	0.001	0.001	0.001	0.001	0.000
10	0.041	0.031	0.018	0.012	0.009	0.008	0.006	0.006
11	0.002	0.002	0.001	0.001	0.001	0.002	0.004	0.004
12	0.005	0.005	0.004	0.003	0.003	0.003	0.002	0.002
13	0.016	0.015	0.012	0.011	0.009	0.008	0.007	0.007
14	0.172	0.157	0.131	0.117	0.088	0.088	0.068	0.068
16	0.075	0.070	0.058	0.049	0.038	0.035	0.028	0.028
17	0.027	0.024	0.020	0.017	0.012	0.014	0.011	0.011
18	0.011	0.010	0.008	0.007	0.005	0.005	0.003	0.003
19	0.013	0.014	0.012	0.010	0.008	0.007	0.006	0.006
20	0.055	0.062	0.061	0.062	0.054	0.051	0.043	0.043
21	0.046	0.053	0.054	0.056	0.049	0.048	0.041	0.041
22	0.061	0.071	0.073	0.076	0.068	0.067	0.057	0.057
25	0.013	0.015	0.014	0.014	0.012	0.011	0.010	0.010
26	0.023	0.029	0.029	0.028	0.025	0.024	0.022	0.022
27	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table 4.1 (Continued)

Peak Number	Initial	Resuspension Event Number					
		1	3	5	7	9	11
28	0.003	0.005	0.004	0.004	0.003	0.003	0.002
29	0.016	0.019	0.022	0.025	0.024	0.024	0.023
30	0.013	0.016	0.017	0.020	0.019	0.019	0.018
31	0.008	0.012	0.014	0.016	0.015	0.015	0.015
32	0.026	0.034	0.040	0.046	0.048	0.047	0.044
33	0.000	0.001	0.001	0.001	0.001	0.003	0.004
34	0.007	0.009	0.010	0.012	0.012	0.012	0.012
35	0.018	0.025	0.030	0.037	0.038	0.039	0.039
36	0.017	0.023	0.028	0.035	0.037	0.038	0.038
37	0.001	0.001	0.001	0.002	0.002	0.002	0.002
38	0.007	0.011	0.012	0.013	0.015	0.015	0.020
39	0.009	0.016	0.017	0.017	0.022	0.023	0.028
40	0.007	0.011	0.012	0.012	0.016	0.016	0.020
41	0.024	0.035	0.040	0.046	0.051	0.050	0.061
42	0.001	0.001	0.002	0.002	0.002	0.002	0.003
43	0.001	0.001	0.001	0.001	0.002	0.002	0.002
44	0.004	0.005	0.006	0.008	0.009	0.009	0.010
46	0.034	0.047	0.060	0.075	0.079	0.080	0.090
47	0.001	0.002	0.002	0.003	0.003	0.003	0.004
48	0.001	0.002	0.004	0.007	0.008	0.008	0.010
49	0.002	0.003	0.004	0.006	0.006	0.006	0.007
50	0.005	0.008	0.010	0.013	0.015	0.015	0.017
51	0.024	0.035	0.043	0.053	0.059	0.058	0.066
52	0.002	0.003	0.003	0.004	0.005	0.005	0.005
53	0.017	0.020	0.036	0.048	0.064	0.085	0.097
54	0.000	0.0201	0.001	0.001	0.001	0.001	0.001

Table 4.1 (Continued)

Peak Number	Initial	Resuspension Event Number					
		1	3	5	7	9	11
55	0.000	0.000	0.000	0.000	0.000	0.000	0.000
56	0.000	0.000	0.000	0.000	0.000	0.000	0.000
57	0.004	0.000	0.007	0.009	0.011	0.006	0.013
58	0.004	0.000	0.008	0.009	0.011	0.005	0.013
59	0.000	0.000	0.000	0.000	0.000	0.000	0.000
60	0.001	0.000	0.002	0.002	0.003	0.001	0.003
61	0.000	0.000	0.001	0.001	0.001	0.000	0.002
62	0.000	0.000	0.000	0.000	0.000	0.000	0.000
63	0.002	0.000	0.004	0.005	0.007	0.003	0.007
64	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Peak number in chromatogram



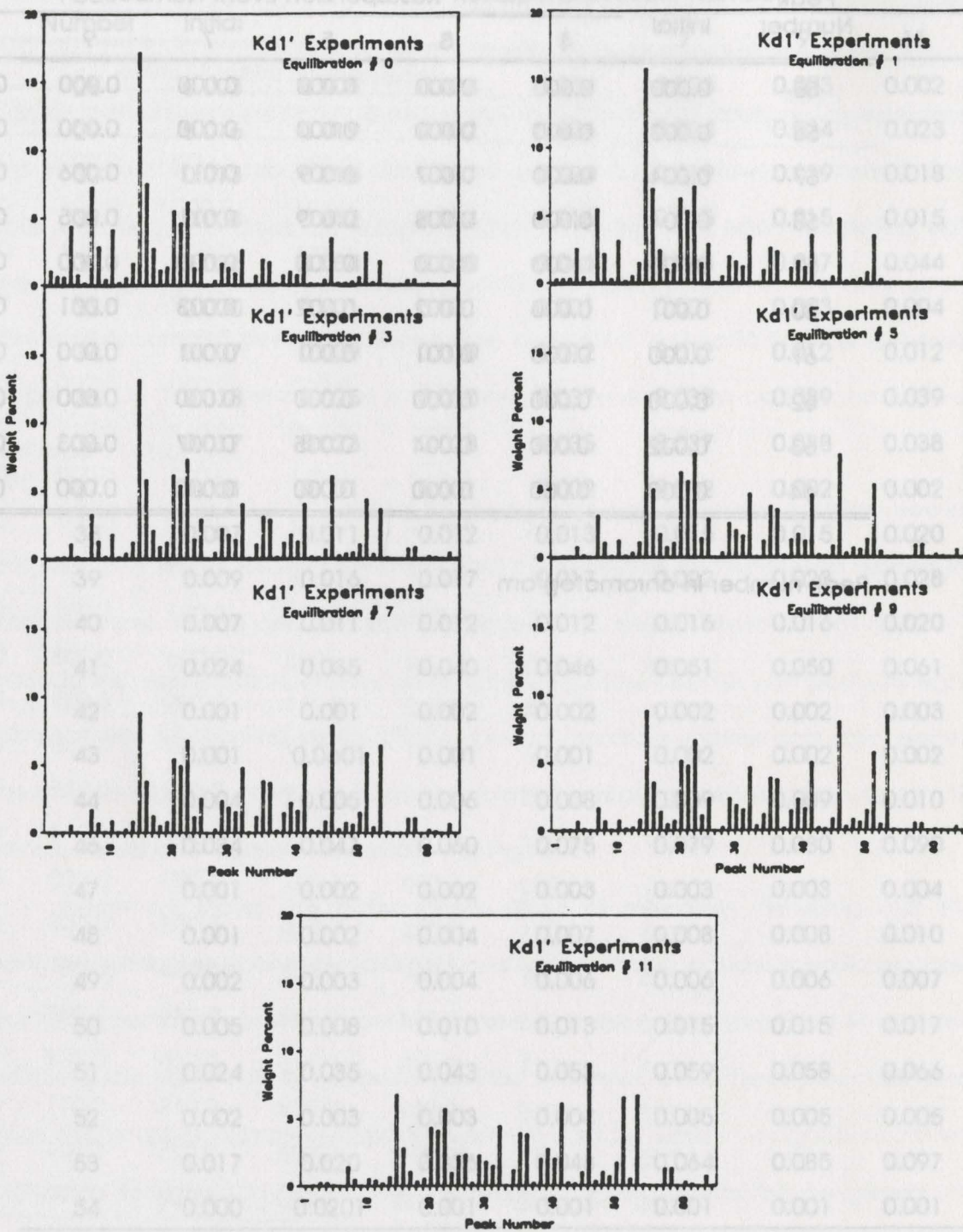


Figure 4.1. Observed weight-percent compositions of sediments resulting from  $K_{d1}$ ' equilibrations.

net loss of PCBs, especially the lower chlorinated congeners. Trends in Table 4.1 and Figure 4.1 are consistent with sediment data from Lake Hartwell, which show higher concentrations of the less-chlorinated PCBs near the point source, and decreasing amounts of less-chlorinated PCBs with increasing distance down the lake system (Germann, 1988).

Data from the  $K_{d2}'$  experiments are summarized in Table 4.2 and Figure 4.2. Again, fractional compositions and weight percent summaries are given. While identical sediments were used for both  $K_{d1}'$  and  $K_{d2}'$  experiments, instead of resuspending a contaminated sediment with PCB free water (washing the sediments), the  $K_{d2}'$  experiments contacted a previously uncontaminated sediment with lake water containing 100 mg PCB/L. This allows evaluation of the continual resuspension of lake sediments in lake water containing high levels of PCBs that were released during upstream resuspension events.

Although the overall appearance of the individual plots between  $K_{d1}'$  and  $K_{d2}'$  experiments are different, the overall effect is the same. As the number of resuspension events increases, the observed weight per cent of the less-chlorinated PCBs decrease (lower HP numbers). Conversely, the higher-chlorinated PCBs (higher HP number) increase in weight percent with increasing exposure to PCB-laden water. It appears that the lower-chlorinated congeners are adsorbed quickly, but become a smaller fraction of the total as higher-chlorinated congeners become adsorbed more.

Peak 14 accounts for the highest individual weight percent in the majority of the plots. This results from a high weight percent in the original Aroclor mixture and a relatively high  $K_d$  as compared with structurally similar PCBs. This peak is present in Lake Hartwell sediments, but is present in relatively lower proportions compared to laboratory experiments, possibly due to biodegradation in field samples. The resuspension experiments have shown that significant changes in the congener composition of

TABLE 4.2  
SUMMARY OF OBSERVED PCB FRACTIONAL COMPOSITION  
IN  $K_{d2}$  EXPERIMENTS

Peak Number	Resuspension Number									
	1	2	3	4	5	6	7	8	9	10
1	0.011	0.008	0.006	0.006	0.005	0.004	0.005	0.004	0.003	0.003
2	0.007	0.006	0.005	0.005	0.004	0.003	0.004	0.003	0.003	0.003
3	0.006	0.006	0.005	0.005	0.004	0.004	0.004	0.003	0.003	0.003
4	0.050	0.044	0.038	0.037	0.031	0.028	0.029	0.027	0.022	0.025
5	0.008	0.007	0.006	0.005	0.005	0.004	0.004	0.004	0.004	0.004
6	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.001	0.001	0.000
7	0.084	0.079	0.069	0.074	0.060	0.053	0.054	0.053	0.048	0.048
8	0.031	0.027	0.028	0.028	0.024	0.021	0.021	0.021	0.017	0.017
9	0.004	0.004	0.004	0.004	0.003	0.003	0.003	0.003	0.002	0.002
10	0.045	0.041	0.038	0.038	0.033	0.030	0.031	0.029	0.025	0.026
11	0.002	0.002	0.001	0.002	0.002	0.002	0.002	0.002	0.002	0.002
12	0.006	0.006	0.005	0.006	0.005	0.005	0.005	0.005	0.004	0.005
13	0.016	0.016	0.015	0.016	0.015	0.015	0.015	0.015	0.013	0.013
14	0.170	0.174	0.168	0.167	0.163	0.153	0.154	0.151	0.136	0.144
16	0.078	0.076	0.076	0.076	0.074	0.070	0.068	0.070	0.063	0.065
17	0.026	0.026	0.027	0.026	0.024	0.023	0.012	0.028	0.025	0.022
18	0.011	0.010	0.011	0.011	0.010	0.010	0.010	0.011	0.009	0.009
19	0.015	0.015	0.014	0.016	0.015	0.014	0.014	0.014	0.013	0.013
20	0.059	0.062	0.062	0.066	0.067	0.064	0.068	0.066	0.064	0.067
21	0.047	0.050	0.050	0.054	0.056	0.054	0.057	0.056	0.054	0.057
22	0.061	0.066	0.067	0.071	0.074	0.072	0.076	0.074	0.073	0.076
25	0.014	0.014	0.014	0.015	0.015	0.015	0.015	0.015	0.014	0.015
26	0.026	0.028	0.028	0.029	0.030	0.029	0.028	0.028	0.027	0.030
27	0.000	0.000	0.000	0.000	0.000	0.00	0.000	0.000	0.000	0.000
28	0.004	0.004	0.005	0.005	0.004	0.004	0.004	0.004	0.004	0.004
29	0.014	0.016	0.016	0.017	0.018	0.018	0.019	0.019	0.020	0.021
30	0.012	0.013	0.013	0.014	0.015	0.015	0.016	0.016	0.017	0.017
31	0.009	0.010	0.010	0.010	0.011	0.012	0.009	0.012	0.013	0.013
32	0.027	0.026	0.028	0.027	0.030	0.067	0.031	0.032	0.034	0.033

Table 4.2 (Continued)

Peak Number	Resuspension Number									
	1	2	3	4	5	6	7	8	9	10
34	0.007	0.007	0.007	0.008	0.009	0.009	0.009	0.009	0.010	0.010
35	0.018	0.017	0.019	0.019	0.021	0.022	0.023	0.023	0.026	0.027
36	0.015	0.014	0.015	0.016	0.018	0.019	0.020	0.020	0.023	0.023
37	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
38	0.006	0.007	0.006	0.007	0.010	0.008	0.009	0.009	0.011	0.010
39	0.010	0.010	0.008	0.009	0.014	0.012	0.014	0.014	0.016	0.015
40	0.007	0.007	0.005	0.006	0.009	0.008	0.009	0.009	0.011	0.011
41	0.022	0.023	0.023	0.023	0.031	0.028	0.031	0.031	0.036	0.035
42	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.002
43	0.001	0.000	0.001	0.000	0.001	0.001	0.001	0.001	0.001	0.001
44	0.003	0.003	0.003	0.003	0.003	0.003	0.004	0.004	0.005	0.004
46	0.025	0.028	0.028	0.028	0.032	0.032	0.037	0.038	0.046	0.043
47	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.002
48	0.001	0.000	0.001	0.002	0.002	0.003	0.003	0.004	0.004	0.004
49	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.003	0.003
50	0.002	0.000	0.002	0.000	0.002	0.000	0.006	0.005	0.007	0.006
51	0.022	0.030	0.024	0.029	0.028	0.033	0.027	0.028	0.034	0.033
52	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.002	0.002	0.002
53	0.003	0.002	0.001	0.011	0.008	0.018	0.034	0.023	0.031	0.018
54	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
55	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
56	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
57	0.003	0.003	0.003	0.003	0.003	0.002	0.004	0.002	0.006	0.005
58	0.002	0.001	0.002	0.002	0.002	0.001	0.003	0.001	0.005	0.004
59	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
60	0.001	0.001	0.001	0.000	0.000	0.000	0.000	0.001	0.001	0.001
61	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
62	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
63	0.002	0.001	0.001	0.000	0.001	0.001	0.000	0.000	0.003	0.001
64	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

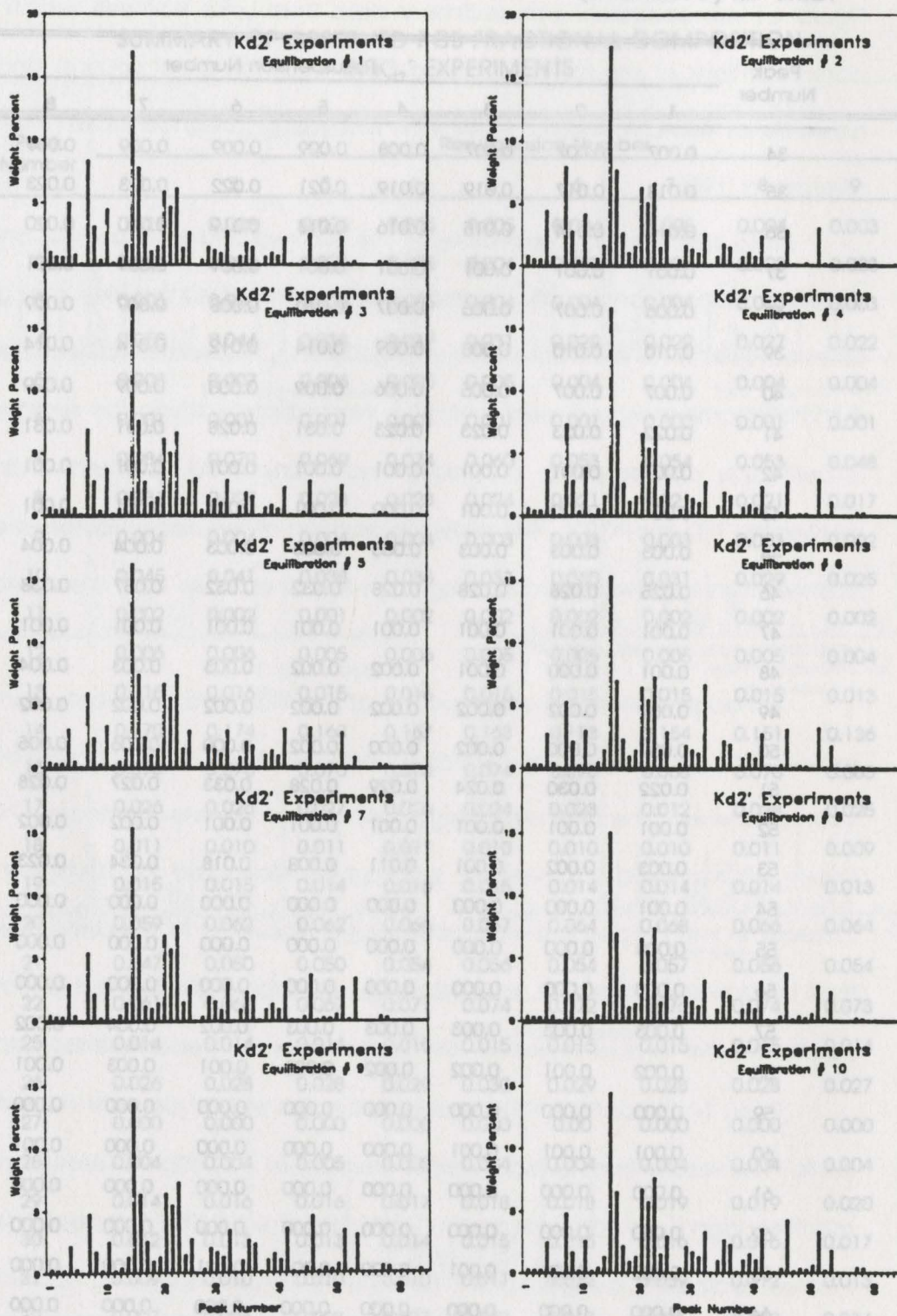


Figure 4.2. Observed weight-percent compositions of sediments resulting from  $K_{d2}'$  equilibrations.

contaminated sediments occur with consecutive mixing events using either PCB-free water or PCB-contaminated water as the resuspending fluid. These compositional changes occurred in the absence of biodegradation since all biological growth was inhibited by  $\text{HgCl}_2$ . While the results from both experiments are similar to PCB trends found in Lake Hartwell sediments, significant differences exist. These can be observed by comparing Figures 4.1 and 4.2 to Figure 4.3, as discussed below.

#### Qualitative Modeling of Environmental Weathering in Lake Hartwell Sediments

Experimental data presented in the previous section showed that significant changes in the congener composition of PCBs in sediments could be explained by chemical and physical processes in the absence of biodegradation. However, when the results from the  $K_d$ ' experiments are compared with compositional changes in PCBs recovered from Lake Hartwell sediments (refer to Figures 4.1-4.3), several discrepancies exist. These differences will be discussed individually.

First, it was observed that several predominant peaks normally present in GC analysis of Aroclor 1016 are entirely missing in Lake Hartwell sediments. They are peaks 2, 3, 15, and 27. The absence of these peaks can be explained by selective degradation by microorganisms utilizing known pathways (Erickson, 1986). Since numerous researchers have noted selective oxidation of specific PCB congeners, it has been assumed that the missing compounds were aerobically biodegraded to non-PCB compounds. This assumption is supported by recent investigations which have found high degradation rates for PCBs corresponding to IUPAC numbers 6, 7, 9, and 28 (Finkbeiner and Hamilton, 1987; Bopp, 1986; Bernard *et al.*, 1987a, 1987b). These compounds account for peak numbers 2, 3, and 15. Peak number 27, the only other prominent peak missing in the Lake Hartwell chromatograms, contains 2,2',3,4- and 2,3',5,5'-TCB. Although no reports were found which have studied biodegradation of

contaminated sediments occur with consecutive mixing events using either PCB-free water or PCB-contaminated water at the resuspension fluid. These compositional changes occurred in the absence of biodegradation since all biological growth was inhibited by HgCl<sub>2</sub>. While the results from both experiments are similar to PCB trends

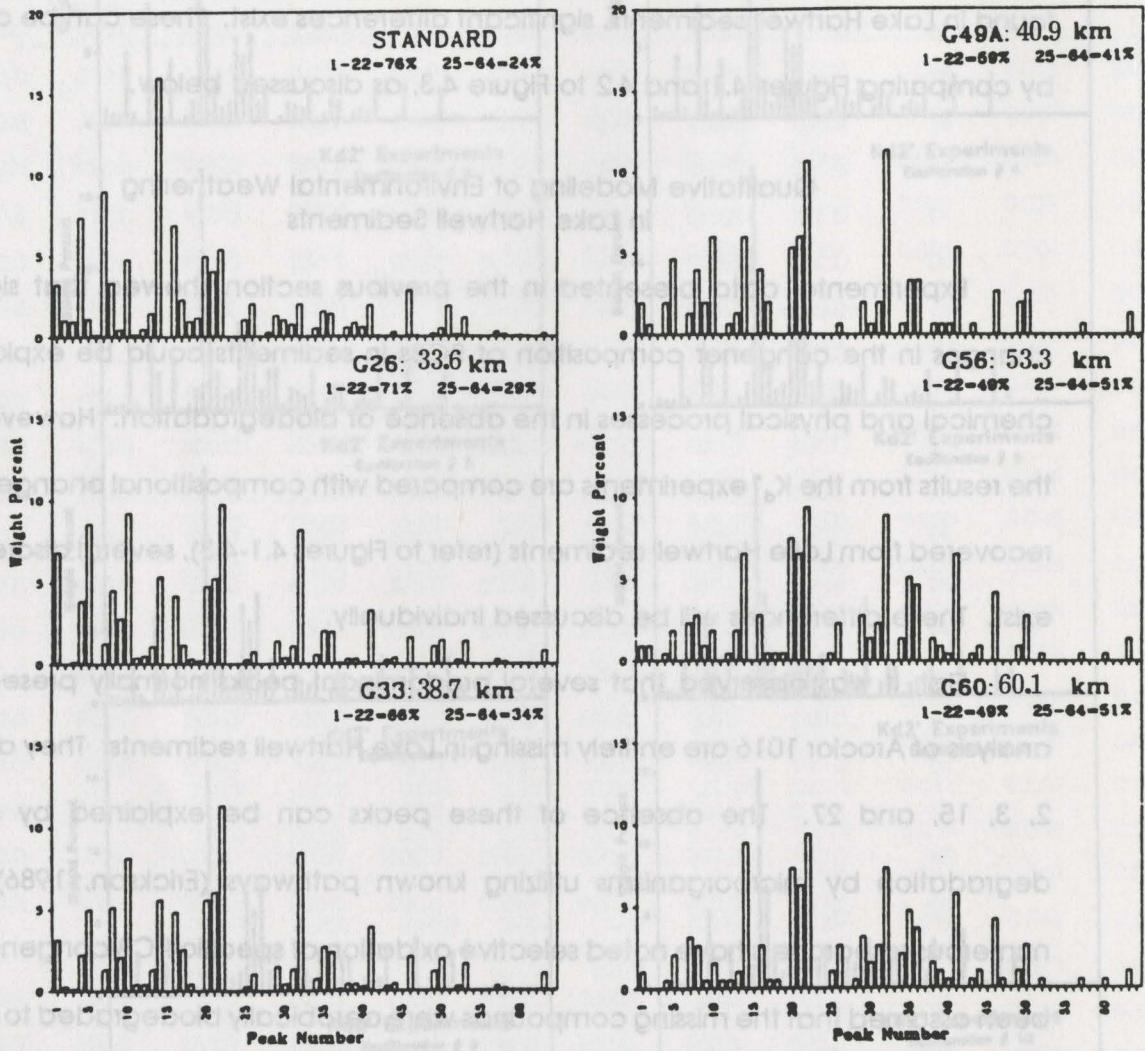


Figure 4.3. Observed weight-percent compositions of selected Lake Hartwell sediments. Figure taken from Germann (1988).

these particular compounds, PCBs with similar chlorination patterns can be aerobically degraded (Finkbeiner and Hamilton, 1987; Bernard *et al.*, 1987a, 1987b). Consequently, the assumption that these compounds were biodegraded is probably correct, and since these compounds have been absent in all Lake Hartwell sediment samples analyzed to date, they will not be included in any model considerations. All predominant PCBs (0.5 weight percent) known to be present in Aroclors 1016 and 1254, but not recovered from Lake Hartwell sediments, are accounted for in the peaks discussed above.

Another discrepancy between the laboratory data and field results is that, intuitively, the sediments sampled near the point source should reflect a fingerprint (i.e., weight-percent distribution) that approximates that of the Aroclor inputs to the system. Figure 4.3 shows the weight-percent distribution of an Aroclor mixture matching the estimated Aroclor contamination in Lake Hartwell (Billings, 1976). When this reference plot is compared with the weight-percent plot of a sample collected near the point source, large differences in PCB composition can be noted (refer to Figure 4.3). One explanation for these discrepancies is based on the history of PCB contamination emitted from the point source. The majority of the effluents from the point source were via a large retention or sedimentation basin. Accordingly, assuming that a large or unlimited source of PCBs was available in the basin, the resulting composition of PCBs in the effluent from the basin was determined both by the original Aroclor released to the basin and any differentiation of congeners in the basin; for example, based on solubilities. Experimental data from Dunnivant (1988) show that PCB solubilities generally decrease with increasing chlorination but are also dependent on specific chlorine substitution patterns within an homologous series (dichloro-, trichloro-, etc.). It follows that water emitted from the retention basin should preferentially contain more of the less-chlorinated PCBs. This is consistent with the results obtained from the  $K_d$ '



experiments discussed above and actual sediment samples taken from Lake Hartwell (refer to Figure 4.3 taken from Germann, 1988). These observations are the basis for the qualitative modeling approach discussed below.

A qualitative model was developed using the assumptions discussed earlier; specifically that (a) the absence of certain PCB congeners in the Lake Hartwell sediments can be explained by congener-specific microbial degradation, and (b) the input of PCBs to the lake system is not a direct function of the Aroclors discharged at the point source but is related to congener-specific differentiation that occurred in the settling basin, probably related to aqueous solubilities of individual congeners. The initial input to the model, consequently, is a function of these two assumptions.

In developing the model, a theoretical 4:1 mixture of Aroclors 1016 and 1254 was used to select the PCB congeners that should be present in the input to the settling basin (Albro *et al.*, 1979, 1981; Billings, 1976). Next, compounds which should have been present in the Lake Hartwell sediments based on the input calculations, but were not, were assumed to be selectively biodegraded (Figure 4.3; Germann, 1988) and were deleted from the list. These compounds represented peaks 2, 3, 15, and 27. Also, peaks having a weight-percent less than 0.5% of the total were not included in the model.

Relative mass contributions were assigned to each of the remaining compounds (GC peaks) as described below. Solubility data from Burkhard (1984) were used since PCBs released as Aroclors are subject to their solubilities as subcooled liquids instead of the solubilities as solids (Dunnivant, 1988). Comparisons between the two data sets confirm that when the theoretical data from Burkhard *et al.* (1985) are converted to solubilities as solids, the data are in good agreement with minor exceptions (Dunnivant, 1988). Partial congener (peak) solubilities were considered to be a function of the maximum solubility for each congener (peak) and were determined by dividing each

maximum congener solubility (Burkhard, 1984) by the sum of the maximum individual solubilities for all the PCB congeners theoretically present. Next, a relative weighted solubility was calculated for each peak (congener) by multiplying the maximum congener solubility (from Burkhard, 1984) by the fraction of the sum of all peak solubilities. Therefore, a weighted solubility for each congener (peak) was obtained. The complete data set (weighted solubilities and sediment/water partition coefficients) and an example calculation is given in Appendix E. This data set was used as the input to the qualitative model. It should theoretically be similar to the contaminated water released from the settling basin into the tributary to Lake Hartwell during the years of highest PCB usage.

The resulting solubility data were entered into a spreadsheet containing congener-specific water/sediment partition coefficients. The partition coefficients used in the spreadsheet were a mean of 10 individual  $K_d$ ' determinations measured in the  $K_{d1}$ ' and  $K_{d2}$ ' experiments discussed earlier (Appendix J). Apparent partition coefficients did not change with increasing number of resuspension events and were statistically identical between the  $K_{d1}$ ' and  $K_{d2}$ ' experiments. The spreadsheets were used to iteratively calculate the change in weight-percent compositions of PCBs associated with sediments in a series of theoretical resuspension events. A 1000 mg/L sediment suspension was used in all of the theoretical resuspension events. Output data from the model were summarized as weight percents and are shown in Figures 4.4 and 4.5. Individual data are not presented, but are stored on computer disks and are available upon request (Elzerman, 1992).

The data show a strong similarity to the data of Germann (1988) summarized in Figure 4.3. The initial equilibrations mimic the weight-percent patterns found near the point source in Lake Hartwell, which are more highly concentrated with the less-chlorinated PCB congeners. As more resuspensions, which are analogous to remixing

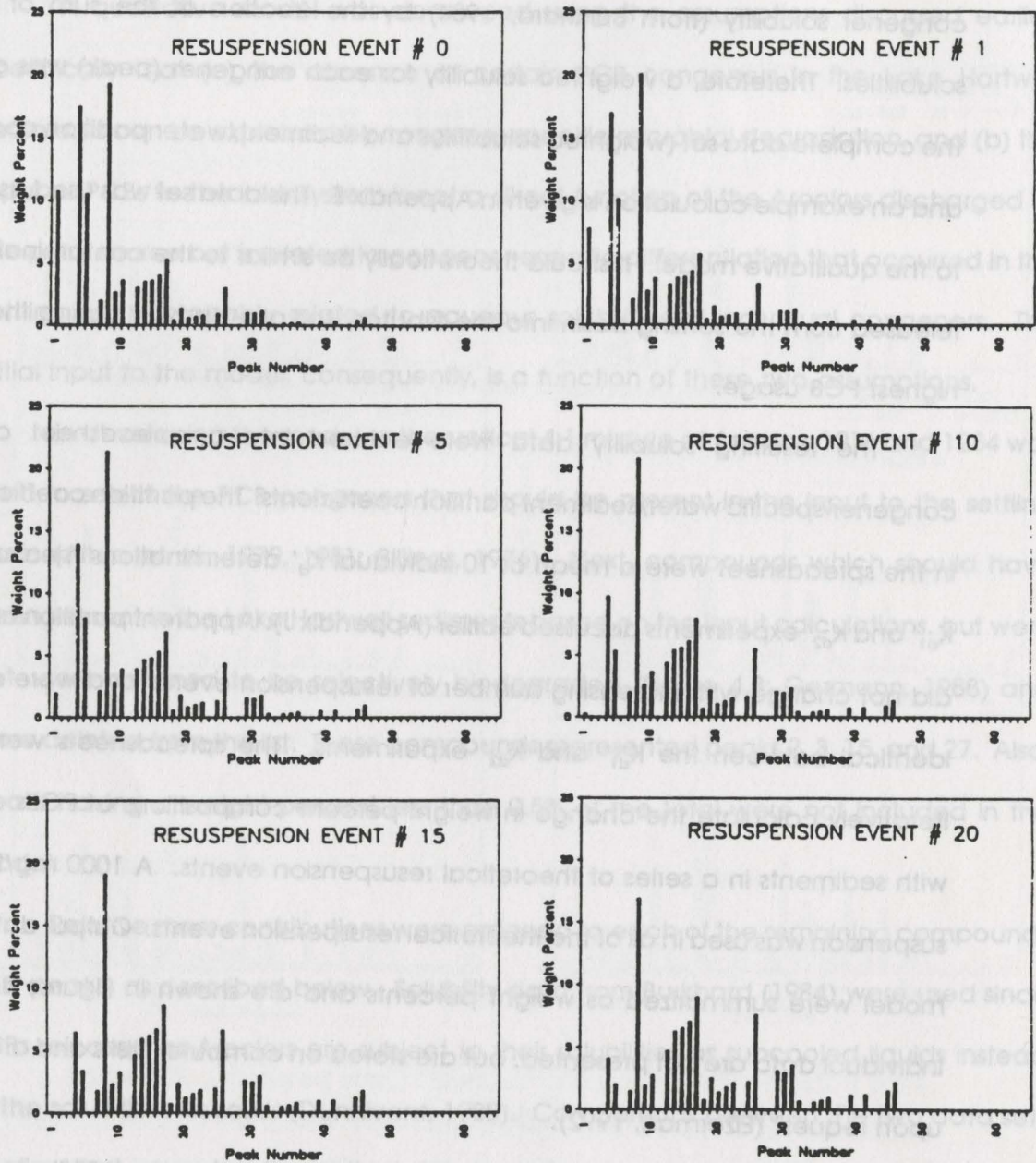


Figure 4.4. Predicted weight-percents from Lake Hartwell sediments during equilibrations 0 to 20.

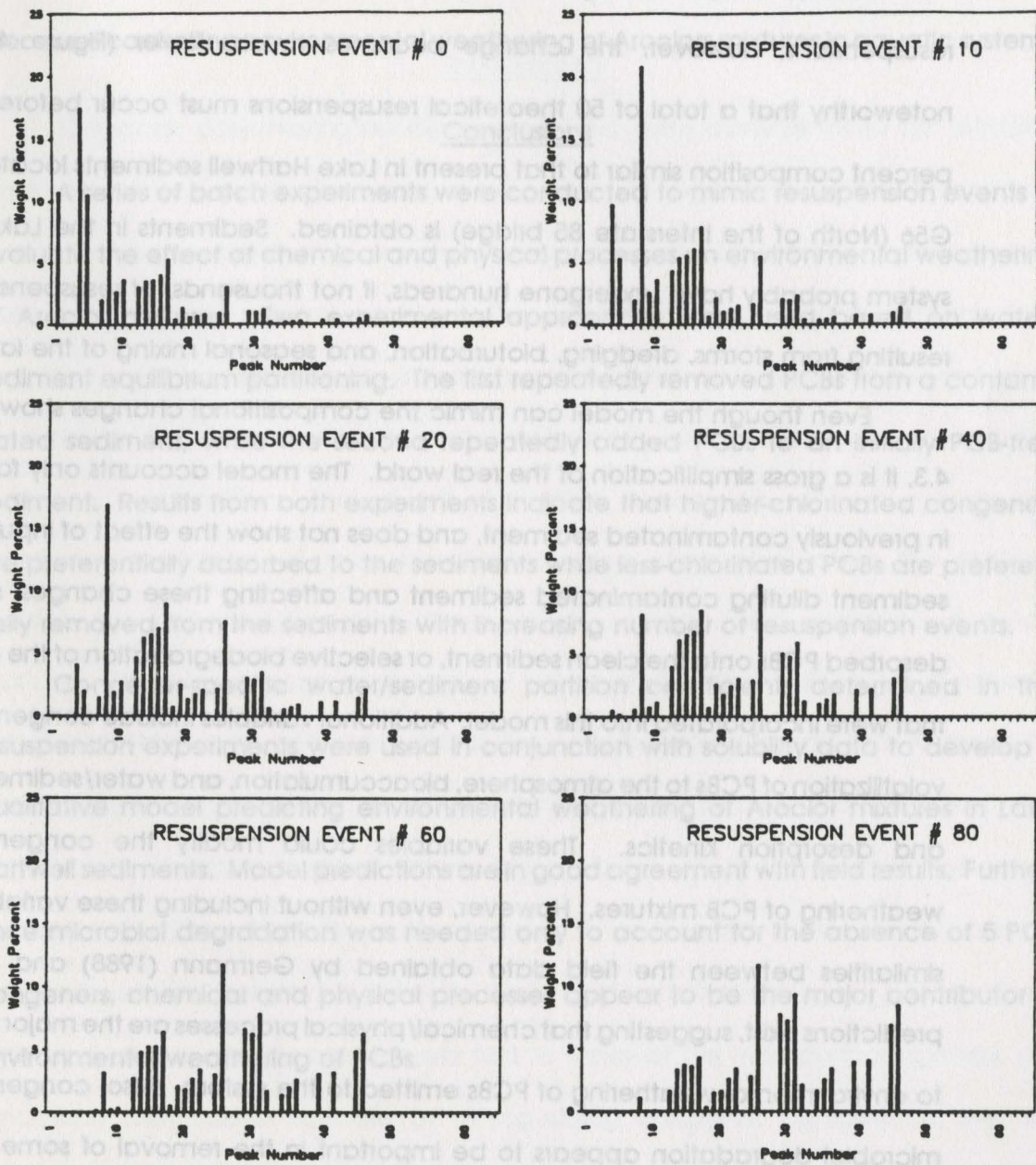


Figure 4.5. Predicted weight-percents for Lake Hartwell sediments during equilibrations 20 to 80.

and transport down the Lake Hartwell system occur, the PCB composition slowly changes to yield compositions containing less dichloro- and trichloro-biphenyls. Again, this appears to be exactly what is occurring in Lake Hartwell.

Initially, a rapid change in weight percents occurs. After approximately 10 resuspensions, however, the change becomes much slower (Figure 4.4). It is noteworthy that a total of 50 theoretical resuspensions must occur before a weight percent composition similar to that present in Lake Hartwell sediments located in core G56 (North of the Interstate 85 bridge) is obtained. Sediments in the Lake Hartwell system probably have undergone hundreds, if not thousands, of resuspension events resulting from storms, dredging, bioturbation, and seasonal mixing of the lake.

Even though the model can mimic the compositional changes shown in Figure 4.3, it is a gross simplification of the real world. The model accounts only for changes in previously contaminated sediment, and does not show the effect of inputs of clean sediment diluting contaminated sediment and affecting these changes, sorption of desorbed PCBs onto the clean sediment, or selective biodegradation of the congeners that were incorporated into this model. Additional variables include congener-specific volatilization of PCBs to the atmosphere, bioaccumulation, and water/sediment sorption and desorption kinetics. These variables could modify the congener-specific weathering of PCB mixtures. However, even without including these variables, strong similarities between the field data obtained by Germann (1988) and the model predictions exist, suggesting that chemical/physical processes are the major contributor to environmental weathering of PCBs emitted to the system. Also, congener specific microbial degradation appears to be important in the removal of some PCBs (e.g. peaks 2, 3, 15, and 27).

In general, the qualitative model presented herein agrees with the conclusions of Burkhard (1984). Less-chlorinated PCBs are selectively removed from the sediment

phase while higher-chlorinated congeners are enriched upon successive resuspensions. Moreover, trends appear to agree with data from the Hudson River sediments, although the Hudson River watershed is more complicated due to the presence of multiple PCB inputs. Chemical and physical processes appear to be the dominant processes controlling environmental weathering of Aroclors mixtures in aquatic systems.

### Conclusions

A series of batch experiments were conducted to mimic resuspension events to evaluate the effect of chemical and physical processes on environmental weathering of Aroclor mixtures. Two experimental approaches were used based on water/sediment equilibrium partitioning. The first repeatedly removed PCBs from a contaminated sediment, while the second repeatedly added PCBs to an initially PCB-free sediment. Results from both experiments indicate that higher-chlorinated congeners are preferentially adsorbed to the sediments while less-chlorinated PCBs are preferentially removed from the sediments with increasing number of resuspension events.

Congener-specific water/sediment partition coefficients determined in the resuspension experiments were used in conjunction with solubility data to develop a qualitative model predicting environmental weathering of Aroclor mixtures in Lake Hartwell sediments. Model predictions are in good agreement with field results. Further, since microbial degradation was needed only to account for the absence of 5 PCB congeners, chemical and physical processes appear to be the major contributor in environmental weathering of PCBs.

## CHAPTER V

### DIFFERENTIAL WEATHERING OF PCB CONGENERS IN LAKE HARTWELL

#### Introduction

Originally, polychlorinated biphenyls (PCBs) were considered to be refractive environmental contaminants because even over prolonged time periods little change in Aroclor composition had been observed in environmental samples. Although PCBs are relatively stable compounds, it was the use of inadequate analytical technology, specifically packed column gas chromatography (Erickson, 1992), that prevented the detection of individual congeners and consequently of significant alternations in PCB congener composition. The advent of capillary column gas chromatography and improved application of mass spectrometry had given researchers the ability to observe the individual behavior of the variety of congeners contained in Aroclor mixtures. There is now a growing body of data which indicates PCBs are weathering (changing relative to congener distributions) in the environment and suggests the possibility that over time some congeners may be degraded and detoxified more rapidly than previously realized (Brown *et al.*, 1987a). Thus, the focus of the current debate has shifted from the existence of PCB weathering to the identification of environmental processes that mediate these compositional changes. Since both the fate and effects of PCBs are actually tied to those of the individual congeners, and analytical techniques capable of distinguishing congener composition are now available, it no longer makes sense just to talk about the determination or fate of Aroclors like they were simple single compounds.

In aquatic systems, current thought tends to group environmental weathering processes into two distinct types: those mediated by biological activity and those due

to physiochemical process. Brown *et al.* (1984) and Bopp *et al.* (1984) showed PCBs in sediments from the upper Hudson River were undergoing a compositional alteration that resulted in decreased proportions of higher chlorinated congeners and increased proportions of lower chlorinated congeners relative to unweathered congener mixtures. Compositional changes were seen with increasing depth in a sediment core, leading to the conclusion that the change was due to microbiologically mediated reductive dechlorination in the anaerobic sedimentary environment (Brown *et al.*, 1987b). Brown *et al.* (1987a; 1987b) proposed a stepwise dechlorination of specific di-, tri-, and tetra-ortho-substituted biphenyls to lower chlorinated congeners of the same ortho substitution patterns. The result of this stepwise dechlorination scenario is the production of 2,2'-DCB, 2,3-DCB, 2,4'-DCB, 2,2',6-TrCB, 2,3',6-TrCB, 2,4',6-TrCB, and 2,2',5',6-TCBs. Supporting this hypothesis is the observation that levels of these terminal dechlorination product congeners were found in upper Hudson River sediments to be three to eight times greater on a relative basis than in the parent Aroclor, while the weight-percent of the higher chlorinated congeners was found to decrease by a factor of two to ten (Brown *et al.*, 1987b).

Bush *et al.* (1987) analyzed water and sediments from the same reach of the Hudson River and also found pronounced differences in congener mixtures between the environmental PCB residues and the source Aroclors. The congener mixtures in the sediment samples were significantly skewed towards the less chlorinated congeners, but no change in PCB composition with depth in sediment was observed. Several of these sediment samples were contaminated with a PCB residue that resembled congener patterns found in the river water. Earlier work (Bush *et al.*, 1985) had identified similar aqueous PCB residues and attributed their presence at the study site to the preferential dissolution of the lower chlorinated congeners (primarily 2-, 2,2'- and 2,6-CB) as the river flowed over contaminated upstream sediments. Thus, they



hypothesized that the composition of the PCBs available for deposition in the downstream sediments had already undergone major changes. This led to the conclusion that the alterations in PCB residue patterns found in bottom sediments were not likely the result of *in situ* weathering processes but were instead due to the scavenging of previously altered mixtures of PCBs from the water column by suspended particles or water-filtering macrophytes growing in the sediments.

Theoretical predictions of physiochemical weathering of PCBs were performed by Burkhard *et al.* (1985). Here the possible changes in congener composition were examined by considering successive batch equilibrations in an air-water-suspended particulate matter (SPM) system using predicted physiochemical properties and the fugacity model (Mackay, 1979). Burkhard *et al.* (1985) found variations in Henry's law constants (HLCs) and sediment-water partition coefficients ( $K_{d,s}$ ) resulted in the most significant differences in congener partitioning behavior, with SPM-water partitioning being the dominant process. The tendency of individual homologous chlorination groups to behave differently in the model systems led Burkhard *et al.* (1985) to conclude that physiochemical processes are a major factor controlling the weathering of PCBs in the environment. Dunnivant (1988) came to similar conclusions based on laboratory batch system investigations and computer simulations of congener fractionation in successive partitioning of congeners in three-phase systems of water, sediment, and air.

The environmental implications associated with physiochemical and biochemical processes make it important to determine which dominate the weathering of PCBs in aquatic systems. Physiochemical weathering should redistribute congeners into different environmental compartments, not eliminating the contamination problem but unequally transferring it elsewhere. On the other hand, biochemical weathering should result in the destruction of congeners, and possible production of others, ideally, but not

necessarily, producing a PCB residue that is less toxic and more easily biodegradable. Thus, knowledge of the dominant transformation or transport processes would enable a more informed decision concerning remediation of PCB-contaminated systems and would improve fate predictions. For example, the remedial action for a biologically mediated system may simply be to allow the PCBs to degrade over time into a less toxic form. Conversely, remediation of contaminated systems dominated by physicochemical modification of the PCB congeners may require an active response in order to prevent the problem from moving into environmental compartments over which there is little or no control.

The Twelve Mile Creek-Lake Hartwell system in northwest South Carolina provides an excellent opportunity to identify the presence and relative importance of physicochemical and biochemical weathering processes in an aquatic system. In the mid-1970s, Lake Hartwell was found to be contaminated with PCBs. The source of the contamination was traced by the South Carolina Department of Health and Environmental Control (SCDHEC) (SCDHEC, 1976) to a capacitor manufacturing plant located on the Twelve Mile Creek tributary 39 km upstream from the top of the lake. The plant was discharging PCB-laden effluent into the creek via two serial settling basins. Sediment samples in these basins were found to have average PCB concentrations of 27,300  $\mu\text{g/g}$  in the upper basin and 7970  $\mu\text{g/g}$  in the lower basin (SCDHEC, 1976). The average total PCB concentration of the effluent in 1976 was 30  $\mu\text{g/L}$ . Subsequent studies of sediments in Twelve Mile Creek and Lake Hartwell have shown maximum concentrations in excess of 150  $\mu\text{g/g}$  (dry weight basis) (Germann, 1988). Total PCB concentrations are highest immediately downstream of the source and decrease with distance (Scarsbrough, 1976; Polansky, 1984; Dunnivant, 1985; Germann, 1988).

Differences in the hydrologic characteristics for the upper and lower portions of Twelve Mile Creek and for Lake Hartwell are believed to have a significant effect on physiochemical and biochemical weathering processes. The upper portion of Twelve Mile Creek (0-32 km) is characterized by relatively shallow waters and high water velocities. In the lower portion (32-39 km), the creek deepens and widens due to the impoundment of Lake Hartwell. Water velocities are much slower in this portion of the creek and a significant portion of the solids load is deposited in the sediments. Flow from Twelve Mile Creek eventually enters the top of Lake Hartwell where it mixes with uncontaminated waters from the Keowee River. Waters then move slowly down this 50 km long reservoir toward the Hartwell Dam.

A summary of the congener-specific data set obtained by Germann (1988) for the lower portion of Twelve Mile Creek and for Lake Hartwell is presented below and is used to evaluate the importance of physiochemical and biochemical weathering processes. As part of this evaluation, steady-state model calculations for physiochemical weathering of PCB congeners are presented and discussed.

### Summary of Congener-Specific Field Data

#### Sample Collection

The samples used in this study were a subset of a total of 85 sediment core samples collected between October 1986 and August 1987 for a larger study on the distribution of PCBs in the Twelve Mile Creek-Lake Hartwell system. Sediment core sampling was done using a Wildco sediment corer (Wildlife Supply Co., Saginaw, MI) containing 5 cm inner diameter polycarbonate tubes. Prior to use, the polycarbonate tubes were washed in a hot detergent bath and rinsed three times with distilled water. After collection, samples were sectioned in 5 cm sections or as changes in sample matrix warranted. Only sediment from the interior of the core not in contact with the corer was saved in order to avoid possible contamination from the polycarbonate and

from sediment fines forced along the wall of the tube. Sectioned samples were stored in solvent rinsed bottles at 4°C until analyzed. Some samples used in this study were collected from reaches of the submerged riverbed (where PCBs were deposited before the reservoir was filled). Sample locations (Figure 5.1) were determined in relation to buoys placed and maintained by the U.S. Army Corps of Engineers. Samples used in this study were limited to those found to be contaminated with at least 1 µg/g of total PCB in order to minimize quantification error during weight-percent calculations.

#### Extraction, Analysis, and Quantification Procedures

Extraction and analysis of the sediments for PCBs were performed using the method developed by Dunnivant and Elzerman (1988) and modified for this study in order to minimize the volume of solvents used and the total extraction time. Three to five grams of sediment were weighed into 150 mL beakers, 50 mL of acetone were added, and the mixture was sonicated while mixing on a magnetic stir plate in an ice-water bath for 5 min at 0.8 relative output using a Fisher Model 300 sonic dismembrator equipped with a standard size probe and a 300 watt generator. The sample was allowed to settle for 5 min and then passed through a Millipore vacuum filter apparatus containing a Gelman Type A glass fiber prefilter into a 250 mL Erlenmeyer flask. The filter cake was rinsed twice with acetone in order to completely remove all of the PCB-containing acetone. The extract was quantitatively transferred to a 250 mL separatory funnel containing 60 mL of double-distilled water, 10 mL of saturated NaCl solution, and 15 mL of iso-octane and then shaken for 3 min at 300 rpm on a New Brunswick Scientific G10 Gyrotory shaker. After the solution settled for 1 hr, the aqueous phase was collected and the iso-octane was placed on a prewashed Na<sub>2</sub>SO<sub>4</sub> column and collected in a 100 mL graduated cylinder. The aqueous phase was then returned to the separatory funnel with 15 mL of clean iso-octane, reshaken, and the iso-octane placed on the Na<sub>2</sub>SO<sub>4</sub> column and collected. The extracts were then composited and

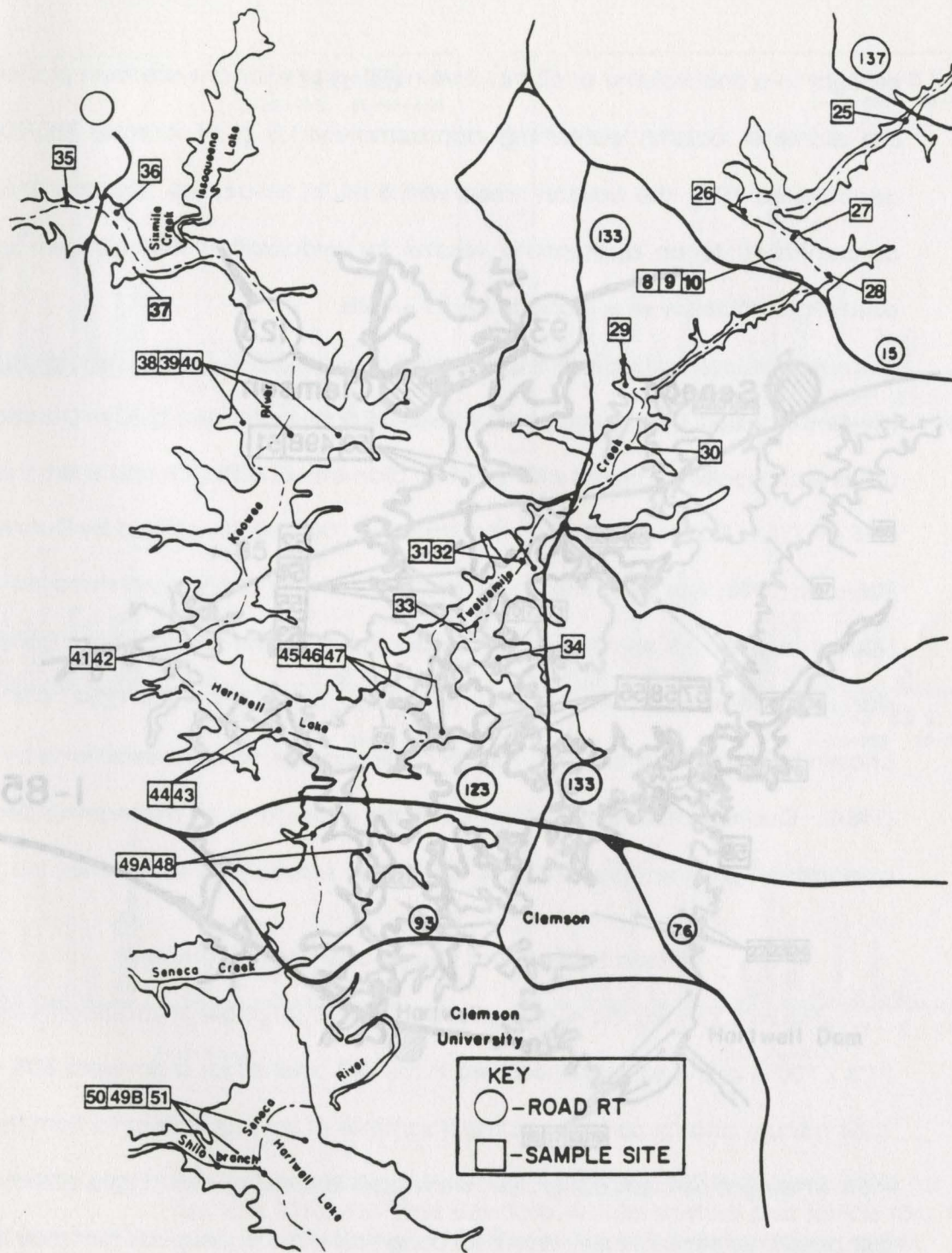


Figure 5.1. Map of the Twelve Mile Creek-Lake Hartwell system showing sample sites and boundaries of the different hydrologic regimes.

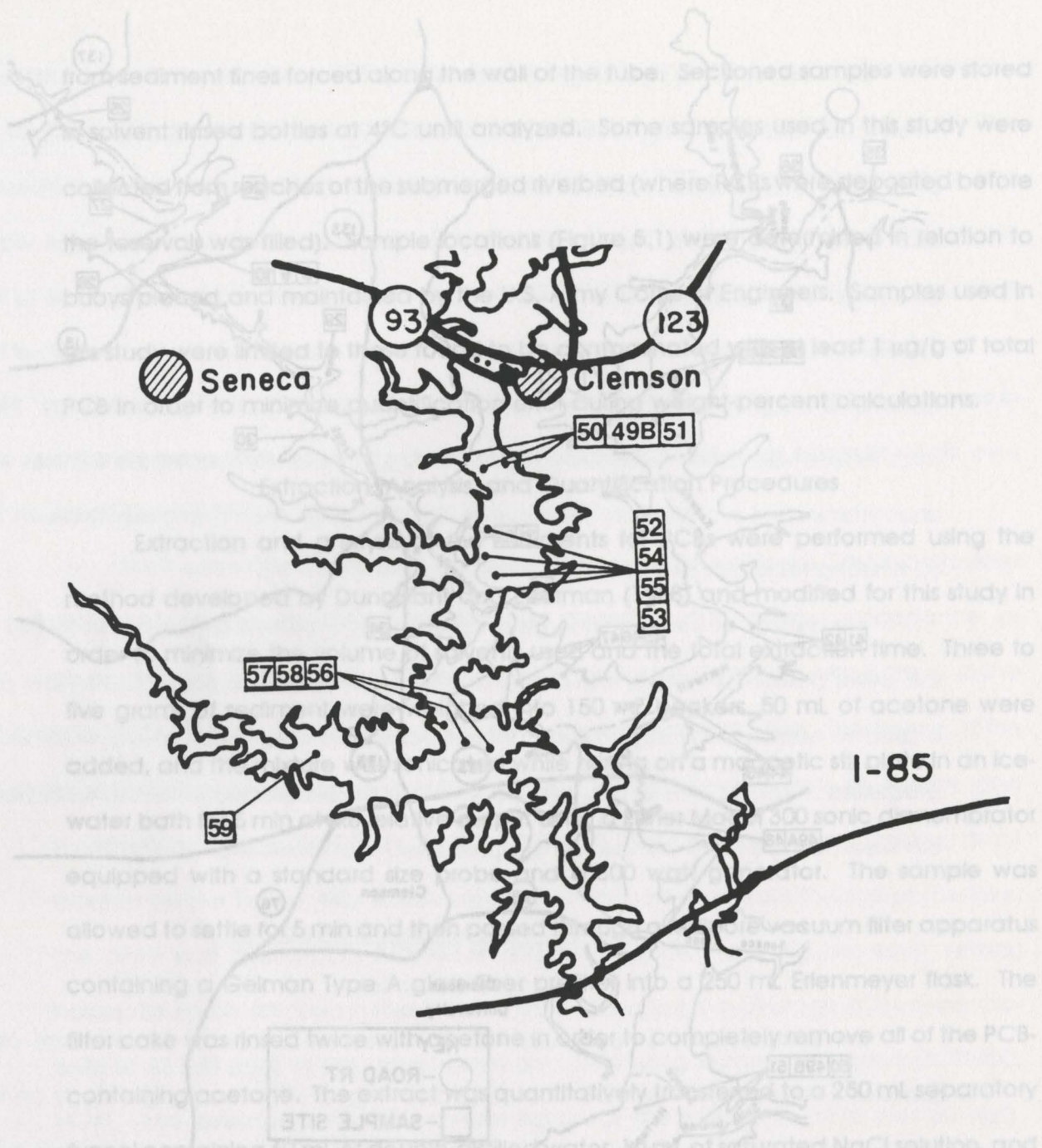


Figure 5.1 (Continued)

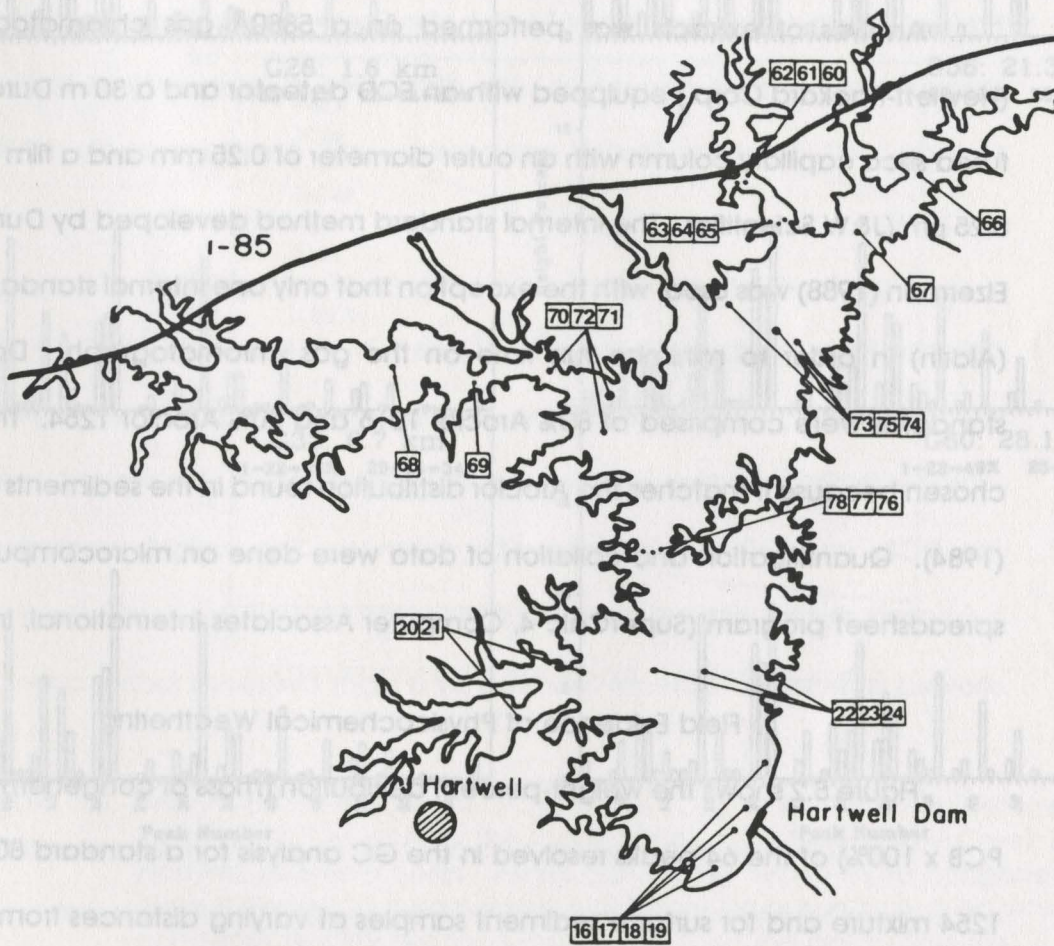


Figure 5.1 (Continued)

brought to a final volume of 60 mL. Five milliliters of extract were then placed on a 1 cm diameter column containing approximately 1.5 g of alumina (80/200 mesh, deactivated 10%), the column rinsed with 5 mL of iso-octane, and the final extract concentrated to an appropriate volume by evaporation with nitrogen gas. The extraction efficiency was found to be  $99 \pm 4.9\%$ .

Analysis of extracts was performed on a 5880A gas chromatograph (GC) (Hewlett-Packard Corp.) equipped with an ECD detector and a 30 m Durabond DB-5 fused silica capillary column with an outer diameter of 0.25 mm and a film thickness of 0.25  $\mu\text{m}$  (J&W Scientific). The internal standard method developed by Dunnivant and Elzerman (1988) was used, with the exception that only one internal standard was used (Aldrin) in order to minimize run time on the gas chromatograph. Daily working standards were comprised of 80% Aroclor 1016 and 20% Aroclor 1254. This ratio was chosen because it matches the Aroclor distribution found in the sediments by Polansky (1984). Quantification and collation of data were done on microcomputers using a spreadsheet program (SuperCalc 4, Computer Associates International, Inc.).

#### Field Evidence of Physicochemical Weathering

Figure 5.2 shows the weight-percent distribution (mass of congener/mass of total PCB x 100%) of the 64 peaks resolved in the GC analysis for a standard 80% 1016/20% 1254 mixture and for surface sediment samples at varying distances from the source. Plots of weight-percent distribution were used instead of actual gas chromatograms because they eliminate any biases for or against a particular peak that may result from absolute levels of total PCB concentration in different samples. In the standard Aroclor mixture, the early eluting peaks (peaks 1-22, representing less chlorinated congeners) account for almost 76% of the total PCB weight while the later eluting peaks (peaks 25-63, representing the higher chlorinated congeners) accounted for the remaining 24%.



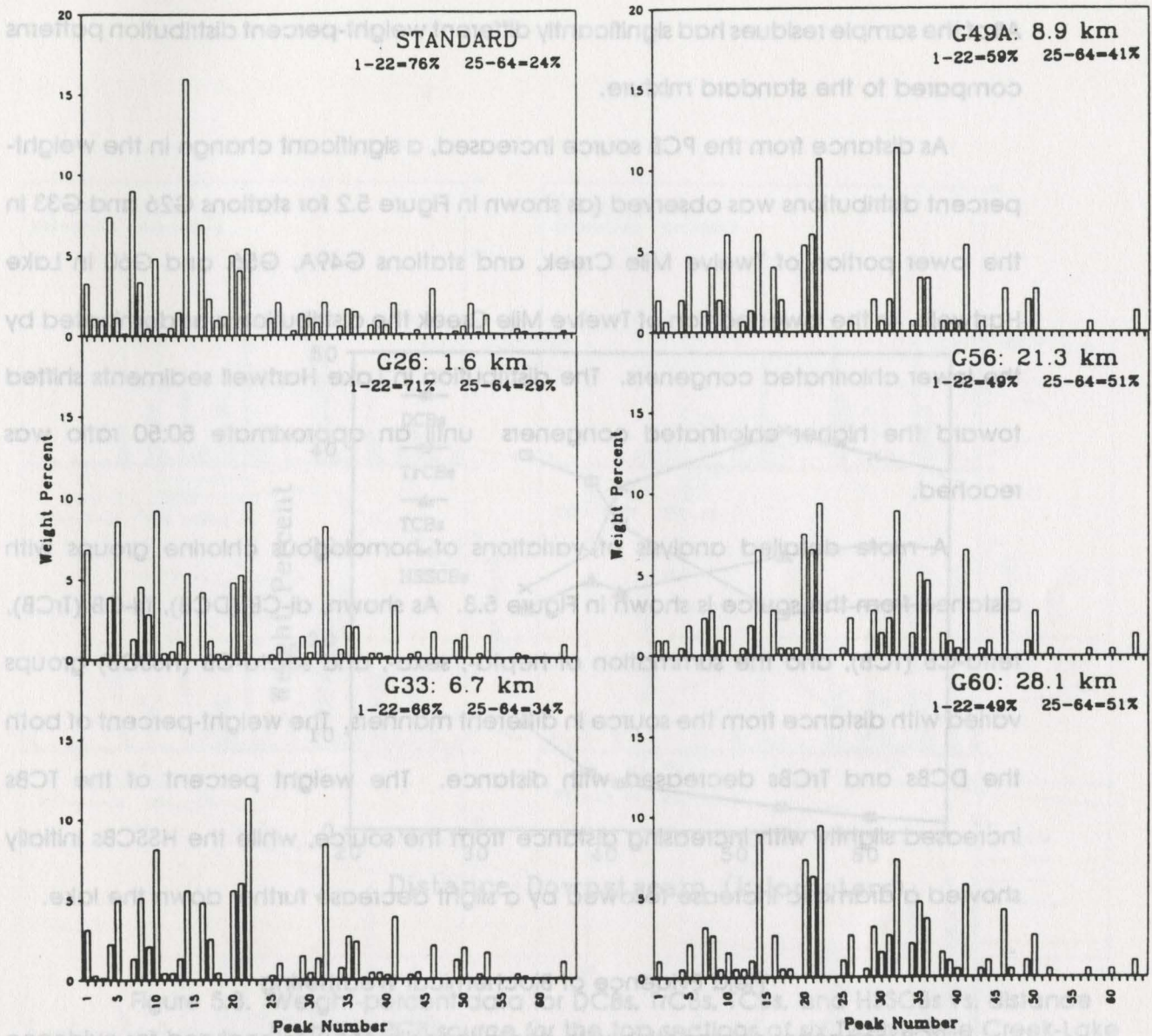


Figure 5.2. Weight-percent (peak mass/total mass x 100%) of each peak for an 80% 1016/20% 1254 standard Aroclor mixture and for the top section of five Twelve Mile Creek-Lake Hartwell sediment cores. Sample location distances from the PCB source and weight-percent summaries for peaks 1-22 and 25-64 are given. Some peaks not quantified due to: (a) chromatographic interferences—GC peaks 24, 27 and 64 or (b) lack of analytical sensitivity—GC peaks 45, 48, 55, 56, 59 and 62. Peak 15 coelutes with peak 14. Peak 23 is the internal standard Aldrin.

All of the sample residues had significantly different weight-percent distribution patterns compared to the standard mixture.

As distance from the PCB source increased, a significant change in the weight-percent distributions was observed (as shown in Figure 5.2 for stations G26 and G33 in the lower portion of Twelve Mile Creek, and stations G49A, G56, and G60 in Lake Hartwell). In the lower portion of Twelve Mile Creek the distribution was dominated by the lower chlorinated congeners. The distribution in Lake Hartwell sediments shifted toward the higher chlorinated congeners until an approximate 50:50 ratio was reached.

A more detailed analysis of variations of homologous chlorine groups with distance from the source is shown in Figure 5.3. As shown, di-CB (DCB), tri-CB (TrCB), tetra-CB (TCB), and the summation of hepta-, sexa-, and septa-CB (HSSCB) groups varied with distance from the source in different manners. The weight-percent of both the DCBs and TrCBs decreased with distance. The weight percent of the TCBs increased slightly with increasing distance from the source, while the HSSCBs initially showed a dramatic increase followed by a slight decrease further down the lake.

#### Field Evidence of Biochemical Weathering

PCB congener composition with depth in sediment was analyzed for evidence of biochemical alteration of the relative congener composition. Congener composition was found to vary significantly with depth in sediments for the lower portion of Twelve Mile Creek (e.g. station G26). In these core samples, the congener composition becomes increasingly dominated by the lower chlorinated congeners with increasing depth in the sediment (Figure 5.4). This trend was absent in the less contaminated sediments further down Lake Hartwell.

Figure 5.5 shows a more detailed analysis of variations of homologous chlorine groups with depth in sediment, which again reveals two seemingly different systems for

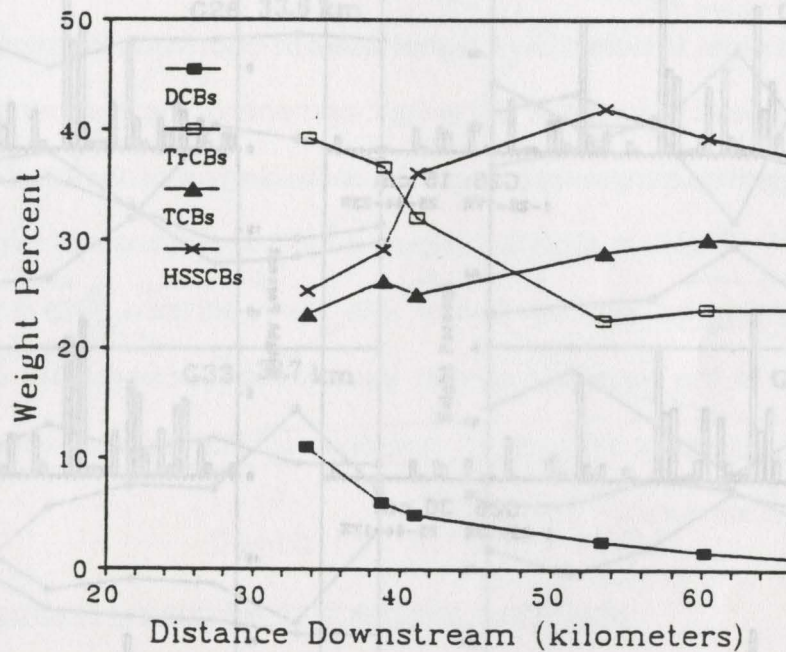


Figure 5.3. Weight-percent data for DCBs, TrCBs, TCBs, and HSSCBs vs. distance from the PCB source for the top sections of six Twelve Mile Creek-Lake Hartwell sediment cores. Peaks containing two or more congeners were assigned to a homologous chlorination group based on which congener accounted for a majority of the total peak mass (as reported by Albro and Parker, 1979; Albro *et al.*, 1981). Peaks unable to be accurately classified (26, 28 and 31) were excluded.

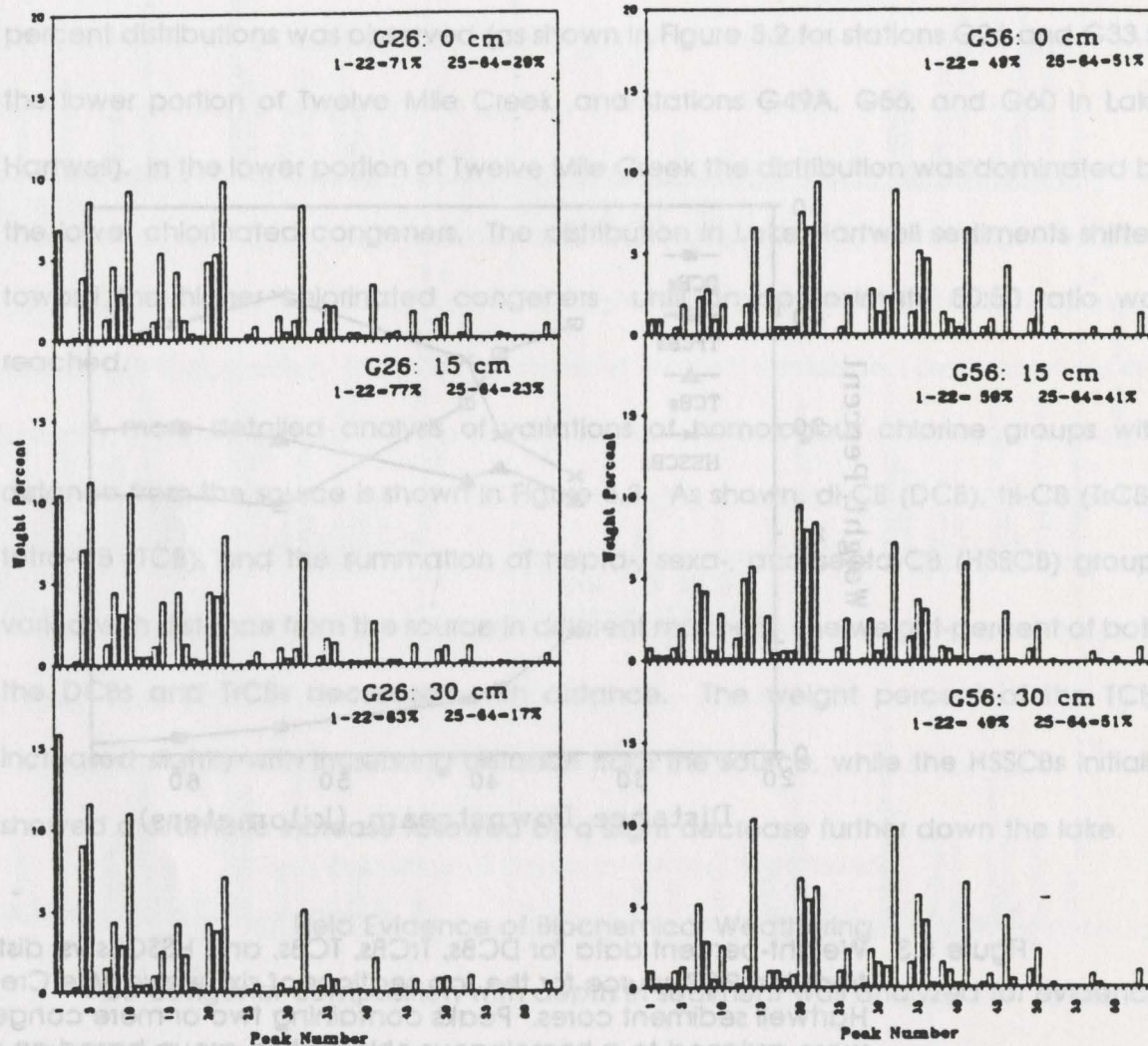


Figure 5.4. Weight-percent data for each peak for three sections of two representative cores, G26 (for the lower portion of Twelve Mile Creek) and G56 (for Lake Hartwell). Depth in core and weight-percent summaries for peaks 1-22 and 25-64 are given. Refer to Figure 2 for sample locations and identification of peaks not quantified and sample locations.

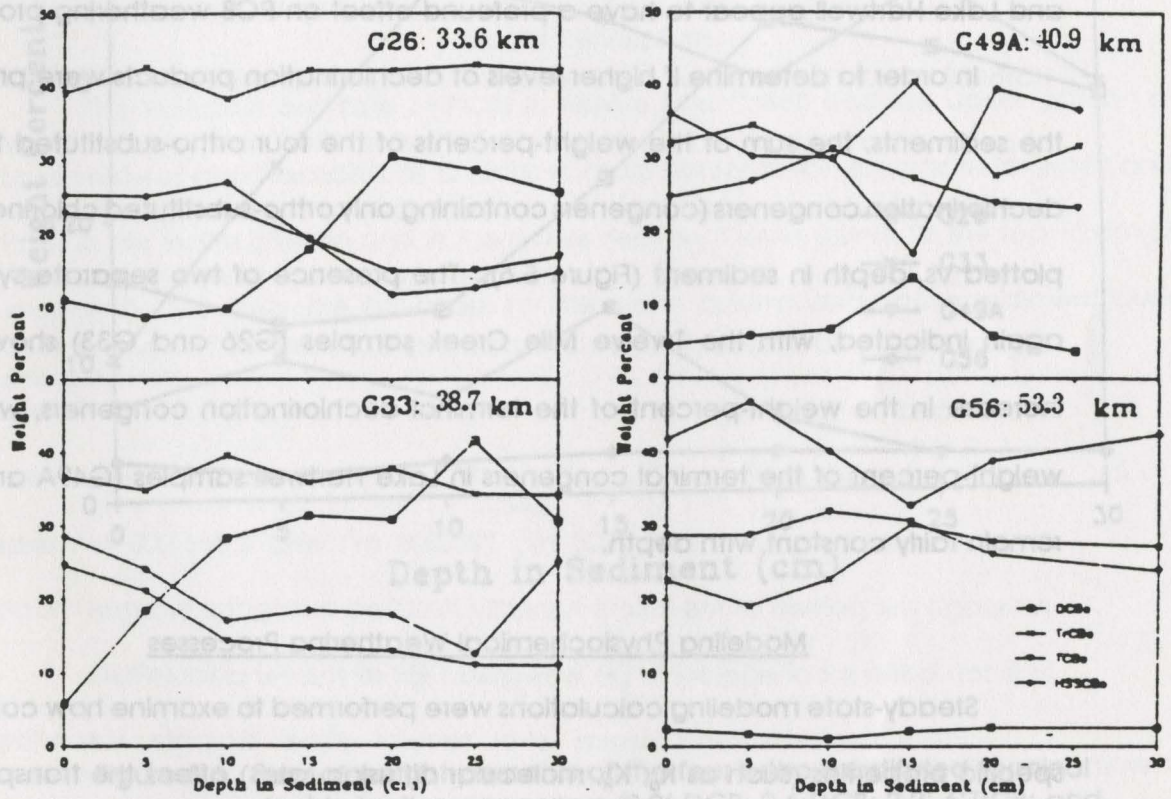


Figure 5.5. Weight-percent data for DCBs, TrCBs, TCs, and HSSCBs vs. depth in core for four Twelve Mile Creek-Lake Hartwell sediment cores. Distance of sample location from the PCB source is indicated. Refer to Figure 3 for description of homologous chlorination groups.

the lower portion of Twelve Mile Creek and for Lake Hartwell. The Twelve Mile Creek samples (G26 and G33) showed DCB levels increasing, TrCBs remaining constant, and TCBS and HSSCBs decreasing with depth. The Lake Hartwell samples (G49A and G56) did not show similar changes in congener composition with depth. Although stations G33 and G49A are less than 3 km apart, the different flow regimes in Twelve Mile Creek and Lake Hartwell appear to have a profound effect on PCB weathering processes.

In order to determine if higher levels of dechlorination products were present in the sediments, the sum of the weight-percents of the four ortho-substituted terminal dechlorination congeners (congeners containing only ortho-substituted chlorines) were plotted vs. depth in sediment (Figure 5.6). The presence of two separate systems is again indicated, with the Twelve Mile Creek samples (G26 and G33) showing an increase in the weight-percent of the terminal dechlorination congeners, while the weight-percent of the terminal congeners in Lake Hartwell samples (G49A and G56) remain fairly constant with depth.

#### Modeling Physiochemical Weathering Processes

Steady-state modeling calculations were performed to examine how congener-specific properties (such as  $K_d$ ,  $K_H$ , molecular diffusion rates) affect the transport and fate of PCBs. A basic description of the model, along with modeling results, is presented below to further explain the importance of physiochemical weathering processes in controlling the fate and distribution of PCB congeners in Twelve Mile Creek and the upper portion of Lake Hartwell.

#### Background Information

For model calculations, Twelve Mile Creek is divided into an upper and lower reach (as shown in Figure 5.1). In the upper reach (0-32 km), the channel is relatively shallow (ca. 0.4 m) with an average width of 25 m. The average annual flow in the

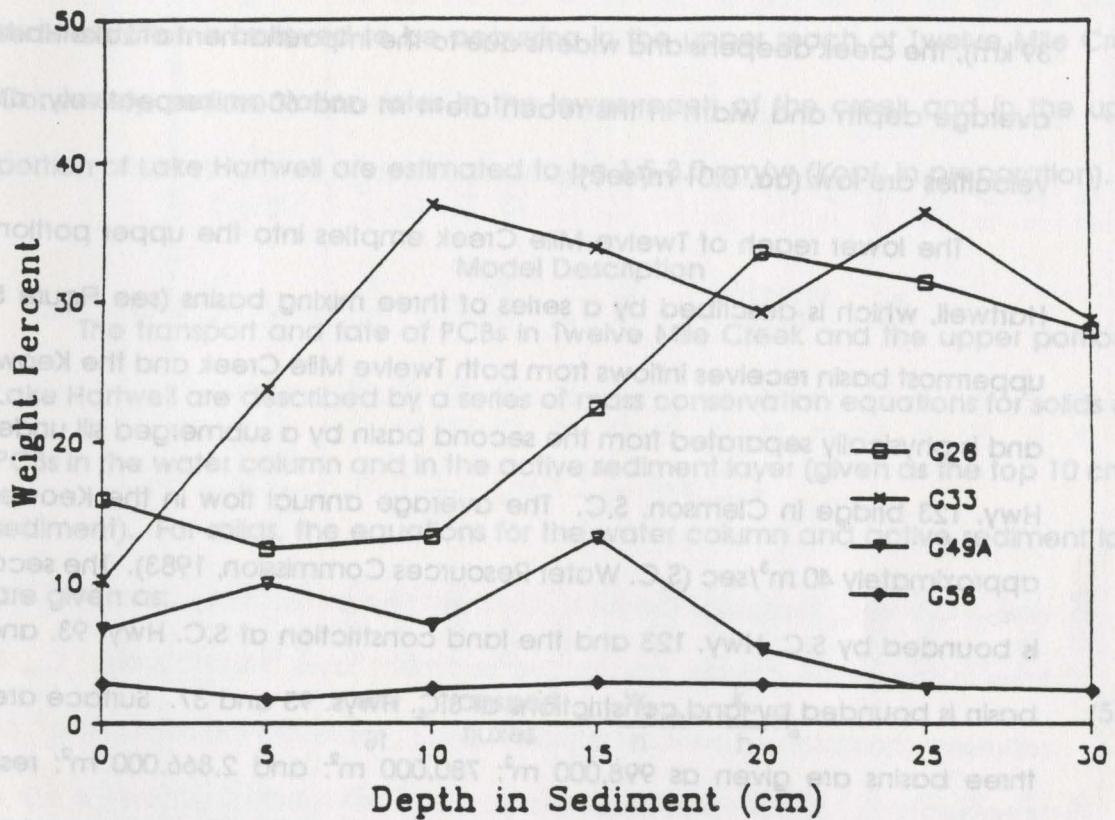


Figure 5.6. Sum of weight-percents of the four ortho-substituted terminal dechlorination congeners (2,2'-DCB, 2,6-DCB; 2,2',6'-TrCB; and 2,2',6,6'-TCB) vs. depth in core.

creek is given as  $6 \text{ m}^3/\text{sec}$  (S.C. Water Resources Commission, 1983) and water velocities in the upper reach are relatively high (ca.  $0.6 \text{ m}/\text{sec}$ ). In the lower reach (32-39 km), the creek deepens and widens due to the impoundment of Lake Hartwell. The average depth and width in this reach are 4 m and 60 m, respectively, and water velocities are low (ca.  $0.01 \text{ m}/\text{sec}$ ).

The lower reach of Twelve Mile Creek empties into the upper portion of Lake Hartwell, which is described by a series of three mixing basins (see Figure 5.1). The uppermost basin receives inflows from both Twelve Mile Creek and the Keowee River, and is physically separated from the second basin by a submerged sill under the U.S. Hwy. 123 bridge in Clemson, S.C. The average annual flow in the Keowee River is approximately  $40 \text{ m}^3/\text{sec}$  (S.C. Water Resources Commission, 1983). The second basin is bounded by S.C. Hwy. 123 and the land constriction at S.C. Hwy. 93, and the last basin is bounded by land constrictions at S.C. Hwys. 93 and 37. Surface areas of the three basins are given as  $998,000 \text{ m}^2$ ;  $780,000 \text{ m}^2$ ; and  $2,866,000 \text{ m}^2$ ; respectively. Although this portion of the lake is typically stratified during the warmer months, water in each basin is considered to be well-mixed for all model calculations.

Initial measurements made over several years indicate suspended solids concentrations in Twelve Mile Creek vary from  $20 \text{ mg}/\text{L}$  to several hundred milligrams per liter and are comprised primarily of clay- and silt-sized particles with average settling velocities in the range of  $0.16$  to  $7.8 \text{ m}/\text{day}$ . The large variation in solids concentrations is primarily due to land erosion and sediment resuspension during storm events. Organic content of suspended solids in Twelve Mile Creek and the upper portion of Lake Hartwell is approximately 2% by weight (U.S. EPA, 1992). Solids concentrations in the top sediment layers (0-10 cm) are in the range of  $300 \text{ g}/\text{L}$  (Germann, 1988). Due to the low organic carbon content of the sediments, the top sediment layers are assumed to remain aerobic and biochemical weathering through



reductive dechlorination is not expected to be significant. Based on bottom profile measurements performed by the U.S. Army Corps of Engineers (1983), little or no net sedimentation is believed to be occurring in the upper reach of Twelve Mile Creek. Conversely, sedimentation rates in the lower reach of the creek and in the upper portion of Lake Hartwell are estimated to be 1.5-3.0 cm/yr (Kopf, in preparation).

#### Model Description

The transport and fate of PCBs in Twelve Mile Creek and the upper portion of Lake Hartwell are described by a series of mass conservation equations for solids and PCBs in the water column and in the active sediment layer (given as the top 10 cm of sediment). For solids, the equations for the water column and active sediment layer are given as:

$$\frac{\partial m}{\partial t} + \text{transport fluxes} = -\frac{w_s}{h}m + \frac{k_u}{h}m_a \quad (5.1)$$

$$\frac{\partial m_a}{\partial t} = \frac{w_s}{\delta_a}m - \frac{k_u}{\delta_a}m_a - \frac{k_b}{\delta_a}m_a \quad (5.2)$$

where  $m$  and  $m_a$  are solids concentrations in the water column and active sediment layer, respectively;  $w_s$  is the settling velocity (m/day);  $h$  is the mean water depth;  $\delta_a$  is the thickness of the active bed layer;  $k_u'$  is the resuspension rate coefficient (m/day); and  $k_b'$  is the sediment burial rate (m/day). For model calculations, the average suspended solids concentration entering the creek is assumed to be 50 g/m<sup>3</sup>. The average suspended solids concentration in the Keowee River input is taken as 25 g/m<sup>3</sup> to reflect the effect of solids removal in Lake Keowee. The average settling velocity for the entire system was assumed to be 0.5 m/day. The settling flux in the upper reach of the creek is balanced by an equivalent resuspension flux, yielding a no net sedimentation condition for this portion of Twelve Mile Creek. In the lower reach of the

creek and the upper portion of the lake, resuspension is not considered and the flux of solids settling to the active sediment layer is balanced by the burial term. Based on this set of model parameters, calculated sedimentation rates for the lower reach of Twelve Mile Creek and the upper portion of Lake Hartwell are in the range of 1.2-3.0 cm/yr.

For PCBs, separate equations are written for 36 congener classes as follows:

$$\frac{\partial C}{\partial t} + \text{transport fluxes} = -\frac{k'_v}{h} C_{dis} - \frac{w_s}{h} \Gamma m + \frac{k'_u}{h} \Gamma_a m_a - \frac{k'_r}{h} [C_{dis} - C_{a_{dis}}] \quad (5.3)$$

$$\frac{\partial C_a}{\partial t} = \frac{w_s}{\delta_a} \Gamma m - \frac{k'_u}{\delta_a} \Gamma_a m_a - \frac{k'_b}{\delta_a} \Gamma_a m_a + \frac{k'_r}{\delta_a} [C_{dis} - C_{a_{dis}}] \quad (5.4)$$

where C and C<sub>a</sub> represent the total (dissolved plus particulate) congener concentrations in the water column and active sediment layer, respectively; C<sub>dis</sub> and C<sub>a<sub>dis</sub></sub> represent the dissolved concentrations; Γ and Γ<sub>a</sub> represent the solid phase concentrations (μg/g); k'<sub>v</sub> is the volatilization rate coefficient (m/day); and k'<sub>r</sub> is the dissolved exchange rate coefficient between the water column and sediment layer pore waters (m/day). In these equations, dissolved and solid phase congener concentrations can be expressed in terms of the total congener concentrations using the equilibrium partitioning relationship (K<sub>d</sub>=Γ/C<sub>dis</sub>) and the total congener mass concentration equation (C=C<sub>dis</sub>+Γm). Note that photochemical degradation of PCBs, which has been observed to occur in laboratory systems (Hutzinger *et al.*, 1972; Baxter and Sutherland, 1984), is not being considered in the model since conclusive evidence for its significance in natural aquatic systems such as Lake Hartwell has yet to be presented.

A listing of the 36 congener classes, along with corresponding values for chemical modeling parameters, is given in Table 5.1. This choice of congener classes is consistent with analytical measurements for congener separation using the Hewlett-Packard gas chromatography system. For classes containing two or more congeners,

TABLE 5.1

## CHEMICAL MODELING PARAMETERS FOR PCB CONGENER CLASSES

Hewlett Packard Number	IUPAC Number	Percent of Total Discharge <sup>a,b</sup>	Molecular Diffusion in Water <sup>c</sup> (cm <sup>2</sup> /s)	Molecular Diffusion in Air <sup>d</sup> (cm <sup>2</sup> /s)	log K <sub>H</sub> <sup>e</sup> (atm-m <sup>3</sup> /mol)	log K <sub>ow</sub> <sup>f</sup> (mL/g)	log K <sub>oc</sub> <sup>g</sup> (mL/g)
1	4,10	3.23	5.43E-06	0.0543	-3.48	4.66	5.11
2	7,9	1.06	5.43E-06	0.0543	-3.44	5.07	5.45
3	6	0.98	5.43E-06	0.0543	-3.49	5.06	5.45
4	8	7.30	5.43E-06	0.0543	-3.52	5.07	5.45
5	14,19	1.15	5.21E-06	0.0525	-3.36	5.09	5.47
7	18	8.90	5.15E-06	0.0520	-3.50	5.24	5.60
8	15,17	3.33	5.21E-06	0.0525	-3.47	5.26	5.61
9	27	0.47	5.15E-06	0.0520	-3.39	5.44	5.76
10	16,32	4.75	5.15E-06	0.0520	-3.51	5.29	5.64
12	25	0.51	5.15E-06	0.0520	-3.53	5.66	5.95
13	25	1.46	5.15E-06	0.0520	-3.50	5.67	5.95
14	31	3.97	5.15E-06	0.0520	-3.56	5.67	5.95
15	28	11.84	5.15E-06	0.0520	-3.54	5.67	5.95
16	20,33,53	6.80	5.11E-06	0.0516	-3.59	5.59	5.89
17	22	2.29	5.15E-06	0.0520	-3.72	5.58	5.88

Table 5.1 (Continued)

Hewlett Packard Number	IUPAC Number	Percent of Total Discharge <sup>a,b</sup>	Molecular Diffusion in Water <sup>c</sup> (cm <sup>2</sup> /s)	Molecular Diffusion in Air <sup>d</sup> (cm <sup>2</sup> /s)	log K <sub>H</sub> <sup>e</sup> (atm·m <sup>3</sup> /mol)	log K <sub>ow</sub> <sup>f</sup> (mL/g)	log K <sub>oc</sub> <sup>g</sup> (mL/g)
18	45	0.95	4.91E-06	0.0493	-3.45	5.53	5.84
19	39,46	1.19	5.09E-06	0.0513	-3.51	5.76	6.03
20	52	4.81	4.91E-06	0.0493	-3.50	5.84	6.10
21	43,49	3.95	4.91E-06	0.0493	-3.45	5.84	6.10
22	47,48,75	5.30	4.91E-06	0.0493	-3.41	5.93	6.17
25	44	1.06	4.91E-06	0.0493	-3.64	5.75	6.02
26	37,42	1.97	5.10E-06	0.0515	-3.76	5.82	6.08
27	41,72	2.04	4.15E-06	0.0520	-3.39	5.44	5.76
29	74	1.31	4.91E-06	0.0493	-3.67	6.20	6.40
30	70,76,98	0.88	4.90E-06	0.0492	-3.67	6.19	6.39
31	66,95	0.72	4.86E-06	0.0490	-3.64	6.18	6.38
32	55,91,12	1.77	4.71E-06	0.0481	-3.37	6.41	6.57
34	84,92	0.48	4.70E-06	0.0481	-3.60	6.14	6.35
35	101	1.39	4.70E-06	0.0481	-3.61	6.38	6.55
36	79,99,113	1.27	4.71E-06	0.0481	-3.60	6.38	6.55
39	87	0.76	4.70E-06	0.0481	-3.74	6.29	6.47

Table 5.1 (Continued)

Hewlett Packard Number	IUPAC Number	Percent of Total Discharge <sup>a,b</sup>	Molecular Diffusion In Water <sup>c</sup> (cm <sup>2</sup> /s)	Molecular Diffusion In Air <sup>d</sup> (cm <sup>2</sup> /s)	log K <sub>H</sub> <sup>e</sup> (atm-m <sup>3</sup> /mol)	log K <sub>ow</sub> <sup>f</sup> (mL/g)	log K <sub>oc</sub> <sup>g</sup> (mL/g)
41	77,110	1.72	4.70E-06	0.0481	-3.71	6.39	6.56
44	108	0.28	4.70E-06	0.0481	-3.76	6.71	6.82
46	106,118,14	2.48	4.64E-06	0.0476	-3.79	6.72	6.83
51	153,168	1.66	4.51E-06	0.0465	-3.64	7.04	7.10
53	138,158	1.02	4.51E-06	0.0465	-3.87	6.85	6.94
SUM		95.07					

<sup>a</sup>Based on weighted-averages assuming a 4:1 mixture of Aroclors 1016 and 1254.

<sup>b</sup>Based on congener composition data for Aroclor 1016 (Albro *et al.*, 1979) and Aroclor 1254 (Albro *et al.*, 1981).

<sup>c</sup>Estimated using the method of Hayduk and Laudie as given in Lyman *et al.* (1990).

<sup>d</sup>Estimated using the method of Fuller, Schettler and Giddings as given in Lyman *et al.* (1990).

<sup>e</sup>Based on values given in Dunnivant (1988).

<sup>f</sup>Based on values given in Hawker and Connell (1988).

<sup>g</sup>Estimated from octanol-water partition coefficients using the empirical correlation given by Karickhoff (1981).

parameter values are based on a weighted-average assuming a 4:1 mixture of Aroclors 1016 and 1254. This composition closely matches the original mixture of Aroclors released into the Twelve Mile Creek-Lake Hartwell system (Billings 1976).

Volatilization rates are determined from information given in Table 5.1 using the two layer model of the air-water interface where:

$$\frac{1}{k_v'} = \frac{1}{k_l'} + \frac{RT}{K_H k_g'} \quad (3.5)$$

In Eq. 5.5,  $k_l'$  and  $k_g'$  represent the mass transfer rate coefficients for the water and air side of the interface, respectively (m/day);  $K_H$  is the Henry's law coefficient (atm·m<sup>3</sup>/mol);  $R$  is the universal gas constant (atm·m<sup>3</sup>/mol·°K); and  $T$  is temperature (taken as 293°K). For the upper reach of Twelve Mile Creek,  $k_l'$  is calculated using the O'Connor-Dobbins formula for free-flowing streams (O'Connor and Dobbins, 1958). For the lower reach of Twelve Mile Creek and the upper portion of Lake Hartwell,  $k_l'$  is determined from the oxygen transfer rate coefficient (taken as 0.5 m/day for light wind conditions) times the square root of the ratio of molecular diffusion rates for the PCB congener and for oxygen in water. For the entire system,  $k_g'$  is given as the water evaporation rate coefficient (taken as 500 m/day) times the square root of the ratio of molecular diffusion rates for the PCB congener and for water vapor in air. In the upper reach of Twelve Mile Creek, resistance on the water and air side of the interface are both important in controlling volatilization of PCBs. In the lower reach of the creek and the upper portion of Lake Hartwell, volatilization rates are primarily controlled by mass transfer rates on the water side of the interface.

For transport terms in Eqs. 5.1 and 5.3, the upper and lower reaches of Twelve Mile Creek are treated as one-dimensional advective (plug flow) systems. The upper basin of Lake Hartwell is modeled as a series of completely-mixed reactors, with inflows into the first reactor from Twelve Mile Creek and the Keowee River. Analytical solutions

for steady-state distributions of solids and PCB congeners in the water column and the active sediment layer are determined using approaches outlined in O'Connor (1988a,b,c). Note that, since  $K_d$  values for a specific congener class are taken to be equivalent for the water column and active sediment layer, the solutions are independent of  $k_r'$  values.

### Modeling Results

Steady-state calculations for PCB distributions in Twelve Mile Creek and the upper portion of Lake Hartwell were performed assuming a daily loading of 6.6 kg/day from the Sangamo Electric site. This loading rate is based on the average quantity of PCBs purchased by Sangamo during 1970-75 (Kopf, in preparation) and the assumption that 0.5% of the PCBs entered the Twelve Mile Creek-Lake Hartwell system. A 4:1 mixture of Aroclors 1016 and 1254 is considered for the input. Under these loading conditions, calculated values for particulate concentrations vary from approximately 100  $\mu\text{g/g}$  near the source to 40  $\mu\text{g/g}$  in the lower reach of Twelve Mile Creek (Figure 5.7). Particulate concentrations in the upper portion of Lake Hartwell are further reduced to approximately 5  $\mu\text{g/g}$  due to mixing of contaminated waters from Twelve Mile Creek with uncontaminated waters from the Keowee River. This calculated distribution of PCB contamination in sediments is consistent with field observations, and concentrations shown in Figure 5.7 are roughly a factor of two greater than the 1987 field measurements for sediment concentrations in the lower reach of Twelve Mile Creek and the upper portion of Lake Hartwell.

Calculations for the relative distribution of congeners in the system is summarized in Figure 5.8 in terms of weight percentages for di-CB (DCB), tri-CB (TrCB), tetra-CB (TCB), and the summation of hepta-, sexa-, and septa-CB (HSSCB) groups. Results show that weight percentages for DCB and TrCB decrease in the upper reach of the creek, indicating preferential removal of these compounds. Since PCB removal in the upper

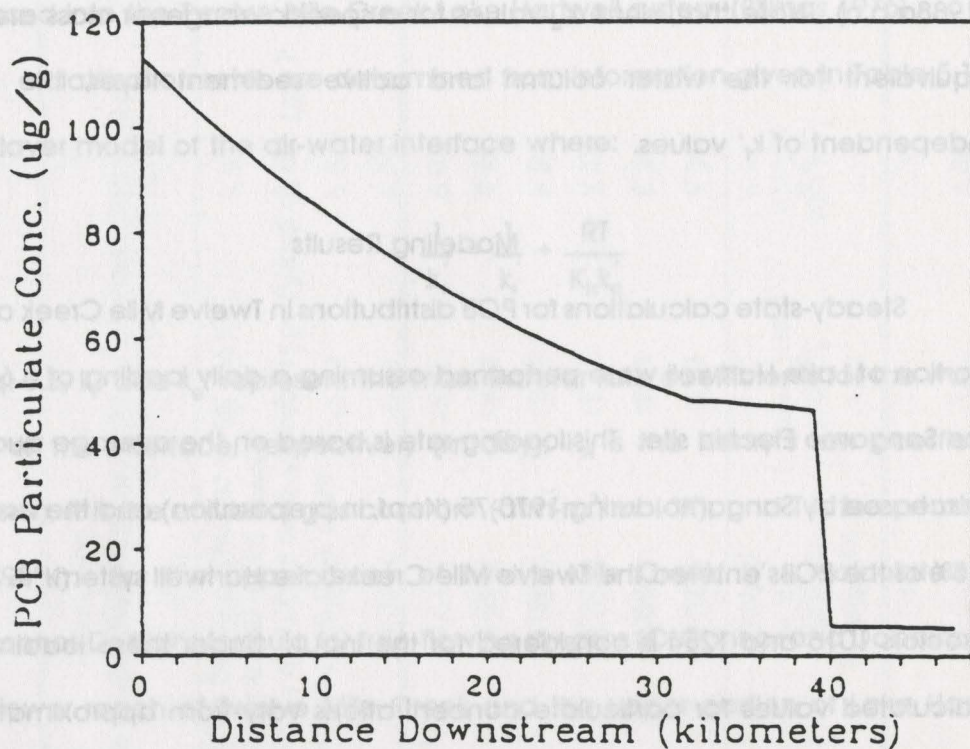


Figure 5.7. Model results for PCB particulate concentrations in Twelve Mile Creek-Lake Hartwell sediments vs. distance from the source.



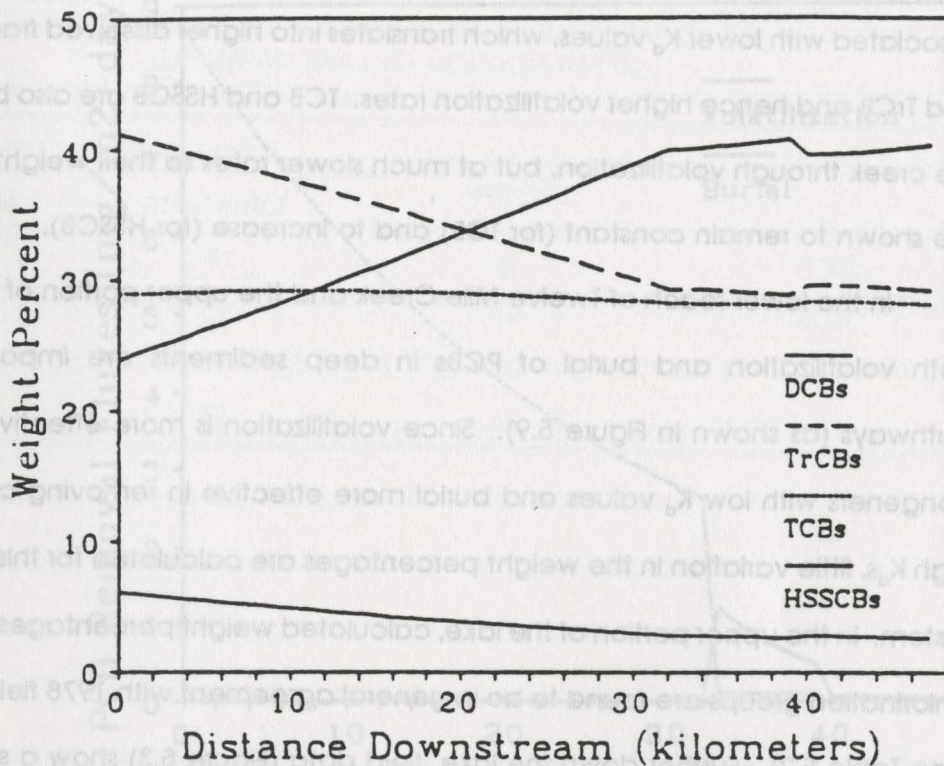


Figure 5.8. Model results for relative weight percentages of DCBs, TrCBs, TCBs and HSSCBs vs. distance from the source.

reach is due to volatilization (due to our specifying that no net deposition is occurring in this reach), preferential removal of the lower chlorinated biphenyls is primarily associated with lower  $K_d$  values, which translates into higher dissolved fractions for DCB and TrCB and hence higher volatilization rates. TCB and HSSCB are also being lost from the creek through volatilization, but at much slower rates so their weight percentages are shown to remain constant (for TCB) and to increase (for HSSCB).

In the lower reach of Twelve Mile Creek and the upper portion of Lake Hartwell, both volatilization and burial of PCBs in deep sediments are important removal pathways (as shown in Figure 5.9). Since volatilization is more effective in removing congeners with low  $K_d$  values and burial more effective in removing congeners with high  $K_d$ s, little variation in the weight percentages are calculated for this portion of the system. In the upper portion of the lake, calculated weight percentages for the various chlorination groups are found to be in general agreement with 1978 field observations (see Table 5.2). Further down the lake, field data (Figure 5.3) show a slight reduction in HSSCB indicating that burial may be the preferred pathway for PCB removal.

Overall, the steady-state model for physiochemical weathering provides a good description of observed variations in congener distributions for surficial sediments in the Twelve Mile Creek-Lake Hartwell system. In general, results show that lower chlorinated congeners are more effectively removed by volatilization, whereas higher chlorinated congeners are preferentially removed by burial in the deeper sediments. These trends however may be masked by time variable processes. For example, during periods of increased PCB loading, "chromatographic separation" would likely occur in the system with lower chlorinated congeners migrating down the creek and into the lake at faster rates due to their lower  $K_d$  values. Under these conditions, the downstream sediments would likely contain higher weight percentages for the lower chlorination groups. As steady-state conditions are approached (and higher chlorinated congeners have

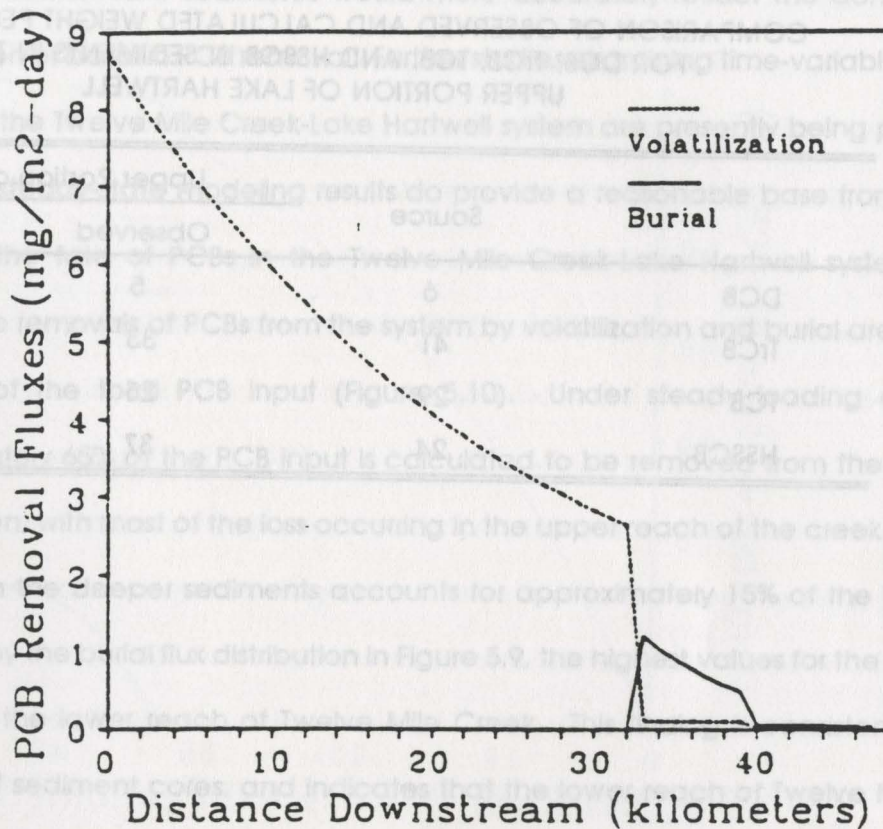


Figure 5.9. Model results for PCB removal by volatilization and burial fluxes in the Twelve Mile Creek and the upper portion of Lake Hartwell.

#### Possible Importance of Biochemical Weathering

Conflicting evidence is presented in Figures 5.4 and 5.5 regarding biochemical weathering of PCB residues in the Twelve Mile Creek-Lake Hartwell system. The samples from the lower portion of Twelve Mile Creek (G26 and G33) both show an increase in DCBs and a corresponding decrease in TCBS and HSCBs with depth in the sediment.

TABLE 5.2

COMPARISON OF OBSERVED AND CALCULATED WEIGHT PERCENTAGES  
FOR DCB, TrCB, TCB, AND HSSCB IN SEDIMENTS IN THE  
UPPER PORTION OF LAKE HARTWELL

	Source	Upper Portion of Lake Hartwell	
		Observed	Model Results
DCB	6	5	3
TrCB	41	33	29
TCB	29	25	28
HSSCB	24	37	40

Overall, the steady-state model provides a good approximation of the physical and chemical processes in the sediments of the upper portion of the Twelve Mile Creek and the upper portion of Lake Hartwell. The model results indicate that lower chlorinated congeners are more effectively removed by volatilization, whereas higher chlorinated congeners are preferentially removed by burial in the deeper sediments. These trends however may be masked by time variable processes. For example, during periods of increased PCB loading, "chromatographic separation" would likely occur in the system with lower chlorinated congeners migrating down the creek and into the lake at faster rates due to their lower  $K_p$  values. Under these conditions, the downstream sediments would likely contain higher weight percentages for the lower chlorination groups. As steady-state conditions are approached (and higher chlorinated congeners have

sufficient time to migrate downstream), the relative weight percentages of chlorination groups in downstream sediments would more accurately reflect the dominance of volatilization or burial in PCB removal. Further studies examining time-variable behavior of PCBs in the Twelve Mile Creek-Lake Hartwell system are presently being performed.

The steady-state modeling results do provide a reasonable base from which to evaluate the fate of PCBs in the Twelve Mile Creek-Lake Hartwell system. Here, cumulative removals of PCBs from the system by volatilization and burial are shown as percents of the total PCB input (Figure 5.10). Under steady loading conditions, approximately 65% of the PCB input is calculated to be removed from the system by volatilization, with most of the loss occurring in the upper reach of the creek. Removal by burial in the deeper sediments accounts for approximately 15% of the PCB input. As shown by the burial flux distribution in Figure 5.9, the highest values for the PCB burial flux are in the lower reach of Twelve Mile Creek. This finding is consistent with our analyses of sediment cores, and indicates that the lower reach of Twelve Mile Creek serves as an effective sediment trap for part of the contamination. However, based on these steady-state calculations, approximately 15% of the PCB discharge would pass under S.C. Hwy. 37 and would continue to migrate down the Lake Hartwell toward the Hartwell Dam. Dilution of PCBs particularly by inflows from Coneross Creek, Eighteen Mile Creek, Twenty-Six Mile Creek, and the Tugaloo River would however be effective in reducing PCB concentrations. Note that the remaining 5% of the PCB input is contained in congener classes that were not considered in our model calculations.

#### Possible Importance of Biochemical Weathering

Conflicting evidence is presented in Figures 5.4 and 5.5 regarding biochemical weathering of PCB residues in the Twelve Mile Creek-Lake Hartwell system. The samples from the lower portion of Twelve Mile Creek (G26 and G33) both show an increase in DCBs and a corresponding decrease in TCBS and HSSCBs with depth in the sediment.

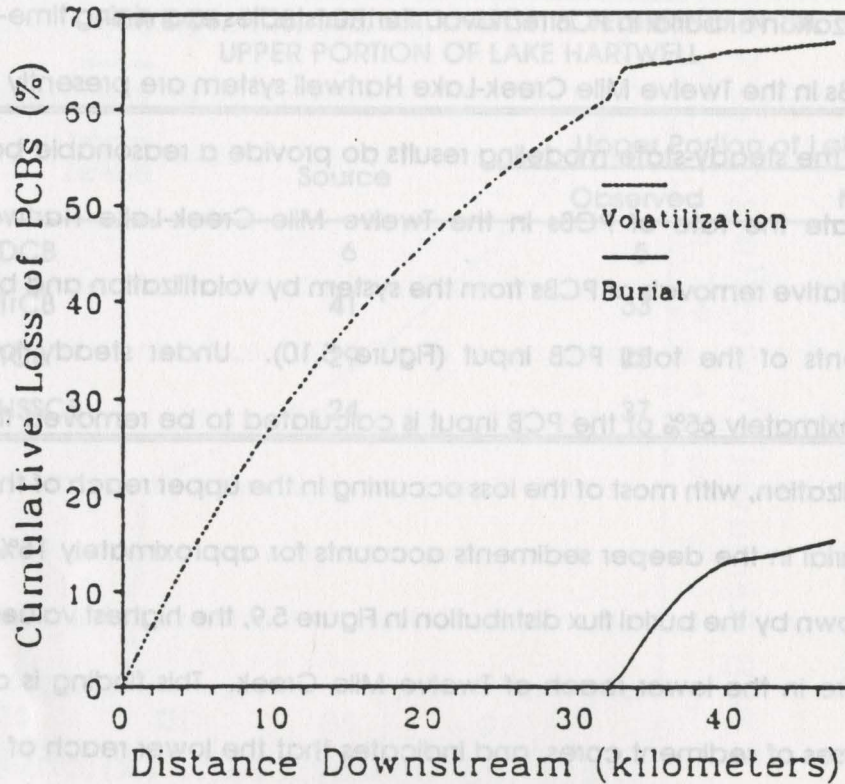


Figure 5.10. Model results for the cumulative loss of PCBs by volatilization and burial in Twelve Mile Creek and the upper portion of Lake Hartwell.

Similar changes have been reported for sediments from the upper Hudson River (Bopp *et al.*, 1984; Brown *et al.*, 1984; Brown *et al.*, 1987b) and have been attributed to *In situ* microbially-mediated reductive dechlorination (Brown *et al.*, 1987a,b).

#### Conclusions

The reductive dechlorination hypothesis is based on the premise that microbial action on PCB congeners is sterically selective for the chlorines in the meta and para positions on the biphenyl rings (i.e., 3,3',4,4',5, and/or 5'), resulting in the cleaving of the chlorines in these positions (Brown *et al.*, 1987b). If this occurs, the terminal dechlorination products of the microbially resistant ortho-substituted congeners in the anaerobic environment should be 2,2'-DCB, 2,6-DCB, 2,2',6-TrCB, and 2,2',6,6'-TCB. Thus, the weight-percent of these congeners should increase with depth as dechlorination of the higher chlorinated congeners progresses. This expected increase in weight-percent for the terminal dechlorination congeners however is only observed in the two Twelve Mile Creek samples (Figure 5.6). For the Lake Hartwell samples (G49A and G56) the individual chlorine substitution groups and the terminal dechlorination congeners remain relatively constant with depth, inferring that biochemical weathering is not occurring.

Differences in biodegradative ability between the Twelve Mile Creek and Lake Hartwell samples may be explained by considering the reductive dechlorination scenario in which PCBs are used as electron acceptors by anaerobic microorganisms. In Lake Hartwell sediments, PCB concentrations are low (due to mixing of PCBs with uncontaminated waters from the Keowee River). At low concentrations, the ability of PCBs to serve as electron acceptors may be diminished compared to other reducing agents (e.g. organic carbon molecules). As a result, no change in PCB congener composition would be observed with sediment depth. For higher concentrations in the Twelve Mile Creek sediments, PCBs may be a significant fraction of the electron

receiving capacity, resulting in more cleaved chlorines, and hence observable biochemical weathering of PCBs.

Similar results for biodegradative and nonbiodegradative zones were previously reported by Bopp *et al.* (1984) for the Hudson River. Based on the occurrence of altered residues in the more highly contaminated upper Hudson River sediments, Bopp *et al.* (1984) concluded that reductive dechlorination may not be significant at PCB concentrations less than approximately 150  $\mu\text{g/g}$ . This value is much higher than the maximum concentrations seen in both the Lake Hartwell (16 and 7  $\mu\text{g/g}$ ) and Twelve Mile Creek (26 and 40  $\mu\text{g/g}$ ) cores.

Two possibilities are given below to explain why biochemical weathering may be occurring at much lower residue concentrations in the Twelve Mile Creek sediments. First, the organic carbon content in the Twelve Mile Creek sediments may be significantly lower than that of the Hudson River, causing the PCBs to make up a larger fraction of the electron receiving capacity and resulting in the biodegradation of PCBs with depth. Second, any biochemical weathering occurring in the Twelve Mile Creek and the Hudson River may be mediated by different types of microorganisms and/or vary due to differences in temperature-dependent metabolic rates. Temporal variations in the PCB loading rate, along with chromatographic separation of congeners migrating down the creek, may also be important in explaining the congener distributions in sediments. However, it is difficult to imagine conditions that would lead to such an abrupt change in the sedimentary core records of stations G33 and G49A, which are less than 3 km apart.

At this time no conclusive evidence exist to support the hypothesis of reductive dechlorination of PCBs in the sedimentary environment of Twelve Mile Creek and Lake Hartwell. Sediment core data for the lower portion of Twelve Mile Creek however do suggest that some degradation of the higher chlorinated groups is occurring. Further



research is needed to confirm or refute this claim and to quantify the possible significance of reductive dechlorination on the ultimate fate of PCBs in the sediments.

### Conclusions

Field data for the Twelve Mile Creek-Lake Hartwell system indicate that sediments in Twelve Mile Creek contain significantly higher PCB concentrations than those in Lake Hartwell, and that a greater degree of weathering has occurred in Twelve Mile Creek. Steady-state modeling calculations for physiochemical weathering processes provide a good description of this observed behavior, supporting the view that physiochemical weathering plays the dominant role in determining the fate of PCBs. In general, modeling results show that a preferential depletion of the lower chlorinated congeners occurs when volatilization is the primary removal mechanism. Conversely, when burial in deep sediments is the dominant removal mechanism a preferential depletion of the higher chlorination groups is expected. These trends however may sometimes be masked by temporal variations in PCB loading and the effects of congener-specific transport, which together may result in a chromatographic separation with lower chlorination groups migrating at faster rates through the system.

Sediment core data suggests that biochemical weathering through reductive dechlorination may also be occurring, but is limited to sediments in the lower portion of Twelve Mile Creek. The overall importance of biochemical weathering on the ultimate fate of PCBs however is difficult to assess at this time but is believed to be of secondary importance.

## Appendix A

### Theses, Dissertations and Papers Related to Project from Environmental Systems Engineering, Clemson University

1. Coates, J. T. Sorption Equilibrium and Kinetics for Selected Polychlorinated Biphenyls on River Sediments. [Ph.D. Dissertation]. Clemson, SC: Environmental Systems Engineering, Clemson University; 1984.
2. Coates, J. T.; Ezzeman, A.W. Desorption kinetics for selected PCB congeners from river sediments. *J. Contam. Hydrol.*; 1986; 1:191-210.
3. Dunnivant, F. M. Congener-Specific PCB Chemical and Physical Parameters for Evaluation of Environmental Weathering of Aroclors [Ph.D. Dissertation]. Clemson, SC: Environmental Systems Engineering, Clemson University; 1988.
4. Dunnivant, F. M. Determination of Polychlorinated Biphenyl Concentrations in Selected Sediments Using a Sonication Extraction Technique. [M.S. Thesis]. Clemson, SC: Environmental Systems Engineering, Clemson University; 1985.
5. Dunnivant, F. M.; Coates, J. T.; Ezzeman, A. W. Experimentally determined Henry's law constants for 17 PCB congeners. *Environ. Sci. Technol.*; 1988; 22:445-453.
6. Dunnivant, F. M.; Ezzeman, A. W. Aqueous solubility and Henry's law constant data for PCB congeners. **APPENDICES** Quantitative structure-property relationships (QSPRs). *Chemosphere*; 1988; 17:525-541.
7. Dunnivant, F. M.; Ezzeman, A. W. Determination of PCBs in sediments using sonication extraction and capillary column GC/EC detection with internal standard calibration. *J. Assoc. Offic. Anal. Chem.*; 1987; 71:551-555.
8. Dunnivant, F. M.; Ezzeman, A. W.; Jurs, P. J.; Hasan, M. Quantitative structure-property relationships (QSPRs): Prediction of aqueous solubilities and Henry's law constants for polychlorinated biphenyls (PCBs). *Environ. Sci. Technol.*; (submitted).
9. Dunnivant, F. M.; Polansky, A. L.; Ezzeman, A. W. PCB distributions in a reservoir (Lake Hartwell, SC). *Bull. Env. Contam. Toxicol.*; 1989; 43:670-678.
10. Ezzeman, A. W.; Coates, J. T. Hydrophobic organic compounds on sediments: Equilibria and kinetics of sorption. In: Hites, R.A.; Eisenreich, S.J., eds. *Sources and Fates of Aquatic Pollutants*. Washington, DC: American Chemical Society; 1987; 263-318.
11. Field, R. A.; Ezzeman, A. W.; Vandever, J. Transport of anthropogenic radionuclides in the upper sub-basin of the Savannah River. Clemson, SC: S.C. Water Resources Research Institute, Clemson University; 1986; Report No. 122.

## Appendix A

### Theses, Dissertations and Papers Related to Project from Environmental Systems Engineering, Clemson University

1. Coates, J. T. Sorption Equilibrium and Kinetics for Selected Polychlorinated Biphenyls on River Sediments. [Ph.D. Dissertation]. Clemson, SC: Environmental Systems Engineering, Clemson University; 1984.
2. Coates, J. T.; Elzerman, A.W. Desorption kinetics for selected PCB congeners from river sediments. *J. Contam. Hydrol.*; 1986; 1:191-210.
3. Dunnivant, F. M. Congener-Specific PCB Chemical and Physical Parameters for Evaluation of Environmental Weathering of Aroclors [Ph.D. Dissertation]. Clemson, SC: Environmental Systems Engineering, Clemson University; 1988.
4. Dunnivant, F. M. Determination of Polychlorinated Biphenyl Concentrations in Selected Sediments Using a Sonication Extraction Technique. [M.S. Thesis]. Clemson, SC: Environmental Systems Engineering, Clemson University; 1985.
5. Dunnivant, F. M.; Coates, J. T.; Elzerman, A. W. Experimentally determined Henry's law constants for 17 PCB congeners. *Environ. Sci. Technol.*; 1988; 22:448-453.
6. Dunnivant, F. M.; Elzerman, A. W. Aqueous solubility and Henry's law constant data for PCB congeners for evaluation of quantitative structure-property relationships (QSPRs). *Chemosphere*; 1988; 17:525-541.
7. Dunnivant, F. M.; Elzerman, A. W. Determination of PCBs in sediments using sonication extraction and capillary column GC/EC detection with internal standard calibration. *J. Assoc. Offic. Anal. Chem.*; 1987; 71:551-555.
8. Dunnivant, F. M.; Elzerman, A. W.; Jurs, P. J.; Hasan, M. Quantitative structure-property relationships (QSPRs); Prediction of aqueous solubilities and Henry's law constants for polychlorinated biphenyls (PCBs). *Environ. Sci. Technol.*; (submitted).
9. Dunnivant, F. M.; Polansky, A. L.; Elzerman, A. W. PCB distributions in a reservoir (Lake Hartwell, SC). *Bull. Env. Contam. Toxicol.*; 1989; 43:870-878.
10. Elzerman, A. W.p; Coates, J. T. Hydrophobic organic compounds on sediments; Equilibria and kinetics of sorption. in: Hites, R.A.; Eisenreich, S.J., eds. *Sources and Fates of Aquatic Pollutants*. Washington, DC: American Chemical Society; 1987; 263-318.
11. Fjeld, R. A.; Elzerman, A. W.; Vandeven, J. Transport of anthropogenic radionuclides in the upper sub-basin of the Savannah River. Clemson, SC: S.C. Water Resources Research Institute, Clemson University; 1986; Report No. 122.

12. Germann, G. G. The Distribution and Mass Loading of Polychlorinated biphenyls in Lake Hartwell Sediments [M.S. Thesis]. Clemson, SC: Environmental Systems Engineering; Clemson University; 1988.
13. Germann, G. G.; Elzerman, A. W. Differential weathering of PCB congeners in sediments of Lake Hartwell, SC. *Chemosphere*; (submitted).
14. Horn, M. A. The Distribution of Anthropogenic and Naturally Occurring Gamma Emitting Radionuclides in Bottom Sediments of Hartwell Reservoir [M.S. Thesis]. Clemson, SC: Clemson University; 1987.
15. Kopf, A. C. Modeling the Fate and Distribution of Polychlorinated Biphenyls in Twelve Mile Creek and Lake Hartwell [M.S. Thesis]. Clemson, SC; Clemson University; 1991.
16. Matthews, S. Use of Radionuclides for Modeling Hydrologic Parameters Related to PCB Transport. [M.S. Thesis in Progress]. Clemson, SC: Environmental Systems Engineering; Clemson University; 1991.
17. Polansky, A. L. Determination of PCB Concentrations in Lake Hartwell Sediments [M.S. Thesis]. Clemson, SC: Environmental Systems Engineering; Clemson University; 1984.
18. Reboul, S. Modeling Anthropogenic Radionuclides in Lake Hartwell. [M.S. Thesis]. Clemson, SC: Environmental Systems Engineering; Clemson University; 1987.

## IUPAC NUMBERING SYSTEM USED FOR PCB CONGENERS

IUPAC Number	Chlorine Substitution Pattern on Biphenyl
<b>Monochlorobiphenyls</b>	
1	2
2	3
3	4
<b>Dichlorobiphenyls</b>	
4	2,2'
5	2,3
6	2,3'
7	2,4
8	2,4'
9	2,5
10	2,6
11	3,3'
12	3,4
13	3,4'
14	3,5
15	4,4'
<b>Trichlorobiphenyls</b>	
16	2,2',3
17	2,2',4
18	2,2',5
19	2,2',6
20	2,3,3'
21	2,3,4
22	2,3,4'
23	2,3,5'
24	2,3,6
25	2,3',4
26	2,3',5
27	2,3',6
28	2,4,4'
29	2,4,5
30	2,4,6
31	2,4',5
32	2,4',6
33	2',3,4

Table B-1 (Continued)

13.	IUPAC Number	G. Eitzman, A. W. Dineen Distributions of Lake Hartwell, SC. Clemson University, 1984.	Chlorine Substitution Pattern on Biphenyl
<b>Trichlorobiphenyls (Cont'd.)</b>			
	34		2',3,5
	35		3,3',4
15.	36	Kopf, A. Modeling the Fate and Distribution of Chlorinated Biphenyls in Tyrone Lake Creek and Lake Hartwell [M.S. Thesis, Clemson University, 1997].	3,3',5
	37		3,4,4'
	38		3,4,5
	39		3,4',5
<b>Tetrachlorobiphenyls</b>			
17.	40	Polansky, L. Determination of PCB Concentrations in Lake Hartwell Sediments (M.S. Thesis, Clemson University, 1984).	2,2',3,3'
	41		2,2',3,4
	42		2,2',3,4'
	43		2,2',3,5
18.	44	Rebold, J. Modeling Anthropogenic Radionuclide Inputs to Lake Hartwell. [M.S. Thesis, Clemson University, 1987].	2,2',3,5'
	45		2,2',3,6
	46		2,2',3,6'
	47		2,2',4,4'
	48		2,2',4,5
	49		2,2',4,5'
	50		2,2',4,6
	51		2,2',4,6'
	52		2,2',5,5'
	53		2,2',5,6'
	54		2,2',6,6'
	55		2,3,3',4
	56		2,3,3',4'
	57		2,3,3',5
	58		2,3,3',5'
	59		2,3,3',6
	60		2,3,4,4'
	61		2,3,4,5
	62		2,3,4,6
	63		2,3,4',5
	64		2,3,4',6
	65		2,3,5,6
	66		2,3',4,4'
	67		2,3',4,5
	68		2,3',4,5'
	69		2,3',4,6
	70		2,3',4',5
	71		2,3',4',6
	72		2,3',5,5'

Table B-1 (Continued)

Table B-1 (Continued)

IUPAC Number	Chlorine Substitution Pattern on Biphenyl
<b>Tetrachlorobiphenyls (Cont'd.)</b>	
73	2,3',5',6
74	2,4,4',5
75	2,4,4',6
76	2',3,4,5
77	3,3',4,4'
78	3,3',4,5
79	3,3',4,5'
80	3,3',5,5'
81	3,4,4',5
<b>Pentachlorobiphenyls</b>	
82	2,2',3,3',4
83	2,2',3,3',5
84	2,2',3,3',6
85	2,2',3,4,4'
86	2,2',3,4,5
87	2,2',3,4,5'
88	2,2',3,4,6
89	2,2',3,4,6'
90	2,2',3,4',5
91	2,2',3,4',6
92	2,2',3,5,5'
93	2,2',3,5,6
94	2,2',3,5,6'
95	2,2',3,5',6
96	2,2',3,6,6'
97	2,2',3',4,5
98	2,2',3',4,6
99	2,2',4,4',5
100	2,2',4,4',6
101	2,2',4,5,5'
102	2,2',4,5,6'
103	2,2',4,5',6
104	2,2',4,6,6'
105	2,3,3',4,4'
106	2,3,3',4,5
107	2,3,3',4',5
108	2,3,3',4,5'
109	2,3,3',4,6
110	2,3,3',4',6
111	2,3,3',5,5'

Table B-1 (Continued)

(Continued)

IUPAC Number	Chlorine Substitution Pattern on Biphenyl
<b>Pentachlorobiphenyls (Cont'd.)</b>	
112	2,3,3',5,6
113	2,3,3',5',6
114	2,3,4,4',5
115	2,3,4,4',6
116	2,3,4,5,6
117	2,3,4',5,6
118	2,3',4,4',5
119	2,3',4,4',6
120	2,3',4,5,5'
121	2,3',4,5',6
122	2,3,3',4,5
123	2',3,4,4',5
124	2',3,4,5,5'
125	2',3,4,5,6'
126	3,3',4,4',5
127	3,3',4,5,5'
<b>Hexachlorobiphenyls</b>	
128	2,2',3,3',4,4'
129	2,2',3,3',4,5
130	2,2',3,3',4,5'
131	2,2',3,3',4,6
132	2,2',3,3',4,6'
133	2,2',3,3',5,5'
134	2,2',3,3',5,6
135	2,2',3,3',5,6'
136	2,2',3,3',6,6'
137	2,2',3,4,4',5
138	2,2',3,4,4',5'
139	2,2',3,4,4',6
140	2,2',3,4,4',6'
141	2,2',3,4,5,5'
142	2,2',3,4,5,6
143	2,2',3,4,5,6'
144	2,2',3,4,5',6
145	2,2',3,4,6,6'
146	2,2',3,4',5,5'
147	2,2',3,4',5,6
148	2,2',3,4',5,6'
149	2,2',3,4',5',6
150	2,2',3,4',6,6'



Table B-1 (Continued)

Appendix C

(Continued)

Non-Linear Least Squares Program for Estimating  
Description Data Constants Using Model 3

IUPAC Number	Chlorine Substitution Pattern on Biphenyl
Hexachlorobiphenyls (Cont'd.)	
151	2,2',3,5,5',6
152	2,2',3,5,6,6'
153	2,2',4,4',5,5'
154	2,2',4,4',5,6'
155	2,2',4,4',6,6'
156	2,3,3',4,4',5
157	2,3,3',4,4',5'
158	2,3,3',4,4',6
159	2,3,3',4,5,5'
160	2,3,3',4,5,6
161	2,3,3',4,5',6
162	2,3,3',4',5,5'
163	2,3,3',4',5,6
164	2,3,3',4',5',6
165	2,3,3',5,5',6'
166	2,3,4,4',5,6
167	2,3',4,4',5,5'
168	2,3',4,4',5',6
169	3,3',4,4',5,5'
Heptachlorobiphenyls	
170	2,2',3,3',4,4',5
171	2,2',3,3',4,4',6
172	2,2',3,3',4,5,5'
173	2,2',3,3',4,5,6
174	2,2',3,3',4,5,6'
175	2,2',3,3',4,5',6
176	2,2',3,3',4,6,6'
177	2,2',3,3',4',5,6
178	2,2',3,3',5,5',6
179	2,2',3,3',5,6,6'
180	2,2',3,4,4',5,5'
181	2,2',3,4,4',5,6
182	2,2',3,4,4',5,6'
183	2,2',3,4,4',5',6
184	2,2',3,4,4',6,6'
185	2,2',3,4,5,5',6
186	2,2',3,4,5,6,6'
187	2,2',3,4',5,5',6
188	2,2',3,4',5,6,6'
189	2,3,3',4,4',5,5'

Table B-1 (Continued)

Table B-1 (Continued)

IUPAC Number	Chlorine Substitution Pattern on Biphenyl
Heptachlorobiphenyls (Cont'd.)	
190	2,3,3',4,4',5,6
191	2,3,3',4,4',5',6
192	2,3,3',4,5,5',6
193	2,3,3',4',5,5',6
Octachlorobiphenyls	
194	2,2',3,3',4,4',5,5'
195	2,2',3,3',4,4',5,6
196	2,2',3,3',4,4',5',6
197	2,2',3,3',4,4',6,6'
198	2,2',3,3',4,5,5',6
199	2,2',3,3',4,5,6,6'
200	2,2',3,3',4,5',6,6'
201	2,2',3,3',4',5,5',6
202	2,2',3,3',5,5',6,6'
203	2,2',3,4,4',5,5',6
204	2,2',3,4,4',5,6,6'
205	2,3,3',4,4',5,5',6
Nonochlorobiphenyls	
206	2,2',3,3',4,4',5,5',6
207	2,2',3,3',4,4',5,6,6'
208	2,2',3,3',4,5,5',6,6'
Decachlorobiphenyls	
209	2,2',3,3',4,4',5,5',6,6'

Appendix C

Non-Linear Least Squares Program for Estimating  
Description Rate Constants Using Model 2

```

//UNH2 JOB (S0919440,37,,5), 'DUNNIVANT'.TIME=(,4),REGION=2M
/*ROUTE PRINT TEXT
// EXEC SAS
//G.SYSIN DD *
GOPTIONS DEVICE=VER1200B ROTATE NOCHARACTERS;
OPTIONS NOTEXT82;
TITLE;
DATA LEGEND;
  WHEN='A'; POSITION='0';
  XSYS='2'; YSYS='2';
  LENGTH TEXT S 35;
  LENGTH FUNCTION S 8;
INPUT FUNCTION S X Y COLOR S SIZE TEXT 35.;
IF FUNCTION='LABEL'
THEN DO;
  STYLE='SIMPLEX';
END;
CARDS;
MOVE 30 2000 . . .
CNTL2TXT . . .
LABEL . . . PEN4 1 REP2 = SQUARE
MOVE 30 2500 . . .
CNTL2TXT . . .
LABEL . . . PEN4 1 REP1 = STAR
MOVE 30 3000 . . .
CNTL2TXT . . .
LABEL . . . PEN4 1 LINE = PREDICTED
MOVE 30 3500 . . .
CNTL2TXT . . .
LABEL . . . PEN4 1 TWO COUPLED FIRST ORDER MODELS
;
DATA HCCURVE;
TITLE1 F=SIMPLEX C=PEN4 H=2 'L.H. 1000mg/L SOLUTION';
TITLE2 F=SIMPLEX C=PEN4 H=2 'HP PEAK NUMBER 1 - IUPAC NUMBER 4';
TITLE3 F=SIMPLEX C=PEN4 H=2 '2,2''-DCB';
INPUT Y1 1-7 Y2 8-13 X 14-25;
CARDS;
0 0 0
1383 1652 0.0104
2446 3049 0.0208
3360 3968 0.0313
4397 5080 0.0521
5294 5806 0.0729
6096 6558 0.1146
6898 7317 0.2396
7526 7899 0.7396
7993 8355 1.8347
8266 8653 2.8125
8579 8915 4.819
8870 9240 7.972
9106 9490 12.483
9317 9733 17.927
9498 9955 24.889
9760 10350 36.73
10005 10612 53.93
;
PROC SORT OUT=FIRST;
BY X;
PROC NLIN BEST=1 DATA=FIRST;
PARAMETERS A1=5900 B1=3390 L1=25 M1=1.4;
E1=EXP(-L1*X);
E2=EXP(-M1*X);
MODEL Y1=(A1-A1*E1)+(B1-B1*E2);

```

```

DER.A1=1-E1;
DER.B1=1-E2;
DER.L1=X*A1*E1;
DER.M1=X*B1*E2;
OUTPUT OUT=NEW1 PARMS=A1 B1 L1 M1 PREDICTED=PY1;
DATA LINE1;
SET NEW1;
IF N=1;
DO X=0.0 TO 55 BY 5;
PY1=(A1-A1*EXP(-L1*X))+(B1-B1*EXP(-M1*X));
KEEP X PY1;
OUTPUT;
END;
PROC NLIN BEST=1 DATA=FIRST;
PARAMETERS A2=7488 B2=2780 L2=22.1 M2=0.13;
E3=EXP(-L2*X);
E4=EXP(-M2*X);
MODEL Y2=(A2-A2*E3)+(B2-B2*E4);
DER.A2=1-E3;
DER.B2=1-E4;
DER.L2=X*A2*E3;
DER.M2=X*B2*E4;
OUTPUT OUT=NEW2 PARMS=A2 B2 L2 M2 PREDICTED=PY2;
DATA LINE2;
SET NEW2;
IF N=1;
DO X=0.0 TO 55 BY 5;
PY2=(A2-A2*EXP(-L2*X))+(B2-B2*EXP(-M2*X));
KEEP X PY2;
OUTPUT;
END;
DATA ALL;
SET HCCURVE NEW1 LINE1 NEW2 LINE2;
PROC SORT;
BY X;
PROC PRINT; VARIABLES X PY1 Y1 PY2 Y2;
PROC GLOT DATA=ALL;
AXIS1 LABEL=(A=90 F=SIMPLEX H=2 C=PEN4 'CUMULATIVE MASS PURGED, ng')
VALUE=(H=1 F=SIMPLEX C=PEN4)
ORDER=(0.0 TO 11000 BY 1000)
COLOR=PEN4
MAJOR=(C=PEN4)
MINOR=(N=1 C=PEN4)
OFFSET=(0,0)
WIDTH=2
LENGTH=60 PCT;
AXIS2 LABEL=(F=SIMPLEX H=2 C=PEN4 'PURGE TIME, days')
VALUE=(F=SIMPLEX H=1 C=PEN4)
ORDER=(0.0 TO 55 BY 5)
COLOR=PEN4
MAJOR=(C=PEN4)
MINOR=(N=1 C=PEN4)
OFFSET=(0,0)
WIDTH=2
LENGTH=75 PCT;
PLOT Y1*X=1 PY1*X=2 Y2*X=3 PY2*X=4/OVERLAY
HAXIS=AXIS2 VAXIS=AXIS1 FRAME ANNOTATE=LEGEND;
SYMBOL1 C=PEN5 I=NONE H=2 V=STAR;
SYMBOL2 C=PEN2 I=SPLINE V=NONE L=1;
SYMBOL3 C=PEN5 I=NONE H=2 V=SQUARE;
SYMBOL4 C=PEN2 I=SPLINE V=NONE L=1;
RUN;
/*
//

```

CORRELATION BETWEEN HP NUMBER, IUPAC  
NUMBER, AND WEIGHT PERCENTS

Hewlett Packard Number	IUPAC Number	Weight Percent in 1016 <sup>a</sup>	Weight Percent in 1254 <sup>b</sup>
1	4	3.7775	0.0000
	10	0.1733	0.0000
2	7	1.0050	0.0000
	9	0.2946	0.0000
3	6	1.1870	0.0475
4	8	8.9240	0.0000
5	14	0.3206	0.0000
	19	1.0802	0.0000
6	12	0.0953	0.0000
	13	0.1040	0.0000
7	18	10.8717	0.0550
8	15	0.9271	0.0000
	17	3.1405	0.0000
9	27	0.5801	0.0000
10	16	3.5005	0.0000
	32	2.3104	0.0000
11	54	0.2154	0.0000
12	26	0.6201	0.0000
13	25	1.7903	0.0000
14	31	4.7207	0.5653
15	28	14.4822	0.0000
16	20	3.9906	0.0000
	33	3.0805	0.0000
	53	1.2133	0.1157
17	22	2.8004	0.0000
18	45	1.1339	0.1335
19	39	1.0802	0.0000
	46	0.3742	0.0000
20	52	4.9326	3.8813
21	43	0.5330	0.0000
	49	3.9461	1.4510

Table D-1 (Continued)

Hewlett Packard Number	IUPAC Number	Weight Percent in 1016 <sup>a</sup>	Weight Percent in 1254 <sup>b</sup>
22	47	2.0524	0.4629
	48	1.5989	0.0000
	75	2.7215	0.0000
23	Aldrin	--	--
24	35	0.3801	0.0000
25	44	1.2927	0.0000
26	37	1.8903	0.1570
	42	0.0000	1.9407
27	41	2.2679	0.0000
	72	0.0000	0.8991
28	40	0.2041	0.2315
	103	0.0000	0.2886
29	74	1.5308	0.2671
30	70	0.0000	4.2285
	76	0.0000	0.1602
	98	0.0507	0.0000
31	66	0.1588	1.9941
	95	0.2282	0.0000
32	55	0.0000	0.3828
	91	0.0000	4.9761
	121	0.0000	3.4932
33	56	0.0000	0.1602
34	84	0.0127	1.7118
	92	0.0000	0.6270
35	101	0.0000	6.9466
36	79	0.0000	0.2047
	99	0.0000	6.0708
	113	0.0127	0.0000
37	83	0.0000	0.3185
38	97	0.0000	2.5776
39	87	0.0000	3.7918
40	85	0.0000	2.1397
	120	0.0000	0.1493
	136	0.0000	0.3741

Table D-1 (Continued)

Hewlett Packard Number	IUPAC Number	Weight Percent in 1016 <sup>a</sup>	Weight Percent in 1254 <sup>b</sup>
41	77	0.0000	0.1068
	110	0.0000	8.4693
42	151	0.0000	0.3631
43	135	0.0000	0.2200
44	108	0.2028	0.5474
45	123	0.0000	0.0000
46	106	0.0000	0.3981
	118	0.0000	8.0513
	149	0.0000	3.9499
47	114	0.0000	0.2488
	131	0.0000	0.1540
48	122	0.0000	0.7564
	133	0.0000	0.0330
49	146	0.0000	0.8252
	188	0.0000	0.0844
50	132	0.0000	2.2005
51	105	0.0000	0.0000
	127	0.0000	0.0000
	153	0.0000	3.6528
	168	0.0000	4.6540
52	179	0.0000	0.6749
53	138	0.0000	4.5880
	158	0.0000	0.5061
54	126	0.0000	0.1592
55	187	0.0000	0.5785
56	183	0.0000	1.3981
57	128	0.0000	1.4413
58	167	0.0000	0.2311
	185	0.0000	1.3378
59	181	0.0000	0.3375
60	171	0.0000	0.3616

Table D-1 (Continued)

(Continued) Table D-1

Hewlett Packard Number	IUPAC Number	Weight Percent in 1016 <sup>a</sup>	Weight Percent in 1254 <sup>b</sup>
61	157	0.0000	0.1980
62	192	0.0000	0.2410
63	180	0.0000	0.9160
64	198	0.0000	1.3103
Totals		97.810	99.798

a - Based on data in Albro et al. (1979).

b - Based on data in Albro et al. (1981).



## Appendix E

### Input Data for Resuspension Event Model

Data in the following table were input data to the qualitative model used to describe environmental weathering of Aroclor mixtures in Lake Hartwell sediments. Data of interest are the peak relative solubility and partition coefficient columns. An example calculation for peak number 1 is given.

First, the maximum solubility (in  $\mu\text{g/L}$  as subcooled liquid) for each congener was calculated from data in Burkhard (1984). Next, the maximum solubility for each GC peak was estimated by weighing the solubility of each congener present in a peak. Peaks with only one congener were assumed to contain 100% of that congener. Solubilities for mixed peaks, such as peak number 1, were calculated as shown below:

$$\text{Maximum Peak Solubility} = \frac{\text{Fractional Composition of Congener } i \text{ in Peak}}{\text{Maximum Solubility of Congener}}$$

$$\begin{aligned}\text{Peak Number 1} &= (0.956)(1696) + (0.044)(1704) \\ &= 1696 \mu\text{g/L}\end{aligned}$$

Next, relative peak solubilities were calculated by weighing the solubility of each peak using the sum of all the maximum peak solubilities calculated above (sum =  $9601 \mu\text{g/L}$ ). For peak number 1, the calculation was:

$$\begin{aligned}\text{Relative Peak Solubility} &= 1696 \mu\text{g/L} (1696/9601) \\ &= 300 \mu\text{g/L}\end{aligned}$$

Two exceptions were peaks 5 and 8. Each of these peaks contained one highly soluble congener ( $\approx 1000 \text{ mg/L}$ ) and one less soluble congener ( $\approx 400 \text{ mg/L}$ ). Because these higher-solubility congeners possessed significant weight-percents in the parent Aroclors, each peak was assumed to be saturated with respect to the congener possessing the higher solubility. Thus, peaks 5 and 8 were assumed to be 100% IUPAC

numbers 14 and 15, respectively. These values were used in the qualitative modeling approach in the final paper of the manuscript and represents the relative solubility of each peak present in the point source effluent waters.

Peak solubilities for mixed peaks such as peak number 1 were calculated as shown below:

Maximum Peak Solubility = of Congener 1 in Peak  
 Fractional Composition  
 Maximum Solubility  
 of Congener

Peak Number 1 = (0.95)(1696) + (0.04)(1704)  
 = 1696 ug/L

Next, relative peak solubilities were calculated by weighing the solubility of each peak using the sum of all the maximum peak solubilities calculated above (sum = 9601 ug/L). For peak number 1, the calculation was:

Relative Peak Solubility =  $1696 \text{ ug/L} / (1696 + 9601)$   
 = 300 ug/L

Two exceptions were peaks 5 and 8. Each of these peaks contained one highly soluble congener (~1000 mg/L) and one less soluble congener (~400 mg/L). Because these higher-solubility congeners possessed significant weight-percent in the parent Atoclor, each peak was assumed to be saturated with respect to the congener possessing the higher solubility. Thus, peaks 5 and 8 were assumed to be 100% IUPAC

TABLE E-1

## INPUT DATA FOR RESUSPENSION EVENT MODEL

Hewlett Packard Number	IUPAC Number	Percent Composition Of Congener In Peak <sup>a</sup>	Congener Maximum Solubility ( $\mu\text{g/L}$ ) <sup>b</sup>	Relative Solubility For HP Peak <sup>c</sup>	Partition Coefficient <sup>d</sup> For HP Peak ( $\text{mL}/\mu\text{g} \times 10^5$ )
1	4	95.6	1696.		
	10	4.4	1704.	300.	0.00284
2	7	--	--	e	
	9	--	--	e	0.00641
3	6	--	--	e	0.00705
4	8	100.	1314.	180.	0.00771
5	14	22.9	1050.		
	19	77.1	346.	115.	0.00726
6	12	--	--	f	
	13	--	--	f	0.01390
7	18	100.	348.	12.6	0.01280
8	15	22.8	1020.		
	17	77.2	394.	108.	0.01420
9	27	100.	404.	17.0	0.01260
10	16	60.2	504.		
	32	39.8	400.	22.3	0.0130
11	54	--	--	f	0.02590
12	26	100.	320.	10.7	0.02280
13	25	100.	316.	10.4	0.02700
14	31	100.	316.	10.4	0.02770
15	28	--	--	e	g
16	20	37.2	402.		
	33	48.2	370.		
	53	14.7	92.	12.1	0.0265
17	22	100.	396.	16.3	0.0257
18	45	100.	116.	1.40	0.0258
19	39	74.3	254.		
	46	25.7	114.	3.85	0.0284
20	52	100.	106.	1.17	0.0413
21	43	11.9	130.		
	49	88.1	104.	1.19	0.0482

Table E-1 (Continued)

Hewlett Packard Number	IUPAC Number	Percent Composition Of Congener In Peak <sup>a</sup>	Congener Maximum Solubility ( $\mu\text{g/L}$ ) <sup>b</sup>	Relative Solubility For HP Peak <sup>c</sup>	Partition Coefficient <sup>d</sup> For HP Peak ( $\text{mL}/\mu\text{g} \times 10^3$ )
22	47	32.2	104.	1.30	0.0516
	48	42.7	122.		
	75	25.1	104.		
23	Aldrin				
24	35	--	--	h	g
25	44	100.	130.	1.76	0.0430
26	37	51.3	296.	4.82	0.0498
	42	48.7	130.		
27	41	--	--	e	h
	72	--	--	e	h
28	40	--	--	f	0.0455
	103	--	--	f	
29	74	100.	98.	1.00	0.0831
30	70	95.3	98.	0.99	0.0807
	76	3.6	114.		
	98	1.1	34.		
31	66	90.4	108.	1.06	0.0886
	95	9.6	34.		
32	55	4.3	122.	0.143	0.1200
	91	56.2	34.		
	121	39.5	32.		
33	56	--	--	f	0.0977
	60	--	--	f	
34	84	73.3	40.	0.162	0.0977
	92	26.7	38.		
35	101	100.	36.	0.135	0.1390
36	79	3.3	82.	0.147	0.1590
	99	96.5	36.		
	113	0.2	38.		
37	83	--	--	f	g
38	81	--	--	f	g
39	87	100.	44.	0.202	0.1410
40	85	--	--	f	0.1770
	120	--	--	f	
	136	--	--	f	

Table E-1 (Continued)

Hewlett Packard Number	IUPAC Number	Percent Composition Of Congener In Peak <sup>a</sup>	Congener Maximum Solubility ( $\mu\text{g}/\text{L}$ ) <sup>b</sup>	Relative Solubility For HP Peak <sup>c</sup>	Partition Coefficient <sup>d</sup> For HP Peak ( $\text{mL}/\mu\text{g} \times 10^3$ )
41	77	1.3	94.		
	110	98.7	44.	0.208	0.1420
42	151	--	--	f	0.1520
43	135	--	--	f	g
44	108	100.	28.	0.082	0.4170
45	123	--	--	f	g
46	106	3.2	42.		
	118	64.9	66.		
	149	31.9	13.	0.243	0.208
47	114	--	--	f	g
	131	--	--	f	g
48	122	--	--	f	g
	133	--	--	f	g
49	146	--	--	g	g
	188	--	--	g	g
50	132	--	--	g	g
51	105	--	--	g	g
	127	--	--	g	g
	153	--	--	g	g
	168	--	--	g	g
52	179	--	--	g	g
53	138	--	--	g	g
	158	--	--	g	g
54	126	--	--	f	g
55	187	--	--	g	g
56	183	--	--	g	g
57	128	--	--	g	g
58	167	--	--	g	g
	185	--	--	g	g
59	181	--	--	f	g
60	171	--	--	f	g

Table E-1 (Continued)

Hewlett Packard Number	IUPAC Number	Percent Composition Of Congener In Peak <sup>a</sup>	Congener Maximum Solubility ( $\mu\text{g/L}$ ) <sup>b</sup>	Relative Solubility For HP Peak <sup>c</sup>	Partition Coefficient <sup>d</sup> For HP Peak ( $\text{mL}/\mu\text{g} \times 10^3$ )
61	157	--	--	f	g
62	192	--	--	f	g
63	180	--	--	g	g
64	198	--	--	g	g

a - Percent composition based on weight-percent data from Albro et al. (1979 and 1981).

b - Maximum solubility based on data from Burkhard (1984)

c - Relative solubility as calculated earlier.

d - Partition Coefficients were measured in the  $K_d$  and  $K_d$  experiments. Those shown above are an average of 10 replicates.

e - Indicates congeners that were not present in Lake Hartwell sediments and are known to be readily biodegradable.

f - Indicates congeners present are weight-percents less than 0.5%.

g - Insufficient data were available for calculation of Kds (water or sediment phase concentrations were below detection limit).

h - Indicates that peak was not used in quantitation due to a co-eluting contaminant in GC analysis.

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