Annual Report
to
Ocean Assessment Division / National Ocean Service
National Oceanic and Atmospheric Administration

THE CYCLING OF TOXIC ORGANIC SUBSTANCES IN THE GREAT LAKES ECOSYSTEM

October 1983

Cooperative Program Between

Great Lakes Environmental Research Laboratory
ERL / NOAA
Ann Arbor, Michigan 48104
and
University of Michigan
University of Minnesota
Michigan State University
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DEPARTMENT OF COMMERCE · UNITED STATES OF AMERICA

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1. BACKGROUND

In 1978, the United States and Canada signed a Great Lakes Water Quality Agreement

> "reaffirming their intent to prevent further pollution of the Great Lakes Basin ecosystem owing to continuing population growth, resource development and increasing use of water"

and

> "reaffirming their determination to restore and enhance water quality in the Great Lakes System."

Among its many provisions and recommendations, the agreement states that

> "An early warning . . . shall be established to anticipate future toxic substances problems"

including

> "development and use of mathematical models to predict consequences of various loading rates of different chemicals."

In terms of research, it is stated that

> "in particular, research should be conducted to determine:
>
> (a) The significance of effects of persistent toxic substances on human health and aquatic life;
>
> (b) Interactive effects of residues of toxic substances on aquatic life, wildlife, and human health; and
>
> (c) Approaches to calculation of acceptable loading rates for persistent toxic substances, especially those which, in part, are naturally occurring."

In order to address these national goals and partially fulfill NOAA's responsibilities in the Great Lakes, the Great Lakes Environmental Research Laboratory (GLERL) began a research program in cooperation with the Office of Marine Pollution Assessment (recently renamed the Ocean Assessment Division (OAD) of the National Ocean Services, NOAA), whose goal is the development of a capability to predict the environmental consequences of persistent synthetic organic contaminants in the Great Lakes ecosystem. This program was initiated in late 1979. The understanding of long-term cooperation with OMPA/OAD has allowed GLERL to develop cooperative agreements with several research institutions and to pursue a comprehensive research program focused on a few questions regarding the flow of selected organics within the Great Lakes. Much of the results generated in this program will be transferrable to coastal marine systems.

A predictive capability is synonymous with modeling, and to accomplish this a modeling team has been set up in-house consisting of chemical, toxicological, ecological, and physical scientists. The modeling group is supported by researchers working on primary ecosystem processes. Most of the process research has been conducted at The University of Michigan; however, our program now has expanded to include several research groups, an arrangement that allows for a maximum of flexibility.

2. INTRODUCTION

2.1 Scope of the Problem

The leakage of toxic synthetic organic contaminants into aquatic ecosystems is a well-recognized global problem. The conclusion of a recent workshop on the "Scientific Basis for Dealing With Chemical Toxic Substances in the Great Lakes," cosponsored by GLERL (Sonzogni and Swain, 1980), was that the Great Lakes are particularly susceptible because of high population density, concentration of heavy industry, and slow (decade-century) flushing rates. Similar evaluations have been expressed by the Great Lakes Science Advisory Board (IJC, 1980a), Water Quality Board (IJC, 1980b), and Toxic Substances Committee (IJC, 1980c) of the International Joint Commission. Over 400 toxic contaminants have been identified to date within the Great Lakes ecosystem (IJC, 1980c) and the extent of the hazards for most of these are poorly understood.

While most of these contaminants are perceived to be detrimental to environmental quality, several toxic organics have been identified as the source of serious problems. High concentrations of DDT in Great Lakes fish severely impacted the herring gull population of the basin in the late 1960s and early 1970s. This once common predator is now beginning to reestablish itself, although high levels of PCB and TCDD may slow its recovery. PCB levels in Lake Michigan sportfish have been significantly above the FDA recommended level of 2 parts per million. It has been estimated that this contamination is costing the State of Wisconsin over $1 million per year (University of Wisconsin, 1980), with costs for the entire basin many times this amount. A report by the National Research Council (NRC, 1979) states that the Great Lakes are the largest reservoir of PCBs in the United States. Another identified problem is mirex in Lake Ontario (Kaiser, 1978; Pickett and Dossett, 1979). This compound, a fire ant pesticide manufactured in the basin, leaked into the lake and contaminated the fish to a level that resulted in New York State ban on their commercial sale. Increased incidences of neoplasia (tumerous lesions) have been found in the fishes of the Great Lakes and tentatively attributed to relatively high concentrations of polynuclear aromatic hydrocarbons (PAH) (Sonstegrad, 1977; Black *et al.*, 1980; Eadie *et al.*, 1982a,b). High levels of dieldrin, toxaphenes, and dioxin have been measured, indicating that other real problems are out there waiting to be found.

2.2 General Nature of the Program

Attempts to model the fate of toxic organic compounds in aquatic ecosystems appear to provide a good first-order estimate of their long-term behavior (Baughman and Lassiter, 1978; Mackay, 1979; Eadie *et al.*, 1981). These models are excellent tools for assembling existing information, testing system sensitivity, and designing a coherent research program. In time, they will be useful tools in the decision-making process as well.

Since its creation in 1974, GLERL has specialized in the design and development of ecosystem models that simulate or predict the physical, chemical, and biological responses of the Great Lakes to imposed stresses. In this program, our efforts to date have focused on the development of system models, supported by the specific process research required to improve, calibrate, and/or validate our mathematical abstractions. Modeling-experimental interactions enable us to make stepwise improvements in our understanding of the cycling, behavior, and fate of synthetic contaminants. Such information is necessary to identify the contaminants that pose the greatest threat to the environment, which organisms or regions within the lakes are most affected, what can be expected in the years ahead, and what can be done to reduce the level of ecosystem stress.

2.3 Program Goal

The goal of this proposed program is to produce a clearer understanding of the cycling of toxic organic compounds in the Great Lakes environment. In order to meet the early warning and load reduction objectives cited in the treaty, we need to be able to predict locations, concentrations, decay rates, residence times, and the eventual sinks of these materials under conditions of long-term, low level leakage into the environment or a major loading from some point source. This information is critical for toxicologists, ecologists, and resource managers to evaluate the potential impacts of particular contaminants that have been introduced into the Great Lakes Region and to provide cost beneficial solutions to the problems in balancing the continued production and use of these compounds with the responsibility of protecting the Great Lakes as a resource. In the final analysis, environmental resource management comes down to a trade-off between "acceptable risks" and "unacceptable costs," and best judgments leading to a suitable balance can only be achieved if the information base is sound.

2.4 Program Objectives

Our primary objective is the development of the necessary tools (models, information base, network of experts, etc.) that will enable us to reliably predict the consequences to the Great Lakes ecosystem of alternative toxic management decisions. This requires the systematic understanding of the major ecosystem processes that affect or are affected by the substance(s) under consideration. Preliminary modeling efforts by ourselves and others and discussions with many experts allowed us to approach the development of these tools in a systematic sense. A diagram of a generalized aquatic ecosystem appears in figure 1.

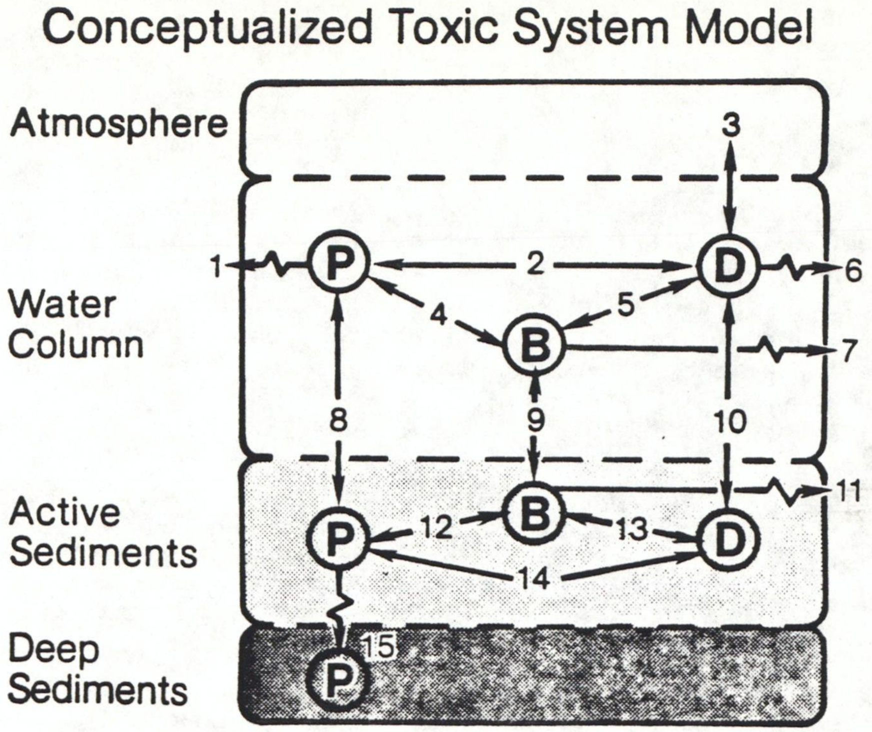

FIGURE 1.--*Conceptualized toxic system model. P represents particle phase, D represents dissolved phase, and B is an abbreviated food web. The 15 process arrows are: photolysis (1 and 6), sorption (2 and 14), air-water exchange (3), grazing and fecal pellet generation (4), filtering (5), biological decomposition (7 and 11), settling and resuspension (8), food web dynamics (9), advective and diffusive mixing (10), benthos-sediment interactions (12 and 13), and burial and bioturbation (15).*

2.5 Approach

Most persistent toxic organics behave similarly in the aquatic environment; they are only slightly soluble and partition onto particulate material, they tend to photodecompose and evaporate as major removal pathways, they are generally resistant to microbial attack and they concentrate in the sediments. This similarity of behavior makes a modeling approach attractive and recently toxic cycling models have begun to appear in the literature. These models require compound-specific experimental rate process information tailored for the ecosystem to which it is applied.

We are employing a systems approach, in which a series of models will be developed. These include the calibration of available equilibrium (Fugacity) and steady state thermodynamic model (EXAMS; EPA) for the Great Lakes: the development of a one-dimensional, time-dependent, process model and the calibration of a two-dimensional time-dependent transport (modified oil spill) model containing first order decomposition, resuspension and sedimentation terms. Our models will be continuously upgraded through the results of our process research experiments, both in-house and under contract, along with other information entering the literature. Carrying out process research and modeling simultaneously will allow us to continually determine the weakest or most sensitive areas in our systems approach and define research necessary to address these specific problems. Ultimately our goal is to combine calibrated ecosystem cycling models with system transport models.

We have concentrated on two classes of toxic organic substances, polynuclear aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB). Field and laboratory studies on the rates of volatilization, photodecomposition, sorption onto particulates indigenous to the Great Lakes, biological decomposition, aggregation and settling were designed and implemented to support our toxic organic cycling model. Our particle dynamics program uses cesium-137 and beryllium-7 as tracers. These compounds are excellent surrogates for hydrophobic organic compounds and there is a large data base on the distribution of these compounds as well as information on their loads to the lakes and decomposition pathways and rates. This wealth of information can be used in the calibration phase of our modeling program.

The 15 process arrows, shown in figure 1, are being studied in our program a shown in the Project/Process Matrix (Table 1). The column marked M is to represent those directly involved in modeling.

2.6 Relevance of our Research Program to Marine Pollution Problems

This topic has already been discussed in the preceding pages in terms of the perception of the International Joint Commission and the Great Lakes Water Quality Agreement. Our modeling and process research goals also match the top priority research needs for the Great Lakes as expressed in the 1981 National Marine Pollution Program Plan and further described in its supporting Working Paper #3, "Report of Great Lakes Region Conference on Marine Pollution Problems."

Although we are not addressing all of the research needs expressed in the above-mentioned documents, we feel that our program is well designed within its level of support to meet a selected subset of these critical needs.

Table 1

PROJECT/PROCESS MATRIX

PI	Description	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	M
GLERL																	
• Eadie	PAH Cycling		X						X		X		X	X	X		X
• Robbins	Radiotracer Applications		X						X		X				X	X	X
• Landrum	Contaminant & Benthic Interactions							X				X	X	X			
• Bennett & Clines	2D & 3D Transport Models								X								X
• McCormick	Vertical Dynamics Modeling			X													X
U.MI																	
• Rice & Meyers	Particle Associated Contaminants		X	X					X						X		
• Simmons	Photolysis	X					X										
• White	Bioturbation												X	X		X	
• Rossmann	Sediment Fluxes															X	
U.MN																	
• Eisenreich	Sed. Accumul. & Diagenesis										X					X	X
MI.ST.																	
• Giesy	Toxic Stress Test												X	X			
ANL																	
• Nelson	Radionuclide Loads																X
ORNL																	
• Breck	Fish Modeling				X	X				X							X

3. SUMMARY OF PROGRAM RESULTS

During the early part of our program, we concentrated our research efforts on processes at the air/water interface (photolysis, air/water exchange, etc.). As our research on air/water processes winds down, we are incorporating this information into our modeling program and improving our parameterizations of processes occurring in that region.

Over the past two years, we have moved a substantial fraction of our effort into processes at the sediment/water interface (uptake by benthic organisms, burial, resuspension, etc.). During the next few years, we will devote the major portion of our program to the bottom boundary which we feel controls the long-term behavior and fate of contaminants in the Great Lakes.

Recent accomplishments are described in the accompanying task reports. Some program highlights include:

1) Equilibrium models that predict the distribution of an organic contaminant based on the contaminant's solubility and a physical description of the ecosystem,

2) Improved understanding and prediction of equilibrium partition coefficients as a function of the concentration of substrate,

3) Estimates of the resuspension rates of sediments and calculations of the flux of reentrained PCBs in Lake Michigan,

4) Estimates of bioconcentrations of contaminants by benthic organisms, along with rates of uptake, depuration, and metabolic decomposition,

5) Improved estimates of the mixing rates in surficial sediments, rates of contaminant burial and early diagenesis,

6) A model of the horizontal movement of sediment-associated contaminants under the influence of wind driven currents,

7) Improved estimates of photodecomposition rates of selected PCB and PAH congeners in lake water,

8) Measurements of PCBs at the air/water interface that suggest significant compound behavioral differences within the microlayer,

9) Analyses of organic matter, nutrients, PCBs, Cs-137 and Be-7 in 1982 traps which shows that the offshore epilimnion is isolated from the pool of resuspendable sediments during the period of stratification, but that winter resuspension is a major source of contaminants to the waters of Lake Michigan,

10) Analysis of an upwelling event allowed a calculation of the magnitude of the injection of nepheloid material into the nearshore surfacr waters. For PCB this estimate is 5-10% of the current atmospheric load estimate,

11) Measurements of PAH uptake rate from sediments by *P. hoyi* indicate a significant fraction of organism's body burden comes directly from sediments, and

12) Substantial input to the IJC regarding PAH management strategy in the Great Lakes; supplying approximately 90% of all Great Lakes PAH data and extensively rewriting the draft recommendation.

Currently major collaborative research investigations are underway in our high sedimentation rate cores, collected in all five Great Lakes (19 principal investigators at eight research institutions) and our sediment trap program (10 principal investigators at four research institutions). Many of our collaborators have other funding sources than GLERL or OAD which serve to amplify all of our respective studies. Both of these projects are providing insight into the movement of particle associated contaminants and on the role of resuspension and burial in regulating contaminant residence times in the Great Lakes.

Our organics cycling program has focused (in house) on the PAH, primarily because of their range of solubilities and their ubiquity. Our work has also indicated that they may be a problem in the Great Lakes. The PAH are primarily products of incomplete combustion of organic matter, are of concern as carcinogens and mutagens, and we have shown that concentration within the Great Lakes ecosystem is very high in comparison with other regions of the world. The benthic invertebrates of the Great Lakes have high measured bioconcentration factors and laboratory studies indicate that the causes are 1) uptake from the highly contaminanted sediment pool and 2) very small depuration rates. We are currently carefully studying the sorption and complexation behavior of PAH and the role of these processes on bioavailability of PAH to organisms. As a direct consequence of our work, we were invited to participate in an International Joint Commission meeting to review the Proposed Aquatic Ecosystem Objective for Polynuclear Aromatic Hydrocarbons in the Great Lakes Ecosystem (Columbus, Ohio, October 28, 1982) and to submit written reviews in November, 1982.

We have supplied a vast majority of PAH numbers to the IJC and they have recommended that PAH be one of the few classes of compounds which should be studied extensively. A copy of a review document on PAH in the Great Lakes is appended to this report.

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5. PRODUCTS

Publications, presentations, and the documentation of models are important products of this program, but other, intangible products must also be considered. Such things include the development of a scientific research team and a network of experts on the cycling, behavior, and fate of contaminants in the Great Lakes. We have provided our results to several working groups of the International Joint Commission and to the State of Michigan, and have published and made presentations to scientifically interested lay groups.

Our last annual report, summarizing results to that date, included a list of 34 publications and 31 presentations. The following list is an update, and indicates that production (as measured in these terms) is increasing.

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6. TASK REPORTS

Following the attached review of PAH in the Great Lakes (which will appear as an appendix to the 1983 International Joint Commission Annual Report) are brief reports from the individual tasks within the program.

A PERSPECTIVE ON POLYCYCLIC AROMATIC HYDROCARBONS IN THE GREAT LAKES[1]

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Introduction

Polycyclic aromatic hydrocarbons (PAH) are a class of compounds with a basic structure consisting of carbon and hydrogen atoms arranged in two or more fused aromatic (benzene) rings. They are of concern because many of the congeners can be carcinogenic and/or mutagenic. The term also covers fused aromatic systems containing a cyclopentene ring or hetero atoms of sulfur or nitrogen. This report will consider only the hydrocarbons, which range from the two-ring compound naphthalene ($C_{10}H_8$) to the seven-ring compound coronene ($C_{24}H_{12}$). Permutations of the spatial orientation of the rings and multiple types of substitution lead to a large number of PAH congeners. Of this large group, those most often reported in environmental samples are illustrated in Figure 1.

PAH are products of the incomplete combustion of organic materials, for example, forest fires or the burning of fossil fuels. As is to be expected from such commonly available source material, PAH are ubiquitous in the environment (Hites *et al.*, 1980), with elevated concentrations reported near urban areas (Laflamme and Hites, 1978; Wakeham *et al.*, 1980a). The predominant compounds found in atmospheric samples (Gordon, 1976; Strand and Andren, 1980) and sediments (Laflamme and Hites, 1978) are the unsubstituted parent compounds (Figure 1). These are primarily generated at temperatures in excess of 400°-500°C. At lower combustion temperatures, alkyl-substituted PAH begin to predominate. This trend is carried to an extreme in the low temperature (100°-150°C) maturation of oil, which contains complex mixtures of substituted PAH (Youngblood and Blumer, 1975).

In the atmosphere, PAH generated in the combustion process are primarily associated with fine particles (Neff, 1979). Recent work indicates that most

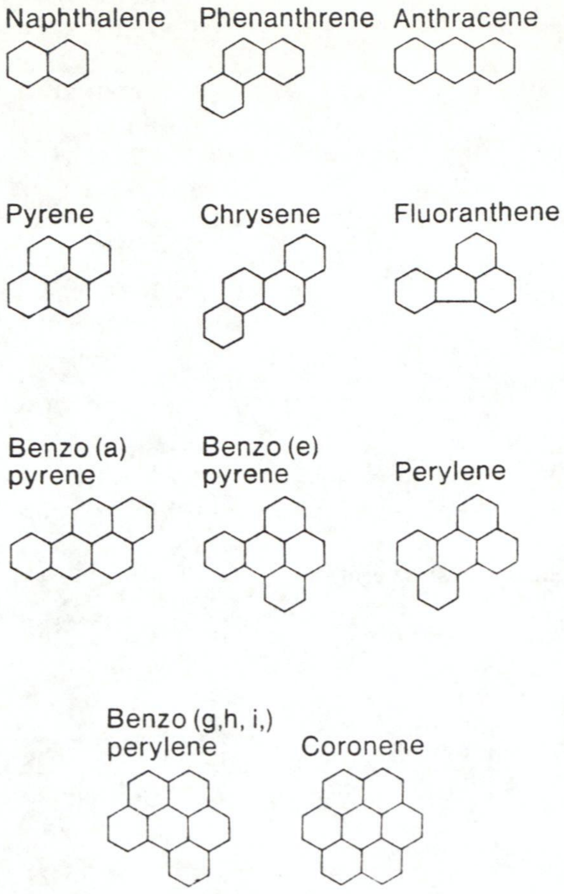

Figure 1. *Ring structures of the most common PAH in environmental samples. By convention, symbols representing the aromatic character of the rings are omitted.*

of the mass of PAH is attached to submicron particles (Miguel and Rubenich, 1979). Particles this size could be expected to have an atmospheric residence time of weeks to months, although this is considerably reduced by washout during precipitation. This still leaves time (days to weeks) for long range atmospheric transport of PAH, contributing to their wide distribution.

There are other sources for some of the PAH. In sediments, perylene concentration has been shown to increase with depth within the core, and it often becomes the most abundant PAH (Wakeham *et al.*, 1980b). Laflamme and Hites (1978) describe some possible quinone pigment precursors that might form perylene in reducing sedimentary environments. Alkylated phenanthrenes occasionally appear in large quantities and are postulated to have two sources in addition to combustion: terpenes associated with pine forests (Laflamme and Hites, 1978) and dehydrogenation of steroids (Wakeham *et al.*, 1980b) within the sediment.

Behavior of PAH in the Aquatic Environment

Solubility dominates the behavior and fate of persistent organic contaminants in the Great Lakes (and other aquatic systems). The distribution of the contaminant within the system is defined by its equilibrium partition coefficient (K_p).

$$K_p = \frac{\text{concentration in particulate phase (ppm)}}{\text{concentration in dissolved phase (ppm).}}$$

Several investigators have recently published on this topic (Chiou *et al.*, 1977; Herbes, 1977; Means *et al.*, 1979, and Karickhoff *et al.*, 1979). The most comprehensive of these studies was a review by Kenaga and Goring (1979), who derived the following relationship:

$$\log K_{oc} = 3.64 - 0.55 \log WS$$

$$n = 106 \text{ compounds} \qquad r = -0.84,$$

where WS = solubility in water (ppm) and $K_{oc} = (100 \times K_p)/(\%$ organic carbon of the substrate).

Reported solubilities of PAH in distilled water (tabulated in Neff, 1979, and in Lee and Grant, 1982) range from approximately 1 ppm for phenanthrene to 0.1 ppb for coronene. Mean solubilities and K_{oc} values calculated from the expression above are listed in Table 1. Log K_{oc} values for pyrene measured by Means *et al.* (1979) averaged 4.82 and those measured by Karickhoff *et al.* (1979) on silts and clay averaged 5.05. These results indicate that the calculated K_{oc} values in Table 1 may be low by as much as an order of magnitude. Measurements made in our laboratory support this.

The equilibrium distribution of PAH in the water column of the Great Lakes, calculated from this information, is illustrated in Figure 2. The fraction of contaminant associated with the dissolved phase is equal to:

$$fd = \frac{1}{1 + K_p * TSM},$$

Table 1. *Summary of water solubility and partitioning information*

Compound	Mean of reported solubilities (mg/kg)[1]	Calculated $\log_{10} K_{oc}$
Naphthalene	31.3	2.82
Phenanthrene	1.24	3.59
Anthracene	0.062	4.30
Pyrene	0.142	4.11
Chrysene	0.0018	5.15
Fluoranthene	0.242	3.98
Benzo(a)pyrene	0.0039	4.97
Perylene	0.0004	5.51
Benzo(ghi)perylene	0.00026	5.61
Coronene	0.00014	5.76

[1] Compiled data from Lee and Grant (1982).

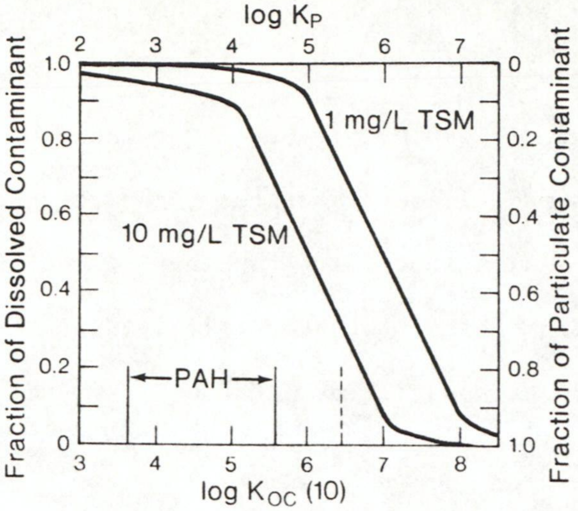

Figure 2.--*The equilibrium distribution of PAH (and other organic contaminants) within the water column of the Great Lakes. The fraction of dissolved contaminant is defined as* $f_d = 1/(1 + K_p{*}TSM)$. K_{oc} *(10) represents the partition coefficient assuming 10% substrate organic carbon, equivalent to* $10{*}K_p$. *The water solubility is calculated from the expression of Kenaga and Goring (1979). (See text.) The region of PAH partitioning is indicated. At equilibrium the PAH are predominately in the dissolved form.*

where TSM represents the concentration of total suspended matter (g/g). The Great Lakes vary in their open lake TSM concentrations as shown below (Bell, 1982):

Lake	Approximate TSM (mg/L)
Superior	0.5-1
Michigan	1-2
Huron	1-2
Erie	4-8
Ontario	2-4

In shallow nearshore regions, TSM concentrations are generally greater by a factor of two or more. The range of TSM illustated in Figure 2 (1-10 ppm) is correct over most of the Great Lakes. In the upper three lakes, approximately

90% of the water column inventory of PAH will be in the dissolved phase. Only in nearshore regions or western Lake Erie will a substantial fraction of the low solubility PAHs be associated with particles.

Decomposition of PAH in the water column is primarily through photo-oxidation (National Academy of Science, 1982). Benzo(a)pyrene (BaP), for example, has a half-life of less than 1.0 hour when exposed to sunlight; however, the near-ultraviolet light that supplies the energy for these reactions is rapidly attenuated within the first few meters of the water column, greatly reducing the amount of BaP removed by this process.

Transport of PAH out of the water column occurs through sorption to particles and particle settling. Fecal pellets were identified as the primary transport vehicle for PAH in a marine bay (Prahl and Carpenter, 1979). Preliminary evidence suggests that fecal pellets play a similar role in Lake Michigan (M. Evans, University of Michigan, personal communication). These are relatively large and have settling speeds of tens of meters per day, rapidly removing PAH from the euphotic zone. Biological decomposition is at a maximum near the sediment/water interface (Gardner *et al.*, 1979; Lee *et al.*, 1981) and competes with burial as the predominant removal mechanism in the Great Lakes.

The distribution of PAH in various sedimentary environments around the world, although complex (Laflamme and Hites, 1978; Hites *et al.*, 1980), is usually dominated by fluoranthene and pyrene in about equal concentrations and is consistent with the hypothesis of a combustion source. Concentrations of these compounds range from a few parts per billion in regions remote from urban environments up to approximately 1 part per million in sediments from the New York Bight. Similarly high concentrations (~1 ppm) were reported for

Lake Washington and three Swiss lakes (all close to urban sources) (Wakeham *et al.*, 1980a). These high sediment concentrations imply that organisms that live or feed in surficial sediments will be exposed to very high concentrations of PAH.

PAH in the Great Lakes

The Great Lakes are the focus of a heavily populated and industrialized region and, as previously described, such areas are expected to receive large loads of PAH. Estimates of the load of PAH to the Great Lakes (Table 2) are similar to maximum estimates of PCB and DDT loads to the same region. Load estimates are based on a very sparse data base, and thus are subject to improvement as more information becomes available. In addition to atmospheric input, tributary input can be estimated from suspended solids load data of

Table 2. *Atmospheric flux of PAH to the Great Lakes (MT/yr)*

	Lake					
Compound	Superior[1]	Michigan[1]	Michigan[2]	Huron[1]	Erie[1]	Ontario[1]
Phenanthrene	4.8	3.4	2.1	3.5	1.5	1.1
Anthracene	4.8	3.4	2.1	3.5	1.5	1.1
Fluoranthene	-	-	3.6	-	-	-
Pyrene	8.3	5.9	4.0	6.1	2.6	1.9
Benzo(a)anthracene	4.1	2.9	3.3	3.0	1.5	1.1
Benzo(a)pyrene	7.9	5.6	4.0	5.8	2.5	1.8
Perylene	4.8	3.3	2.1	3.4	1.5	1.1

[1] Eisenreich *et al.* (1981).

[2] Andren and Strand (1981).

Sonzogni *et al.* (1979) and Sullivan *et al.* (1980) and an estimate of 50 ppb fluoranthene or pyrene for soil from Hites *et al.* (1980). Based on these assumptions, PAH via tributary input is approximately 10% of the level attributed to atmospheric input. Shoreline erosion and diffuse sources would also contribute small amounts, but direct atmospheric input appears to be the major source of PAH to the Great Lakes.

Because of their low solubility and concentration, data on PAH in the water column are very limited. Worldwide concentrations of BaP ranged from approximately 0.1 to 100 ng/L (Neff, 1979). BaP (0.3 ng/L) and total PAH (4.7 ng/L) were found in Lake Erie near Buffalo (Basu and Saxena, 1979). Large volumes of treated municipal drinking water taken from 12 plants using Great Lakes water yielded relatively high concentrations of pyrene (11.2 ± 20.0 and 3.9 ± 10.2 ng/L) and fluoranthene (9.2 ± 12.0 and 10.6 ± 25.0) (Williams *et al.*, 1982). The numbers in parenthesis represent the mean ± 1 standard deviation for winter and summer samples, respectively. Fluoranthene (15 ± 9 ng/L), pyrene (14 ± 6 ng/L), and BaP (7 ± 4 ng/L) were found in filtered offshore waters of southern Lake Michigan (Eadie, 1983). The concentration of these compounds on suspended particles was 2-4 μg/g. At a concentration of 1 mg/L of TSM, more than 75% of these PAH are estimated to be in the dissolved phase.

PAH concentrate in sediments, and there have been several analyses of Great Lakes sediments for these compounds (Table 3). In general, high sediment PAH concentrations are associated with fine-grained, organic rich sediments. Low values in Table 3 are from nearshore, sandy environments.

PAH in Lake Superior sediments are an order of magnitude lower than those in the lower lakes. Lake Michigan sediments have the highest PAH concentration. This observation supports the hypothesis of localized urban sources,

Table 3. *Range of concentrations of PAH in Great Lakes surficial sediments (ng/g dry)*

Compound	Lake Superior[1] (n=1)	Michigan[2] (n=10)	Huron[2] (n=3)	Erie[2,3] (n=4)	Ontario[2,4] (n=5)
Phenanthrene	34	6-1268	11-272	18-431	40-205
Fluoranthene	88	9-1664	33-487	65-285	210-1000
Pyrene	53	8-1430	36-256	57-287	56-1182
BaP	28	4-944	23-294	56-173	76-306

[1] Gischwend and Hites (1981).

[2] Eadie *et al*. (1982b, 1983).

[3] Eadie *et al*. (1982a).

[4] IJC (1977).

since the Lake Superior region is heavily forested and undeveloped, while the region around southern Lake Michigan (where six of the sediments were collected) is heavily industrialized. The distribution of measured PAH congeners in Great Lakes sediments is similar in a gross sense to sediments reported by Hites *et al*. (1980), Laflamme and Hites (1978), Wakeham *et al*. (1980a), Tan and Heit (1981), and Eadie *et al*. (1982a,b) for environments that receive PAH from anthropogenic sources. Characteristically, these are highest in unsubstituted fluoranthene and pyrene, with large concentrations of phenanthrene, chrysene (plus triphenylene), and BaP.

More detailed information on the distribution of PAH in Lake Michigan sediments is presented in Table 4. Stations T1 and T6 are located in regions

Table 4. *Lake Michigan sediment PAH (ng/g dry)*

Station	Phenanthene	Fluoranthene	Pyrene	Chrysene + Triphenylene	BaP
T1	28	34	30	36	33
T2	809	906	733	-	450
T3*	1268	1664	1430	1128	944
T4	308	445	363	319	251
T5	537	794	665	522	248
T6	19	62	38	41	26
T7	298	620	421	554	572
T8	245	419	319	348	571
T11	263	413	318	543	324

*Calculated PAH coefficients of variation (%) for replicate (3-4) analyses of replicate (3) extracts from station T3 are: 27.6, 13.0, 11.6, 19.4, 18.5, respectively

where sediments are not accumulating (Cahill, 1981). The other seven stations are in regions of recent sediment deposition. The distribution of the fluoranthene concentrations for these nine stations (Figure 3) is in general agreement with the map of chlorinated organic contaminants (whose source is also primarily atmospheric) (Frank *et al.*, 1981). It appears that the final sedimentary distribution of PAH and other hydrophobic organics will be controlled by processes that affect the movement of the fine-grained, organic rich sediments to which they are attached.

The information from the previous discussion can be used to estimate a simple steady-state mass balance for PAH in the Great Lakes. Figure 4 illustrates such a calculation for BaP in Lake Michigan. The numbers should be considered uncertain to about ± 50% at this time. The loss of 2.8 MT of BaP per year (calculated by difference) indicates decomposition of approximately 50% of the load. If one divides the concentration in the water by the

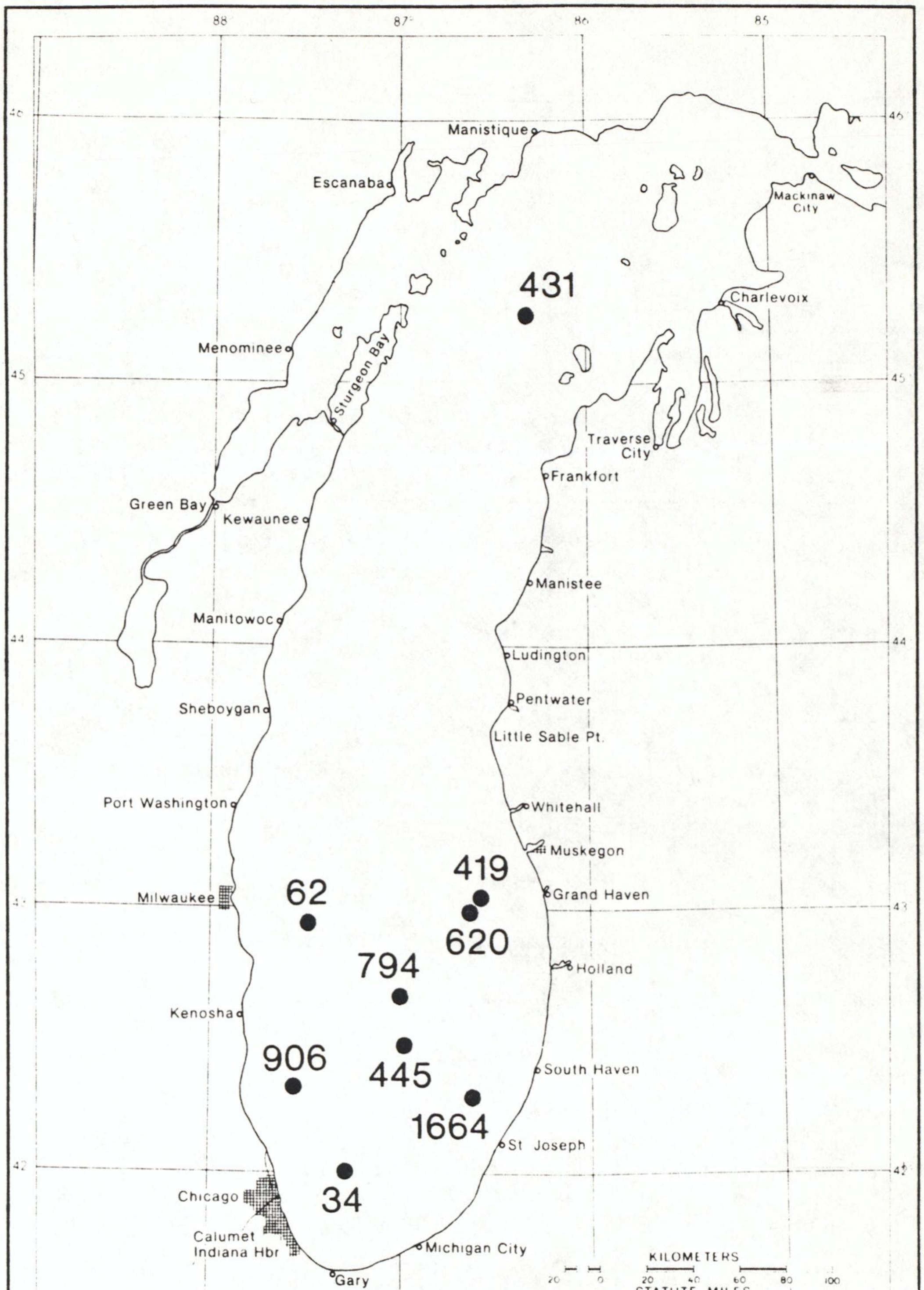

Figure 3. *The distribution of fluoranthene (ng/g) in the surficial sediments of Lake Michigan.*

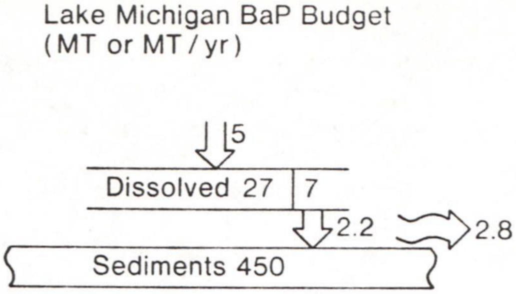

Figure 4. *Lake Michigan benzo(a)pyrene budget. The input (~5 MT/yr) is from Table 2. Concentration in the water column (7 ng/L, 80% dissolved) is from Eadie (1983) multiplied by the volume of the lake and distributed as 27 MT dissolved and 7 MT associated with particulate matter. Sedimentation is estimated from recent accumulation data (Robbins and Edgington, 1975) and trap fluxes (Chambers and Eadie, 1981), both of which are approximately 7 mg/cm^2/yr. This figure was multiplied by the lake area and a BaP concentration of 500 ng/g (Table 2). Sediment inventory was estimated for the upper 3 cm (well mixed, 2.6 g/cm^3, 80% porosity). The losses of approximately 2.8 MT/yr were calculated by difference.*

load, one calculates a relatively long apparent residence time of approximately 7 years for BaP in Lake Michigan water. The large reservoir of BaP in the surficial sediments may act as an important source for the water column through resuspension and diffusion. The load of 5 MT/yr, equivalent to 8.5 ng/cm^2/yr, is higher (by a factor of 35) than that calculated by Gischwend and Hites (1981) from a core in Lake Superior, but lower than their reported fluxes for urban sites.

Biological Effects

The complex mixtures and relatively high concentration of PAH in lake sediment has raised questions regarding the exposure of benthic organisms to these compounds, resultant bioconcentration factors, and the transfer of these compounds up the food chain to fish. In general, fish and some invertebrates have inducible mixed function oxidase systems capable of oxidizing PAH, resulting in low bioconcentration factors. Other invertetrates may lack the appropriate enzymes for biotransformation, resulting in large bioconcentration factors. Neff (1979) summarizes a great deal of information on biological uptake, accumulation, and degradation in the aquatic environment. Recent analyses of oligochaete worms and chironomids from Lake Erie and *Pontoporia* from Lake Michigan (Eadie *et al.*, 1982a,b) have shown that the PAH concentrations in these organisms are similar to those found in the fine-grained fraction of their sedimentary environment. Bioconcentration factors in *Pontoporia hoyi*, the most abundant benthic organism (by mass) in Lake Michigan, ranged from 10^4 to 10^5 with respect to the overlying water concentrations of seven measured PAH. Recent laboratory experiments with this organism confirm these bioconcentration factors for anthracene and BaP (Landrum, 1982). In *Pontoporia* from recent (fine-grained) sediments, concentrations of several PAH exceeded 1 ppm (wet wt.) (Eadie *et al.*, 1982b).

Do these concentrations present a serious threat to Great Lakes fish? The primary concern is the ability of PAH to cause cancer (Jones and Leber, 1979; Gelboin and Ts'o, 1978). Acute toxicity from these compounds is of major significance only in the immediate area of an oil spill. In addition, Leversee *et al.* (1982) recently described a high acute mortality rate for sunfish exposed to ppb concentrations of anthracene in the presence of sunlight. Benzo(a)pyrene adversely affected the hatching and early development of flatfish (Hose *et al.*, 1980) at very low ppb levels.

The limited amount of work on the chronic response of aquatic organisms has been summarized in Neff (1979) and Malins and Hodgins (1981). Both reviews agree that measurable effects of chronic exposure are probably limited to polluted coastal environments or locations of oil spills and that these locations are usually contaminated with a wide variety of pollutants, making it difficult to distinguish between cause and effect.

Since fish can enzymatically oxidize PAH, monitoring the ambient levels of PAH in fish does not measure their exposure. Payne and Fancey (1982) found elevated levels of mixed function oxidase in fish exposed to moderate levels of petroleum hydrocarbons, and they advocate monitoring this enzyme to determine if fish are being stressed by PAH.

Are PAH causing cancer in fish? Sonstegard (1977) found very high incidences of tumorous tissue in Great Lake fish that feed primarily on bottom organisms; yet he didn't detect any such malformations in an analysis of a museum collection of similar Great Lakes fish collected in 1952. The implication is that some carcinogenic or mutagenic agent(s) have been introduced into the Great Lakes since the early '50s. Many compounds or possible combinations of compounds could be those agents; PAH are certainly among them. High incidences of tumorous tissue in the carp and goldfish hybrids of Lake Erie tributaries have been correlated with high concentrations of PAH in sediments (Black *et al.*, 1980a,b). Liver tumors were found in the brown bullhead of the Black River, an input to Lake Erie that is highly contaminated with PAH (Baumann *et al.*, 1982). As mentioned above, these regions are usually contaminated with multiple pollutants that may have additive or synergistic effects with PAH. However, PAH in laboratory studies have induced tumors in fish (Jones and Hoffman, 1957; Schultz and Schultz, 1982; Black, 1982), and fish enzyme systems have been shown to produce carcinogenic metabolites (Neff, 1979). Thus, there is evidence of both chronic effects and carcinogenic/mutagenic responses in fish populations exposed to PAH. These effects are most severe near urban areas and for fish that live or feed on the bottom.

How does this exposure of fish to PAH affect human health? Since fish have the enzymes to biotransform PAH, exposure of bioaccumulated parent compounds will be minimal. While it has been reported that marine fish have levels of BaP up to 5000 ng/kg dry wt., the one reported level in fresh water fish (lake trout) was less than 4 ng/kg dry wt. (Neff, 1979). Based on a consumption of 0.5 kg of fish per day and the daily intake of PAH from other sources (Table 5) (Lee and Grant, 1981), lake trout would contribute less than 2% of the total intake of PAH. Since fish can biotransform PAH, the level of metabolites in fish may be quite high, depending on exposure. Research has not yet been performed to examine these levels, nor has the toxicity of these biotransformation products of PAH been determined. Therefore the hazards and the extent of exposure to the biotransformation products of PAH are unknown.

The Future of PAH in the Great Lakes

Although the seriousness of the exposure of benthic organisms and fish to PAH is currently supported only by circumstantial evidence, it appears that the load of PAH to the Great Lakes and consequent exposure will increase over the next few decades. This will result from increasing population and consequent increasing energy consumption. Regional population data are given in Table 6. Population for the year 2000 is estimated to be approximately 10%

Table 5. *Human exposure to PAH from various environmental sources*

Source	BaP	µg/day carcinogenic PAH	Total PAH
Air	0.00095-0.0435	0.038	0.207
Water	0.0011	0.0042	0.0270
Food	0.16-1.6		1.6-16

Table 6. *Population data for the Great Lakes States (millions)*

	1970[1]	1980[2]	1990[3]	2000[3]	2050[4]
U.S. Total	203,000	222,000	243,000	260,000	316,000
Illinois	11,113	11,418	12,015	12,491	
Indiana	5,196	5,490	5,804	6,069	
Ohio	10,657	10,797	11,570	11,999	
Michigan	8,882	9,258	10,302	10,970	
New York	18,241	17,557	18,528	18,816	
Pennsylvania	11,801	11,913	12,272	12,465	
Minnesota	3,806	4,077	4,382	4,637	
Wisconsin	4,418	4,705	5,156	5,476	
GL States Total	73,394	75,215	80,029	82,923	

[1] U.S. Bureau of Census, 1979.

[2] U.S. Bureau of Census, 1981.

[3] U.S. Bureau of Census (1979), Projection IIA.

[4] Schurr *et al.* (1979), p. 110; no estimates given by state.

larger than the current population, a somewhat slower rate of growth than the country as a whole. It is expected that growth on the Canadian side will be similar.

A study by the National Academy of Sciences (1979, p. 204) has concluded that, because of its availability, coal will be a key element in the United States energy policy well beyond the end of the century. They estimate that three times the present level of production, or about 45 quads (1 quad =

10^{15} BTU), annually will provide one-third to one-half of the nation's energy compared to 18% (14 quads of 78 quads) in 1978. A regional study (Great Lakes Basin Commission, 1981) estimates that, by the year 2000, the use of coal will increase with respect to oil and gas, and that energy production within the basin will increase from 3.1 quads (1975) to 3.9 quads by 1990.

Information summarized for the United States in the late sixties (National Academy of Sciences, 1972) indicates that over 1200 Mt/yr of BaP were emitted each year. This amount was apparently reduced to approximately 300 MT/yr by the mid-1970s (Table 7). This 75% reduction in emissions

Table 7. *Estimated PAH emissions (Mt/yr)*

Period	BaP U.S.[1] late '60s	BaP U.S.[2] 1975	BaP Ontario[3] 1976	Total PAH U.S.[4] mid '70s
Heat and Power				
Coal	431.0	27.0	0.013	184.0
Oil	2.0	2.7	0.052	9.0
Gas	2.0	1.0	0.048	12.2
Wood	40.0	73.0	--	7674.0
Open burning	450.0	>52.0	--	2547.0
Coke production	20.0	110.0	9.33	632.0
Forest fires	140.0	11.0	8.16	1478.0
Mobile sources	22.0	13 0	0.323	2266.0
Grams emitted per capita	6.6	1.4	2.2	70.5

[1] NAS (1972).

[2] Faoro and Manning (1981).

[3] MOE (1979).

[4] Peters *et al.* (1981).

supports the National Air Surveillance Network's (NASN) estimate of a 75% reduction in the atmospheric concentration of BaP at 26 urban sites throughout the United States from 1966 to 1977 (Faoro and Manning, 1981). This decline has been observed at the Great Lakes Basin atmospheric monitoring stations (Figure 5). The decline has been attributed to a reduction in the use of coal and wood in residential heating, although with the recent rise in the price of

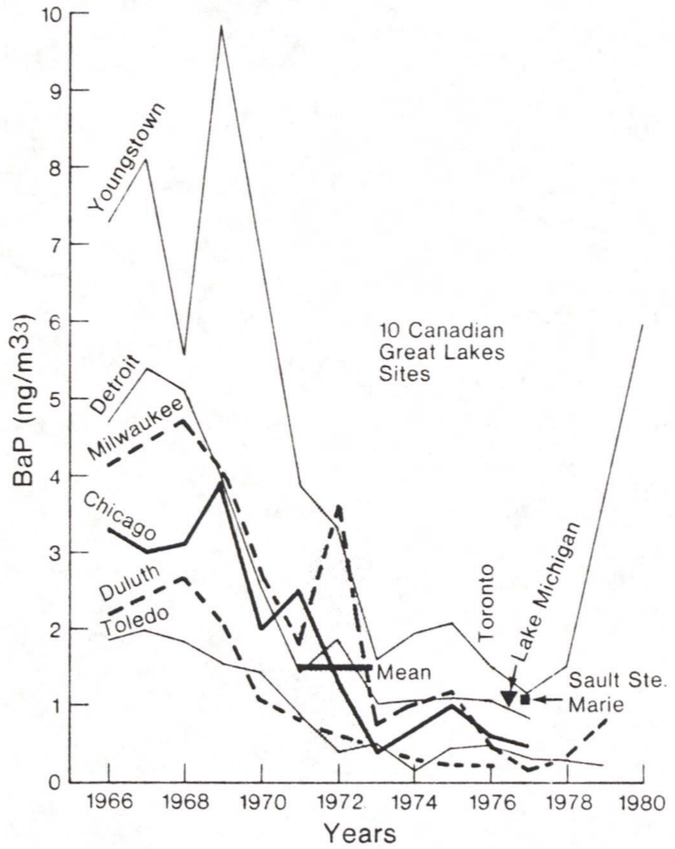

Figure 5. *Atmospheric concentration of benzo(a)pyrene in the Great Lakes Region. Data for United States cities are from the U.S. EPA/NASN (Faoro and Manning, 1981; Ackland, 1982). Data for 10 Canadian cities on the Great Lakes are from the Ontario Ministry of the Environment (MOE) (1979). Each of the 2-year averages falls within the gray zone; the grand mean for all the data is also shown. The Toronto data for 1976 is from Katz* et al. *(1978). The Lake Michigan data are from Strand and Andren (1980). The Sault St. Marie point is from the MOE (1979). Youngstown and Milwaukee both show recent increases in BaP concentrations.*

oil and gas, coal and wood use is again increasing (Peters *et al.*, 1981). Considering changes in sample collection and analysis techniques, it is not clear whether the reported decline in PAH is real or an artifact of the methods employed. Potvin *et al.* (1981) found no significant differences in atmospheric BaP measured between 1971 and 1975 and that between 1975 and 1979 at a site in northern Ontario. What is obvious from the four emission estimates in Table 7 is that there is considerable disagreement about the relative importance of even major sources of BaP. In the late 60s, the major sources were perceived to be open burning of refuse, followed closely by the combustion of coal for heat and power. By the mid '70s, this was altered to coke production in both the United States and Ontario. In the case of total PAH estimates, the major source for this period was the combustion of wood for heat and power. These estimates are rather weak since sampling procedures and analytical intercomparisons are not yet standardized or uniformly efficient for various environments. Bennett *et al.* (1979) found order of magnitude ranges in the PAH concentrations of oil fired power plant emissions (23-2550 ngPAH/m^3) and coal fired power plant emissions (24-378 ng PAH/m^3); thus the use of an average emission factor for each source type is only a gross approximation. In a literature review, Junk and Ford (1980) found 109 organics in coal combustion products and 331 in coal and refuse combustion, but stated that there are probably many more as yet uncollected or unidentified compounds. Many of these could have caused interference in earlier, less specific analytical procedures.

At this time it is unclear to what extent PAH emissions will increase with projected increased fossil fuel combustion. The fact that PAH are associated with submicron particles makes them very difficult to remove from stack gases. Increased use of "dirty" fuels, such as coal and wood, will further increase the potential for PAH production. If regional energy production increases by 25% (3.1 quads to 3.9 quads) as estimated by the Great Lakes Basin Commission (1981) report and if this increase is primarily in the form of coal and wood combustion, then based on the figures in Table 7, we can conservatively estimate an increase of 10% in the loads of PAH to the lake. As long as rates of removal from the ecosystem remain the same or even decrease because of a reduction in primary productivity caused by the Great Lakes phosphorus abatement program, concentrations of PAH within the Great Lakes ecosystem will increase.

Acknowledgments

We would like to thank the crew of the R/V *Shenehon* for their assistance in sample collection; Warren Faust, Nancy Moorehead, and Sheila Nihart for their analytical assistance; and Drs. John Robbins and Wayne Gardner for helpful comments. This work was jointly funded by the Office of Marine Pollution Assessment, NOAA, and the Great Lakes Environmental Research Laboratory, NOAA.

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PROGRESS REPORT

October, 1983

1. Organization: Great Lakes Environmental Research Laboratory
   2300 Washtenaw Avenue, Ann Arbor, MI 48104.

2. Principal Investigator: Brian J. Eadie.

3. Title: Long-term Behavior and Fate of Polycyclic Aromatic Hydrocarbons and Other Toxic Organic Contaminants in the Great Lakes.

4. Project Summary: The objectives of this project are 1) to develop and calibrate long-term toxic cycling models for the Great Lakes and (2) to conduct experiments on processes which affect the transport of synthetic organic compounds across the sediment-water interface.

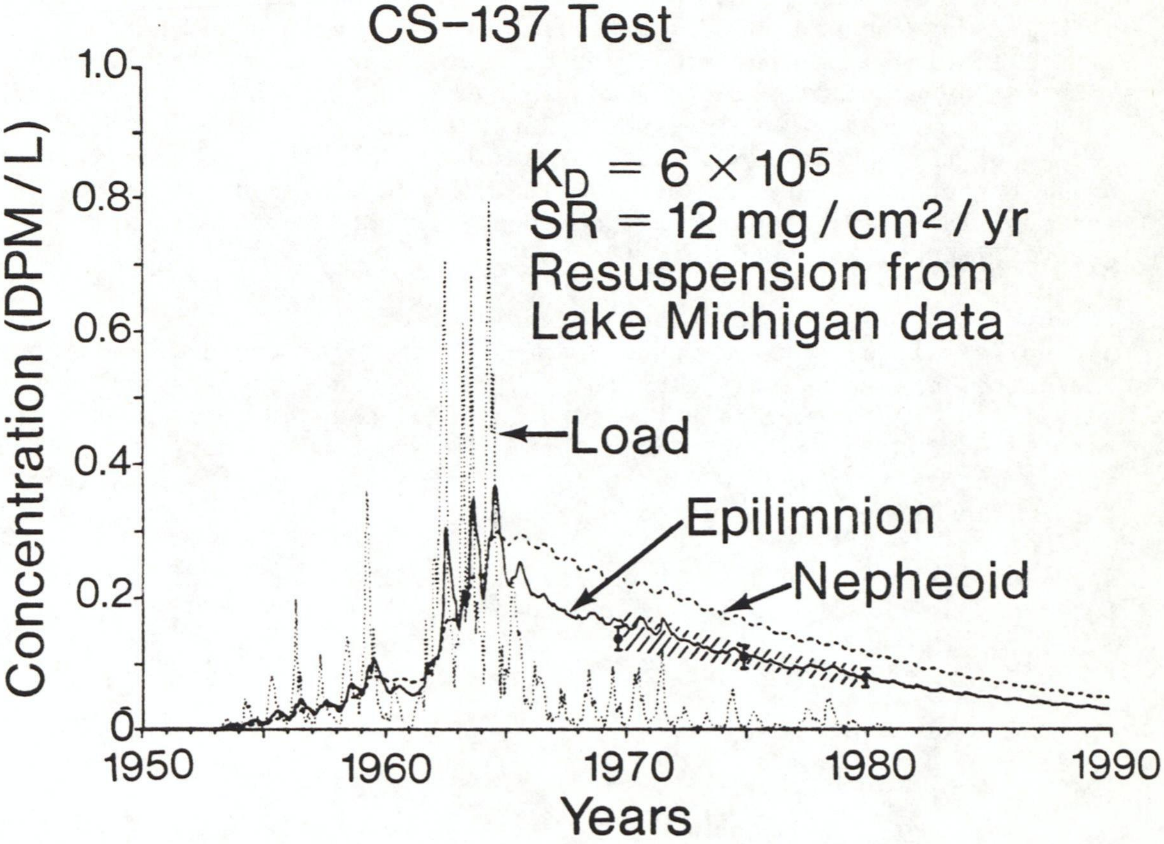
5. Status: Part I. During the past year, efforts have been made to design a toxic cycling model which includes the effect of sediment resuspension and reequilibriation of sediments with the water column. Initial calibration runs for this model have been made using Cesium 137 (a fall-out radionuclide) data. This isotope was employed for several reasons: 1) there are extensive data on the lead (monthly for 30 years), water column and sediment distributions and 2) Cs-137 exhibits similar partitioning behavior to many of the trace organics. Results from these calibration runs are shown in figure 1. The simulation represents southern Lake Michigan for which we have resuspension rates estimated from sediment traps. The model appears relatively insensitive to 50% changes in resuspension. Recent field work with our traps indicates that month to month changes can be nearer to an order of magnitude and may have significant impact on the model. Current results indicate that resuspension is acting as a scrubbing mechanism and is continuing to reduce the annual average concentration of Cs 137 in the water column. Initial efforts to model organics with this simulation have encountered the major problem of lack of load information. We are addressing this through the analyses of carefully studied cores of recent sediments from which we plan to reconstruct lake loads (see report by John Robbins).

   Part II. Sediment trap studies. During the past year there have been three major sediment trap experiments designed to gain a more quantitative estimate of resuspension and particle fluxes in Lake Michigan. The first was an examination of monthly fluxes at a 100 m deep station, 35 km offshore southeastern Lake Michigan. Early analysis of the data indicates significant month to month variation in mass fluxes. Radionuclide analyses show that during stratification, there is no measurable exchange between the resuspended material and the epilimnion - while after fall overturn the injection of resuspended matter into surface waters is large. The second experiment was designed to collect material for the whole winter period at five deep water locations around the lake. This was successful and the traps were redeployed to collect material for the period of stratification. We have shown that during stratification, near surface traps collect fresh material and we believe they can be used to estimate loads to the lake. The third experiment, currently underway, involves the collection of trap samples from the center of the southern basin of Lake Michigan on a biweekly basis from April through November. These samples will be analyzed for nutrients, radionuclides, and aromatic hydrocarbons; such temporal data will greatly improve our modeling efforts.

Polycyclic Aromatic Hydrocarbons: Analyses of PAH have continued. We are using this class of compounds as surrogates for toxic organics because they are relatively easy to analyze for and span a range of solubility of approximately five orders of magnitude. Our laboratory results of PAH in various samples from the Great Lakes has led us to be intimately involved in developing the standards to be set by the International Joint Commission.

Appended is a copy of a paper on PAH in the Great Lakes which we prepared and which will appear as an appendix to the IJC 1983 annual report.

6. Products: See Program list.



Resuspension model calibration run for CS 137. The dotted line represents monthly CS 137 load data. The other two lines, labelled Epilimnion and Nepheoid, are model output. The epilimnion simulation is in good agreement with the nine available data points which all fall within the hatched area. The two "tuning" variables, partition coefficient (K_D) and sediment accumulation rate (SR), are well within reported values ($10^5 > K_D > 10^6$; SR = 10±5).

1. Organization: DOC/NOAA/GLERL

2. Principal Investigator: John A. Robbins

3. Amount of 1983 Funds: In House

4. Total Project Funds to Date: In House

5. Title: Present and historical fluxes of contaminants to Great Lakes Sediments

6. Project Summary: The aim of this study is (1) to build an optimally self-consistent description of sedimentation, bioturbation, diffusion, and reaction for contaminants (inorganics, organic and radionuclides) in a series of cores from each of the Great Lakes to aid development of long-term modeling efforts and (2) to use historical records of contaminant fluxes reconstructed from self-consistent diagenetic models as a form of ground truth for models describing the behavior of contaminants in the water column. To this end sediment cores of high quality (large box cores) are being collected from areas of the open lakes with maximum sedimentation. High sedimentation rates generally improve the time resolution in reconstruction of time-dependent fluxes. Core sections are being analyzed for a host of constituents (major elements, amorphous silicon, phosphorus, diatoms, inorganic and organic contaminants and natural and fallout radionuclides) by many different researchers at several participating institutions.

   Status: Within the past six months there have been several important developments. (1) Box cores from selected sites in Lake Superior were collected by U. S. and Canadian researchers via the *C.S.S. Limnos* (July 12-19, 1983). Materials from cores carefully sectioned aboard ship have been distributed to participants in this study. (2) One Lake Superior core has already been analyzed for fallout ^{137}Cs and reveals surface activities of over 50 dpm/g which far exceed activities found in the other lakes. In cores from eastern Lake Erie, for example, activities are roughly 3 dpm/g. The probably explantion: total ^{137}Cs loading, essentially the same from lake to lake, is diluted by less sediment in Superior than Erie and other lakes. Such results are of importance in modeling the behavior of the radionuclide since its apparently slower burial in Superior can mean a longer persistence in the water column. (3) The distribution of ^{137}Cs has been determined in essentially all the Lake Erie cores collected last year. In addition distributions of ^{7}Be ($t_{\frac{1}{2}}$ = 53.4 days) have been measured in three of these cores.

   An example is provided in the accompanying figure. The activity of ^{137}Cs in this core from the eastern end of Lake Erie extends all the way to the bottom of the box core. In no other location in open waters of the

Great Lakes is the sedimentation rate so high (0.6 g/cm^2 yr ∿ 1.6 cm/yr). The 1963-1964 peak fallout occurs at 33 cm depth. The histogram curve which closely follows the data points, connected by dashed lines, is the theoretical result based on the steady state mixing model indicating roughly 8 cm of long-term mixing. This extent of mixing implies a time resolution of less than five years in this core! The shaded histogram is the distribution expected in the absence of mixing (same sedimentation rate) if transfer from air to sediments were immediate. These periodic departures of the activity from the mixing model results correspond to past 1963-1964 atmospheric testing episodes. Their appearance within the mixed zone indicates that mixing is not complete. The distribution of ^{7}Be in the same core further illustrates that sediment mixing cannot be treated as an instantaneous process at least on seasonal time scales. The activity of this isotope decreases exponentially with depth within the mixed zone. Rates of advective mixing inferred from this profile, compare favorably with the rate calculated from densities of convey-belt feeding zoobenthos at this location. (3) The steady-state mixing model has been modified to properly take account of the conveyor-belt type of sediment redistribution in the Great Lakes. Initial results indicate that details such as those seen in profiles of ^{137}Cs in the eastern Lake Erie cores and ^{7}Be can be described correctly by that approach. (4) In this study field work alone has extended over a three-year period in which Lake Ontario was cored in June, 1981; Huron and Michigan in October, 1981; Erie in 1982; and Superior in 1983. While the field phase of the study is largely complete, the analytical work is expected to continue for several years, with cores collected earliest generally ahead in work-up. Studies on the Ontario and Erie cores are sufficiently far along that there have been several presentations and a publication within this reporting period (see Products below).

Directions: During the next six-month period activities in this study will include (1) planning of the AGU/ASLO (Jan. 1984 New Orleans) session on contaminants, transport and transbioturbation processes in Great Lakes sediments, (2) calibration of the new mixing-sedimentation model and its application to profiles of ^{7}Be and ^{137}Cs, (3) coupling sediment fluxes to whole lake models for ^{137}Cs, (4) applying the mixing-sedimentation model to stable lead profiles, (5) initiating the experiment on the partitioning and mobility of ^{137}Cs (and ^{210}Pb) in sediments, (6) formulating the mixing-sedimentation model for a two-phase system with reaction terms, and (7) continuing radionuclide and stable element analysis of core materials from Superior and Erie.

Products

A. Papers at Meetings

Johansen, K. A. and J. A. Robbins. Use of Be-7, Ce-144, and Cs-137 to characterize short-term mixing processes and rates in Great Lakes sediments. American Society of Limnology and Oceanography Fall Meeting, San Francisco, Calif., December 7-15, 1982.

Robbins, J. A. and K. A. Johansen. Beryllium-7: A tracer of short term sediment mixint processes in the Great Lakes. 26th Conference on Great Lakes Research, International Association for Great Lakes Research, Oswego, N.Y., May 24-26, 1983.

Rossman, R., R. A. Bourbonniere, K. A. Johansen, and J. A. Robbins. Vertical variation of metals in dated Lake Ontario sediment cores. 26th Conference on Great Lakes Research, International Association for Great Lakes Research, Oswego, N.Y., May 24-26, 1983.

Johansen, K. A., R. Rossman, and J. A. Robbins. History of lead and mercury deposition in lead-210 and cesium-137 dated cores from eastern Lake Ontario. 26th Conference on Great Lakes Research, International Association for Great Lakes Research, Oswego, N.Y. May 24-26, 1983.

Eisenreich, S. J., P. D. Chapel, J. A. Robbins, and R. A. Bourbonniere. Chlorinated hydrocarbon concentrations and fluxes in sediment cores from eastern Lake Ontario. 26th Conference on Great Lakes Research, International Association for Great Lakes Research, Oswego, N.Y., May 24-26, 1983.

Johansen, K. A. and J. A. Robbins. Patterns of sedimentation and metal contaminant deposition in southern Lake Huron. Invited paper for the 26th Conference on Great Lakes Research, Oswego, N.Y., May 24-26, 1983.

Schelske, C. L., E. F. Stoermer, D. J. Conley, J. A. Robbins, and R. M. Glover. Sedimentary evidence for anthropogenic modifications of silica cycles in the Great Lakes. 26th Conference on Great Lakes Research, Oswego, N.Y., May 24-26, 1983.

Keilty, T., J. A. Robbins, and D. S. White. Relations between organism densities, organic carbon, and sediment accumulation rates in Lake Michigan. 26th Conference on Great Lakes Research, Oswego, N.Y., May 24-26, 1983.

Keilty, T., E. F. Stoermer, and J. A. Robbins. *Cyclotella comensis* from Lake Huron in Lake Erie sediments: Evidence for near-bottom transport? 26th Conference on Great Lakes Research, Oswego, N.Y., May 24-26, 1983.

Keilty, T. and J. A. Robbins. Are tubificid abundances in Lake Erie sediments controlled by the rate of supply of organic carbon? 46th Annual Meeting of the American Society of Limnology and Oceanography, St. Johns, Newfoundland, June 13-16, 1983.

Rice, C. P., Meyers, P. A., Eadie, B. J., and Robbins, J. A. Sources, transport, and degradation of organic matter components associated with sedimentary particles in Lake Michigan. Sixth International Symposium on Environmental Biology, Santa Fe, New Mexico, October 9-14, 1983.

Johansen, K. A. and Robbins, J. A. The fate of allout ^{137}Cs in Lake Huron. The 28th Annual Meeting of the Health Physics Society, Baltimore, MD, June 19-23, 1983.

B. Seminars

"Long-term behavior of natural and fallout radionuclides in the North American Great Lakes"
Dept. of Oceanography, University of Washington, Seattle, Feb. 10, 1982.

"^{7}Be and ^{137}Cs fluxes in Lake Michigan"
Great Lakes Environmental Research Laboratory, Ann Arbor, Feb. 17, 1982.

"Radioactivity in the Great Lakes"
School of Natural Resources, University of Michigan
Ann Arbor, MI, March 28, 1983.

"Deposition rates and mass distributions of particle associated pollutants in the Great Lakes"
Cranbrook Institute of Science, Workshop on the transport and fate of particle associated pollutants in the Great Lakes, April 12-14, 1983.

"Contaminant Integration Processes in the Great Lakes Ecosystem: the role of Benthic Organisms"
Great Lakes Environmental Research Laboratory
Ann Arbor, MI, April 21, 1983.

"Recent studies of particle transport in Lake Michigan using ^{7}Be"
Radiological and Environmental Research Division
Argonne National Laboratory, Argonne, IL, April 26, 1983.

"Cosmogenic ^{7}Be and fallout ^{137}Cs in Lake Michigan: Behavior of two radionuclides with contrasting half-lives"
Water Chemistry Laboratory
University of Wisconsin, Madison, WI, April 28, 1983.

C. Articles

Eadie, B. J., S. Nihart, and J. A. Robbins. Study of early diagenesis of compounds in Great Lakes sediments is underway. Coastal Oceanography and Climatology News, Recent Events in United States Coastal Waters, Center for Ocean Management Studies, University of Rhode Island, Rhode Island, 4 (1982) 43.

Schelske, C. L., E. F. Stoermer, D. J. Conley, J. A. Robbins, and R. M. Glover. Early eutrophication of the lower Great Lakes: New evidence from biogenic silica in sediments. Science. (In Press June 1983).

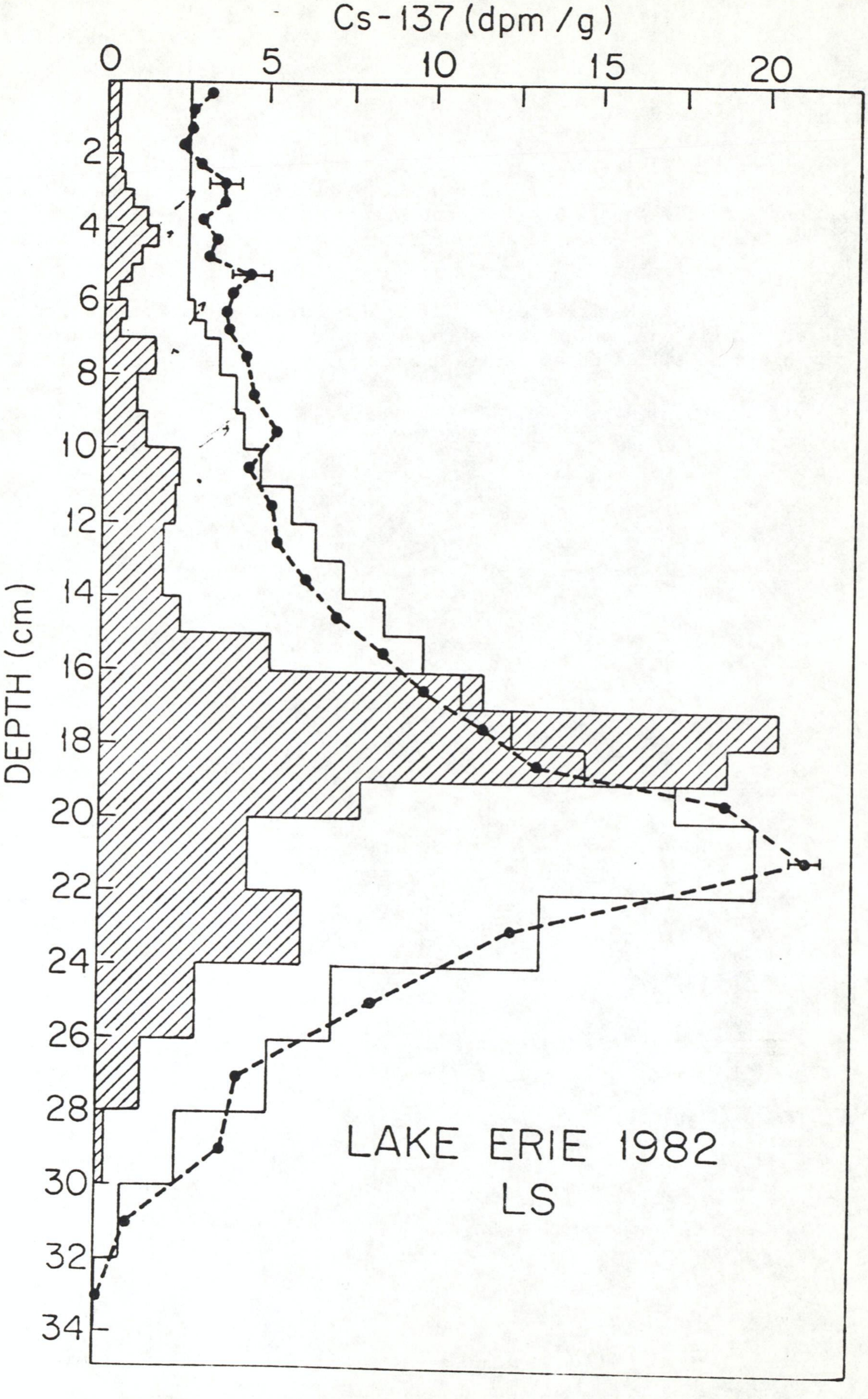

Cs-137 (dpm /g)
0
5
10
15
20
DEPTH (cm)
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
LAKE ERIE 1982
LS

Figure 1a.

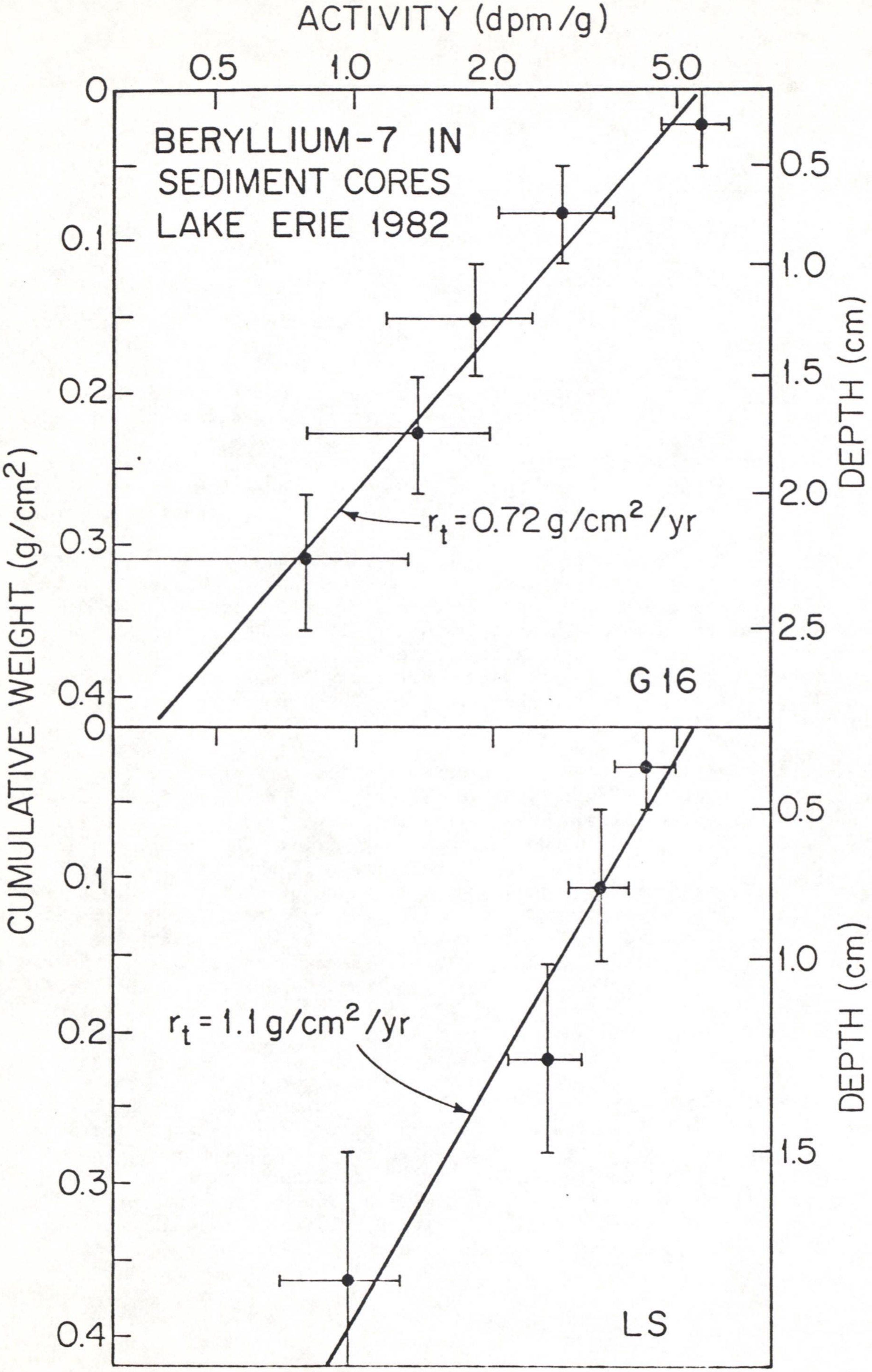

ACTIVITY (dpm/g)
0.5
1.0
2.0
5.0
BERYLLIUM-7 IN
SEDIMENT CORES
LAKE ERIE 1982
CUMULATIVE WEIGHT (g/cm2)
DEPTH (cm)
0
0.1
0.2
0.3
0.4
0.5
1.0
1.5
2.0
2.5
rt = 0.72 g/cm2/yr
G 16
rt = 1.1 g/cm2/yr
LS

Figure 1b.

1. Organization: Great Lakes Research Division
The University of Michigan
2200 Bonisteel Blvd.
Ann Arbor, MI 48109

2. Principal Investigators: Ronald Rossmann and Kjell A. Johansen

3. Amount of 1983 Funds: $47,125.

4. Total Project Funds to Date: $93,231.

5. Title: Determination of Present and Historical Fluxes in High Sedimentation Rate Areas of the Great Lakes.

6. Project Summary: The sedimentary environment of deposition is being described in detail. This includes measurement of sedimentation rates, depth of surficial sediment mixing, dilution of contaminants by non-contaminated sediments, the depth of sediment oxygenation, and the flux of metal contaminants to the sediment. From these data, the post-depositional redistribution (diagenesis, physical mixing) of contaminants is described.

7. Status: Core collection and analyses are proceeding on schedule. The latest set of cores was obtained from Lake Superior during July 1983. Several of these cores have been freeze-dried, and measurement of Cs-137 and Be-7 has begun. Cs-137 analyses of the 1982 Lake Erie cores is complete. Analysis for Ca, Mg, and selected heavy metals used to help describe the Lake Erie sedimentary environment is more than 50 percent complete. Lead-210 analyses have been completed for 7-1/2 of the nine Lake Erie cores.

The Pb-210 profiles from the high sedimentation rate areas of the eastern basin of Lake Erie are strikingly different from Pb-210 profiles obtained in the other Great Lakes. These differences are illustrated in Figure 1 by the Pb-210 profiles in two different box cores. The Pb-210 profile from a high sedimentation rate area of Lake Ontario (Figure 1a) is typical of Pb-210 profiles from the Great Lakes. A region of uniform Pb-210 activity near the sediment-water interface is followed by decreasing Pb-210 activity which is at supported levels at a depth of 34-36 cm. In contrast, the Pb-210 profile from the eastern basin of Lake Erie barely has changed over the same depth interval (Figure 1b). The Pb-210 activity in this profile is fairly uniform to a depth of 15 cm and then begins a very slow decline. Supported Pb-210 levels were not reached at a depth of 42 cm which is the maximum penetration of the box corer.

The difference between the two profiles results from the much higher sedimentation rate in this area of Lake Erie (about 7 cm/yr) as compared to that of the Lake Ontario location (roughly 0.3 cm/yr). Fortunately, the supported levels of Pb-210 can be obtained from the bottoms of 1-1.5 meter long gravity cores obtained at the same locations as the box cores. The determination of the levels of supported Pb-210 activity will enable us to calculate sedimentation rates for the shorter box cores.

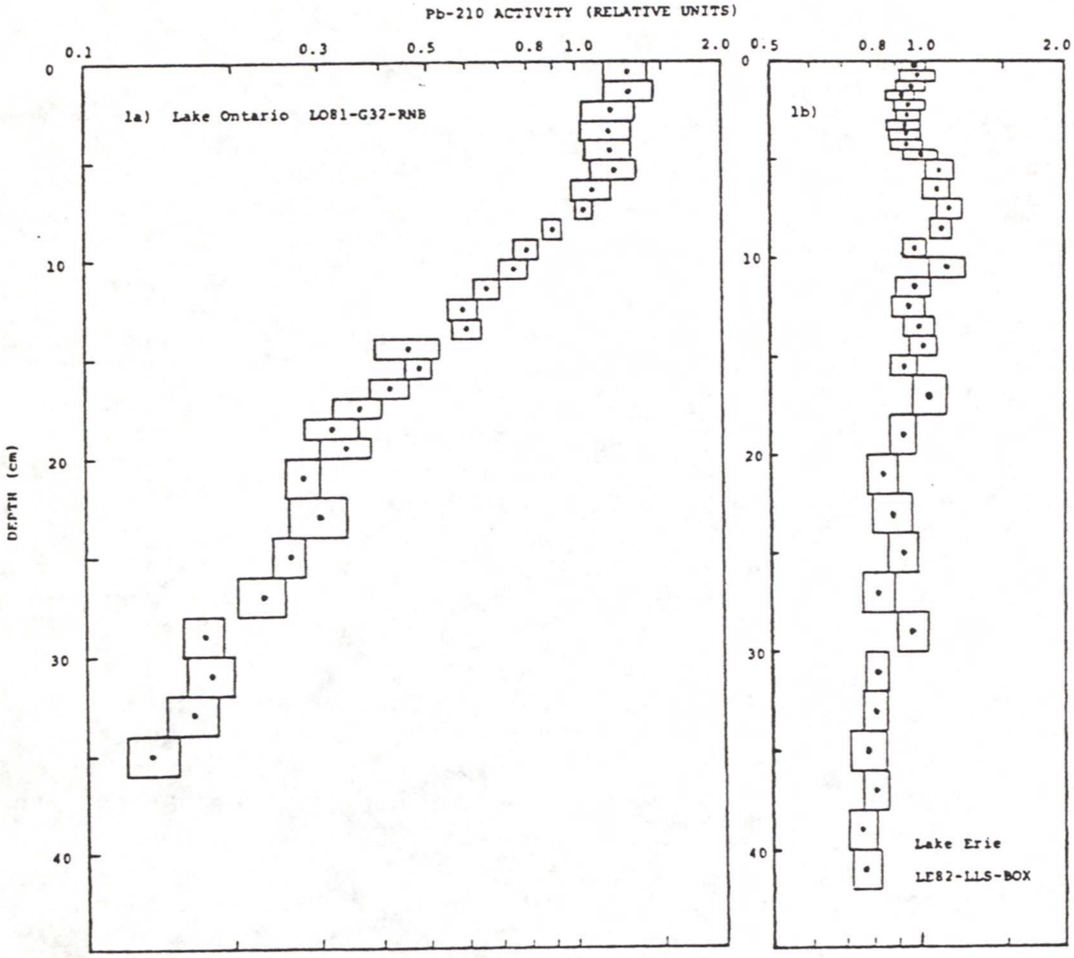


Figure 1. Lead-210 profiles. Height of box equals the sampling interval. Box width equals ± 2 standard deviations based on counting statistics.

PROGRESS REPORT

September, 1983

1. Organization: Environmental Engineering Program
   122 CME Bldg.
   University of Minnesota
   Minneapolis, MN 55455

2. Principal Investigator: Steven J. Eisenreich SJE

3. Amount of 1983 Funds:

4. Total Project Funds to Date:

5. Title: Toxic Organic - Sediment Dynamics in the Great Lakes

6. Project Summary: The overall objective of this research project is to examine the processes responsible for the accumulation, transformations and mobility of toxic organics in sediments of the Great Lakes. To this end, detailed sediment cores obtained with box (Ontario, Erie, Huron, Superior) and benthos corers (Michigan) have been collected in 1981-83 from sites in all of the Great Lakes. Sedimentation rates of neighboring sites vary by factors of 2 to 4. The numerous cores have been sectioned into 0.5 cm (Superior) and 1.0 cm (Ontario, Erie, Huron, Michigan) depth increments and analyses conducted for a variety of hydrophobic organic compounds. Diagenetic processes involving such organics are being studied by analyzing cores for species differing in their ability to partition to sediment of varying organic content. Organics selected for intense study include PCB congeners (K_{ow} = 4-8), DDT-group species, and various other chlorinated hydrocarbons, including α, β,γ-BHC, mirex, and HCB.

   Several box cores from Lakes Erie, Huron and Superior have been analyzed for the above chlorinated species in pore water increments. Pore water was separated by centrifugation/filtration on board ship in 2-cm depth increments, sometimes to depths as low as 10 to 20 cm.

   The Lake Ontario cores and all pore water have been analyzed completely, Lake Michigan data await final determination of sedimentation and mixing parameters, and Lake Huron cores have been analyzed and are now being interpreted. Present emphasis is placed on analysis of Lake Erie cores taken in 1982 and supplemented in 1983 at sites G-16, LE-LS and LE-MS. The value of these cores is emphasized by the depth/time resolution available (1 cm/months).

7. Status: Significant progress has been made in the last year in the analysis and interpretation of box core and pore water data. The Lake Ontario core data will be discussed in detail but results are similar for other lake cores. The sedimentation data for the two cores analyzed based on Pb-210 chronology are:

	LO E-30	LO G-32	
R	0.0443±.0027	0.0795±.0031	$g/cm^2/yr$
W	$\sim$ 0.2	$\sim$ 0.3	cm/yr
S	0.50 ± .08	0.92 ± .10	g/cm^2
t_r^*	11.3	11.6	yrs.

$^*t_r = S/R$

Figures 1a-c show the concentration and flux profiles for PCBs in E-30 and G-32. The data show that the peak in PCB concentration occurs at 3-4 cm in E-30 and 5-6 cm in G-32, both corresponding to the bottom of the mixed depth(s) as calculated from the rapid steady state mixing model employing Pb-210 as the tracer. However, there is resolution in PCB concentrations at depths shallower than S pointing out that steady-state mixing has not occurred for these species. This observation is consistent with the conclusions drawn by J. Robbins (NOAA), that steady-state mixing probably does not occur in time scales less than 10-15 years. When normalized to sediment age, PCB concentrations scale to about the same profile peaking in $\sim$ 1965-1968. Significant PCB concentrations appear first in the sediment profile (both cores) at $\sim$ 1955. Analysis of individual PCB congeners shows that the lighter chlorinated species are significantly more mobile than $N(Cl) \geq 5$. This explanation is consistent with the penetration of t-PCBs to sediment whose age is older than the onset of PCB production and the variation of K_{ow} with chlorine content. Statistical analysis of PCB congener behavior does not support the hypothesis that PCB congeners degrade, either aerobically and anaerobically. Figure 1c shows that the flux of t-PCBs is greater in G-32 than E-30, primarily a result of sediment focusing. The steady-state mixing model in conjunction with the estimated PCB input function adequately describes the PCB profile (Figure 41, p. 83, 3rd year rept.).

The mirex profiles in G-32 and E-30 are consistent with a 1970 plug input into Lake Ontario, with approximately equal sediment concentrations (Figs. 2a,b) leading to fluxes differing in the ratio to their sedimentation rates.

The DDT-group profiles show distinct regions of biological diagenesis. DDT undergoes oxidative transformation to DDE in the water column and oxygenated mixed area, and reductive transformation to TDE(DDD) in anaerobic "pockets" in surficial sediments and at depth. GC-MS analyses document the presence of p,p'-DDT to sediment depths corresponding to > 20 years establishing that transformation rates are affected by sedimentary processes such as adsorption. These data will permit the calculation of DDT transformation rates.

For persistent hydrophobic organics, transport and fate are dominated by associations (sorption/partitioning) with the high surface area, high organic content particles. Thus, the total quantity of hydrophobic organic in sediment cores ($\mu g/m^2$) differing in sedimentation rate should be directly related to the ratio of organic carbon fluxes. Figure 3 shows the relationship of accumulated mass of several different organics in the two cores. The data points cluster closely along the line representing the ratio of the organic carbon sedimentation rate, and not the mass sedimentation rate.

A summary of the pore water data for PCBs is given in Table 1. Concentrations are 10 to 300 times greater in pore water than in overlying lake water. PCBs in pore water are dominated by the lighter congeners while the sediment phase is dominated by the heavier congeners. Calculations suggest that the pore water contribution to sedimentary recycling of PCBs is minimal on a whole-lake process. Preliminary estimates from core data suggest the tortuosity-corrected diffusion coefficient is $\sim 10^{-7}$ cm^2/sec.

The principal short-term objective is to complete analysis of box cores collected in the Great Lakes. Resulting data will be used in conjunction with the newly-developed mixing model of J. Robbins to develop an overall dynamic model of describing the fate, distribution and diagenesis of hydrophobic organics. An important sub-objective is to develop a partitioning model which will describe field observations in water and sediments. The core and pore water data are invaluable in focusing the important aspects of the model and to provide empirical relationships between physical/chemical properties of these organics and environmental behavior. The use of $\sim$ 60 PCB congeners for which K_{ow} values are known (Rapaport and Eisenreich, EST, in press) is particularly valuable.

Figure 1

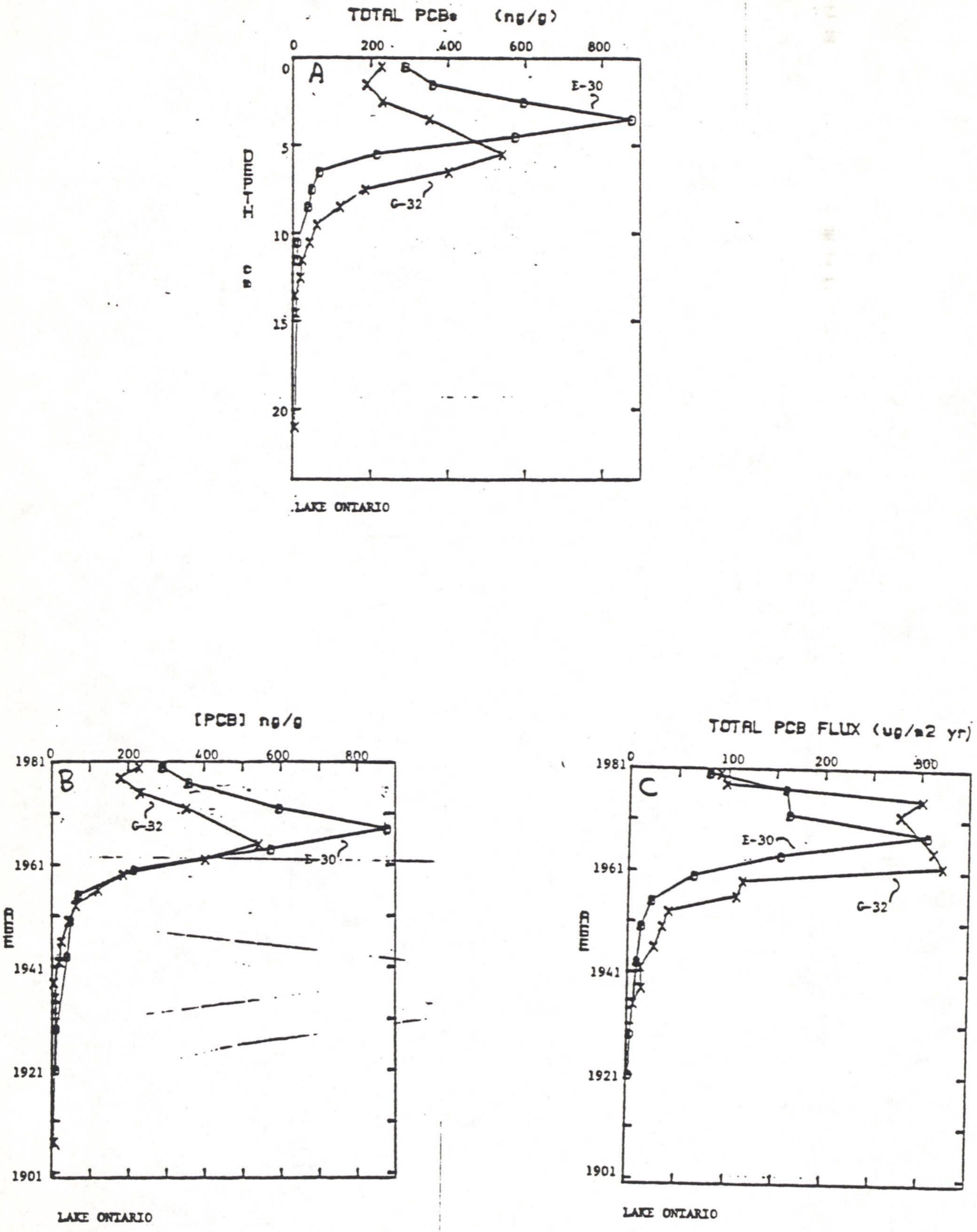

TOTAL PCBs (ng/g)
0
200
400
600
800
A
E-30
G-32
DEPTH
cm
0
5
10
15
20
LAKE ONTARIO
[PCB] ng/g
0
200
400
600
800
B
G-32
E-30
1981
1961
1941
1921
1901
DATE
LAKE ONTARIO
TOTAL PCB FLUX (ug/m2 yr)
0
100
200
300
C
E-30
G-32
1981
1961
1941
1921
1901
DATE
LAKE ONTARIO

Figure 2

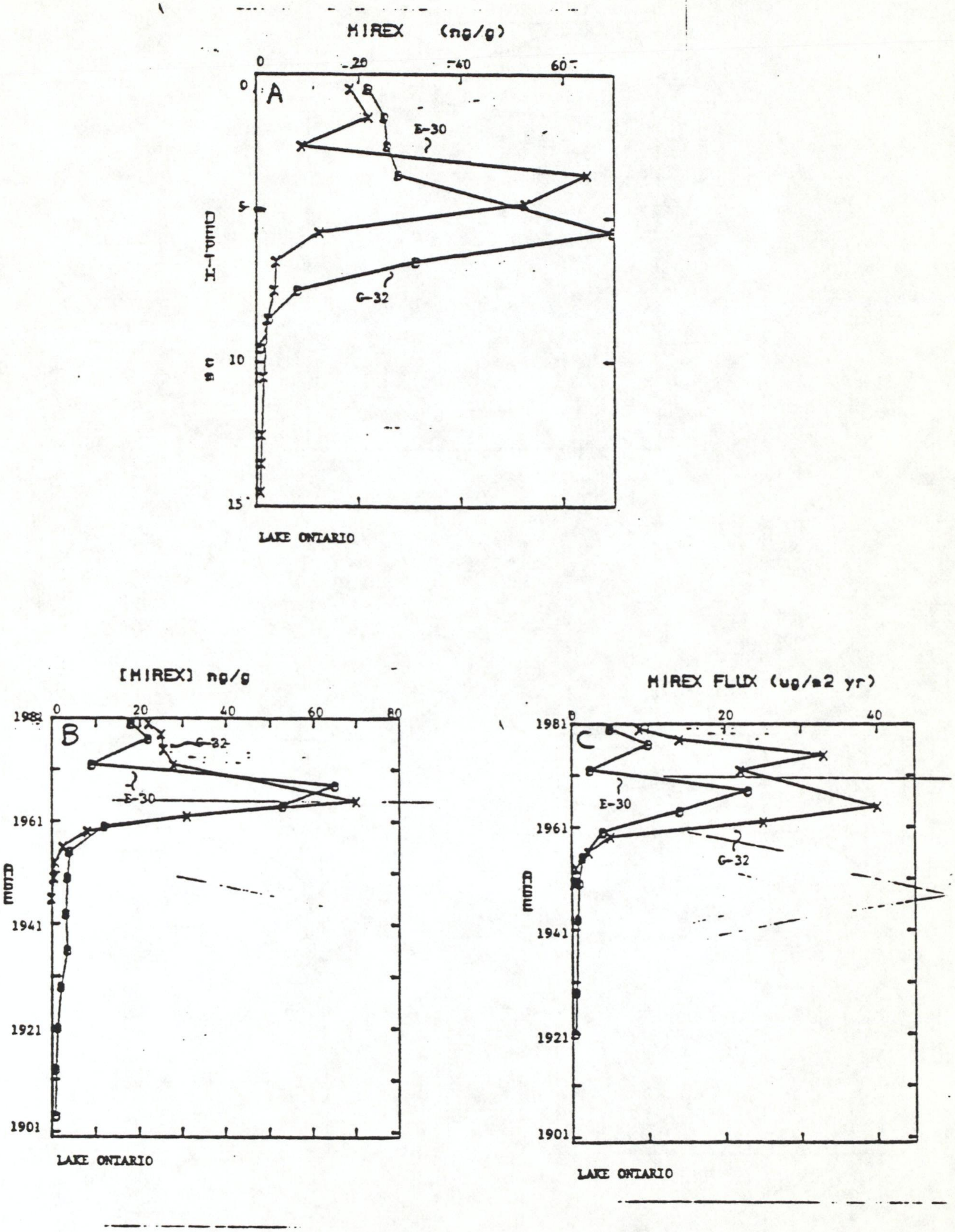

MIREX (ng/g)
0
20
40
60
A
E-30
G-32
0
5
10
15
cm
LAKE ONTARIO
[MIREX] ng/g
0
20
40
60
80
B
G-32
E-30
1981
1961
1941
1921
1901
LAKE ONTARIO
MIREX FLUX (ug/m2 yr)
0
20
40
C
E-30
G-32
1981
1961
1941
1921
1901
LAKE ONTARIO

Figure 3

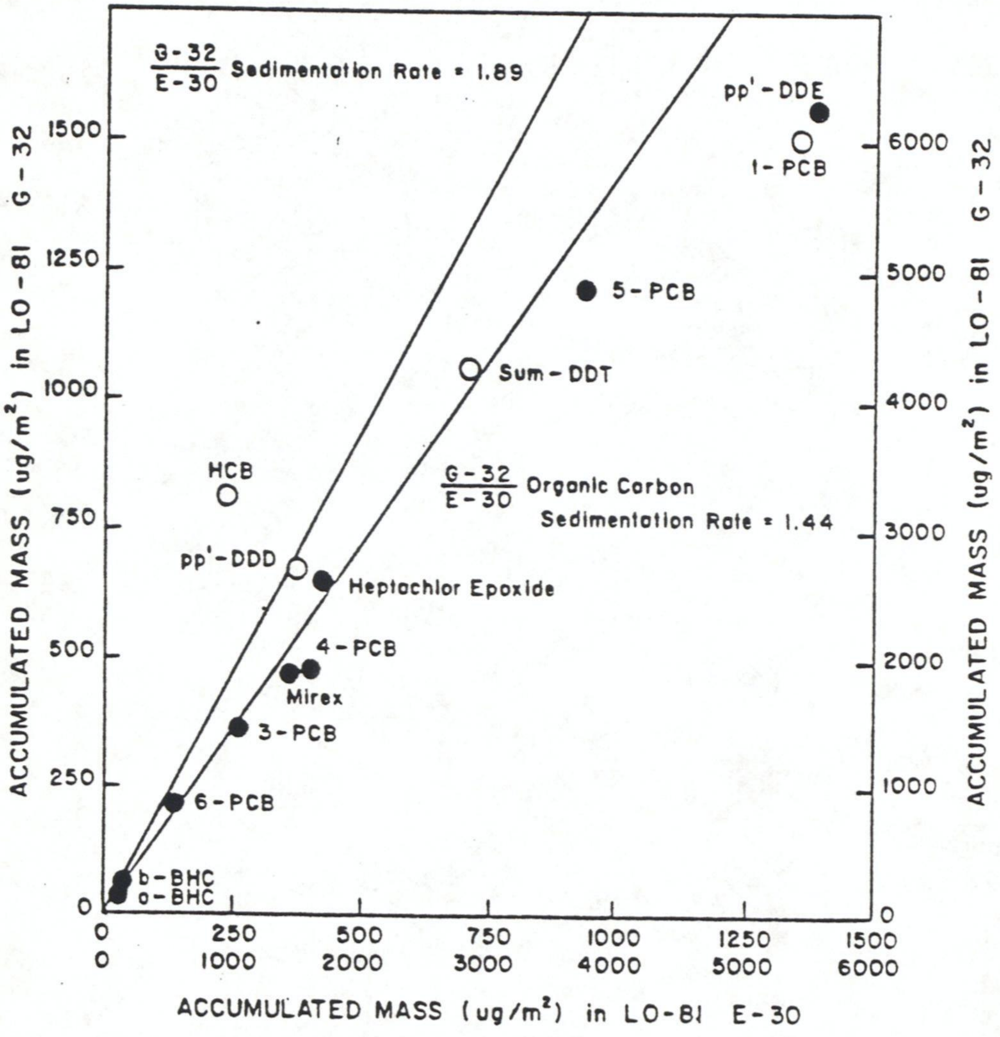

G-32 / E-30 Sedimentation Rate = 1.89
G-32 / E-30 Organic Carbon Sedimentation Rate = 1.44
pp'-DDE
1-PCB
5-PCB
Sum-DDT
HCB
pp'-DDD
Heptachlor Epoxide
4-PCB
Mirex
3-PCB
6-PCB
b-BHC
a-BHC
ACCUMULATED MASS (ug/m²) in LO-81 G-32
0
250
500
750
1000
1250
1500
ACCUMULATED MASS (ug/m²) in LO-81 G-32
0
1000
2000
3000
4000
5000
6000
0
250
500
750
1000
1250
1500
0
1000
2000
3000
4000
5000
6000
ACCUMULATED MASS (ug/m²) in LO-81 E-30

Table 1.

PCBs in Pore Water of Great Lakes' Sediments

Pore Water (ng/l)	Sediment (ng/g)	Kp (ng/g)p/ (ng/g/w	Site ID
Lake Superior			
26	5.0	190	9BX-81
18	7.9	440	19BX-81
12	7.8	640	31BX-81
9-35	9-19		2BX-81
~1	~1700	$\sim 10^6$	Lake
Lake Erie (HS-81)			
72	76	1060	0-2 cm
35	40	1160	2-4 cm
1-5	--	--	Lake
Lake Huron (HS-81)			
39	46	1180	0-2 cm
26	39	1520	2-4 cm
307	21	70	4-6 cm
~1	--	$\sim 10^6$	Lake

ANNUAL PROGRESS REPORT

1. Organization: Great Lakes Environmental Research Laboratory/NOAA, 2300 Washtenaw Avenue, Ann Arbor, MI 48104.

2. Principle Investigator: Dr. Peter F. Landrum.

3. Title: Role of Benthic Invertebrates in the Fate of Pollutants in the Great Lakes.

4. Project Summary: The objectives of this project are to determine the uptake, depuration and biotransformation rate constants for various toxic organics in Great Lakes invertebrates. A further objective is to determine the emperical relationships between the rate constants and environmental parameters such as temperature, pollutant concentration and sediment sorption. The past six months' work has focused on determining the rate constants for three additional polycyclic aromatic hydrocarbons (PAH) from water, the role of sediment sorbed PAH on the uptake by benthic invertebrates and the role of humic acids on the uptake rate constant from water.

5. Status: The uptake and depuration rate constants for three additional PAH, phenanthrene, benzo(a)pyrene, and pyrene, were determined from water. The uptake rate constants are 133±59 $mlg^{-1}h^{-1}$, 148±50 and 208±52 respectively and the depuration rate constants are 0.032±0.0092h^{-1}, 0.0022, 0.0017±0.0007 respectively. The uptake rate constant for pyrene seems unusually high and will require some additional investigation.

   Studies have continued on the uptake of sediment sorbed PAH. The uptake rate constant in *Pontoporeia hoyi* for benzo(a)pyrene (BaP) was small but reasonably reproducable, 0.0022±0.0013 g dry sediment g^{-1} animal h^{-1}. The similar rate constant for phenanthrene was 0.032±0.0092 g dry sediment g^{-1} animal h^{-1}. These rate constants were used in conjunction with the uptake rate constant from water and the depuration rate constant to predict steady state body burdens of phenanthrene and BaP for three different depths in Lake Michigan. The steady state body burdens compared well for the predicted and measured values, Table 1. The sediment-associated BaP is predicted to contribute 8-53% while the sediment-associated phenanthrene was predicted to contribute from 8-88% of the steady state body burden.

   A kinetics model for the bioaccumulation of PAH in *Pontoporeia hoyi* was developed to incorporate the uptake from water and sediment. The rate constants were allowed to vary with season, as had been determined for BaP, and temperature. The seasonal variation with temperature was taken from a relationship determined for whole lake data for Lake Ontario (McCormick, personal communication). From this model the body burden for the *P. hoyi* was predicted to vary with season with the highest concentrations in the winter and spring and declining in the fall (Figure 1).

Field studies are required to verify the seasonal variation in body burden. The average concentrations agree well with field measured values (Table 1).

Studies on the reduction of the bioavailability of PAH by humic acids indicate that Aldrich® humics reduce the uptake of most of the PAH studied. The I_{50} (the concentration of humic acid that reduces the apparent uptake by 50%) was 0.021±0.05 mg L^{-1} (X±1SD, n=5) Aldrich® humic acid for BaP, 0.73±0.012 (n=3) for benz(a)anthracene, 3.3 (n=2) for pyrene. Aldrich® humics could not affect the anthracene uptake sufficiently to reduce the uptake by 50%, however; the I_{25} was 15.8 mg L^{-1}. Phenanthrene uptake was not affected by the Aldrich® humic acid at any concentration studied (16 mg L^{-1}). Calculation of the uptake rate constant, assuming that the compound bound to the humic acid was not bioavailable, and calculating the fraction that was "freely dissolved" from the measured partition coefficient, gave uptake rate constants that were statistically the same as those measured when no humic acids were present. Thus the humic acid bound xenobiotic is unavailable on an acute time frame but will act as a source of reversibly bound compound.

Future studies will focus on the uptake from sediment for *P. hoyi* and continuing to define the seasonal and temperature variability of the rate constants. Additionally, toxicokinetic studies will be started for other benthic organisms and other compounds will be investigated as they become of importance.

6. PRODUCTS

Publications:

Spacie, A., P. F. Landrum, G. L. Leversee (1983). Rates of uptake, depuration, and biotransformation of anthracene and benzo(a)pyrene in bluegill sunfish. *Ecotoxicology and Environmental Safety* 7:330-341.

Haddock, J. D., P. F. Landrum, J. P. Giesy (1983). Factors affecting the extraction efficiency of anthracene from sediments. *Anal. Chem.* 55:1179-1200.

Landrum, P. F., S. M. Bartell, J. P. Giesy, G. J. Leversee, J. W. Bowling, J. D. Haddock, K. LaGory, S. Gerould, and M. Bruno. Fate of anthracene in an artificial stream: A case study. *Ecotoxicology and Environmental Safety*. (In Press.)

Landrum, P. F. (1983). The effect of co-contaminants on the bioavailability of polycyclic aromatic hydrocarbons to *Pontoporeia hoyi*. Polynuclear Aromatic Hydrocarbons: Formation, Metabolism, and Measurement. M. Cooke and A. J. Dennis eds. Battelle Press, Columbus, OH 731-744.

Eadie, B. J., W. R. Faust, P. F. Landrum, N. R. Morehead, W. S. Gardner, and T. Nalepa (1983). Polynuclear Aromatic Hydrocarbons: Formation, Metabolism, and Measurement. M. Cooke and A. J. Dennis eds. Battelle Press, Columbus, OH 437-450.

Manuscripts submitted:

Landrum, P. F., S. R. Nihart, B. J. Eadie, and W. S. Gardner. Reverse phase separation method for determining pollutant binding to Aldrich® humic acid and dissolve organic carbon of natural waters. *Environ. Sci. Technol.* (In Review).

Other contributions:

Seminar "NOAA's Role in the Great Lakes with an emphasis on Toxic Substances" presented: Michigan State University Center for Environmental Toxicology, Pesticide Research Center and Department of Fisheries and Wildlife, March 21, 1983, East Lansing, MI.

Table 1

STEADY STATE PREDICTIONS OF
PAH IN *PONTOPOREIA HOYI*

Compound	Predicted Concentrations		Measured Concentrations	% from Sediment	
Depth	Kinetics Model ng/g	Steady State ng/g	ng/g	Model	Steady State
Benzo(a)pyrene					
60m	1027±434	1079±402	900	46	53
45m	471±189	584±239	400	8	10
23m	286±147	570±237	280	6	8
Phenanthrene					
60m	5197±1781	6474±2611	1500	88	88
45m	912±299	1255±710	650	39	40
23m	454±117	824±634	200	8	8

STEADY STATE PREDICTIONS OF PAH IN *PONTOPOREIA HOYI*

Compound	Predicted Concentrations		Measured Concentrations	% from Sediment	
Depth	Kinetics Model ng/g	Steady State ng/g	ng/g	Model	Steady State
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60m	1027±434	1079±402	900	46	53
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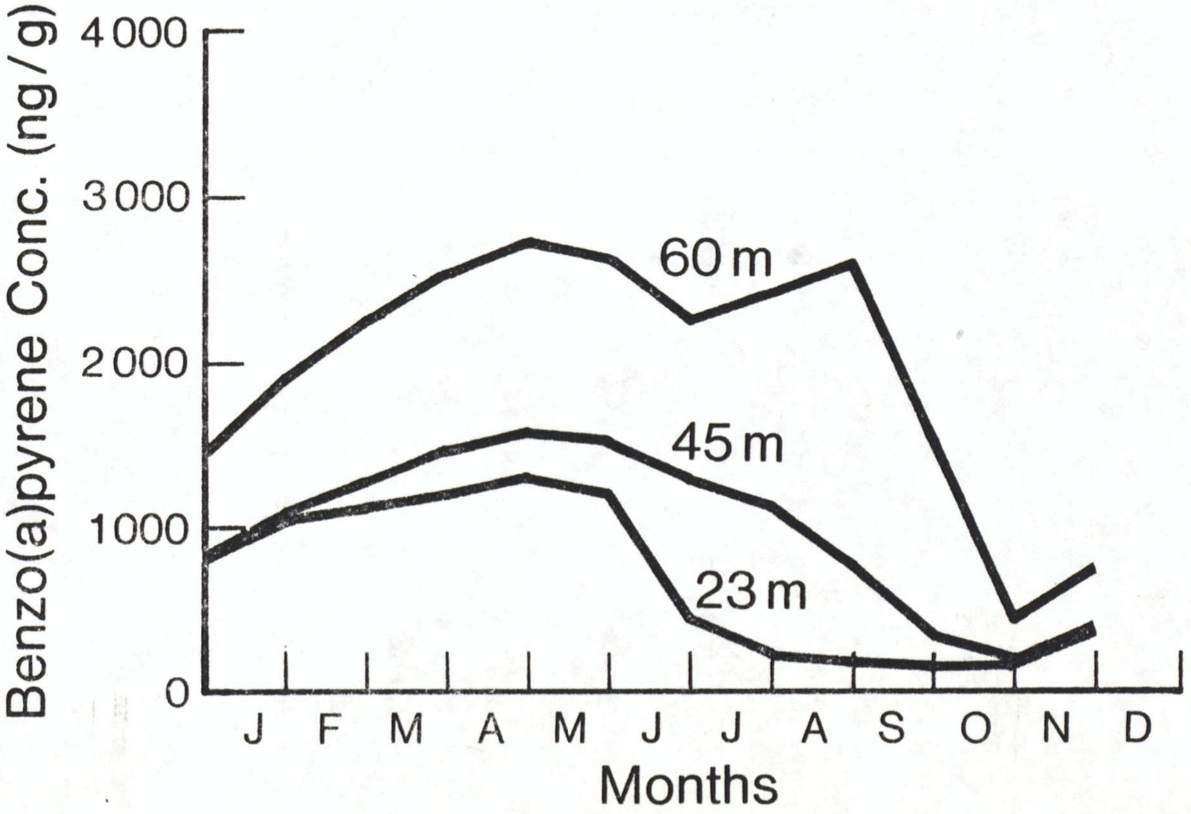
23m	286±147	570±237	280	6	8
Phenanthrene					
60m	5197±1781	6474±2611	1500	88	88
45m	912±299	1255±710	650	39	40
23m	454±117	824±634	200	8	8

Benzo(a)pyrene Uptake by *Pontoporeia hoyi*



PROGRESS REPORT

September, 1983

1. Organization: Great Lakes Environmental Research Laboratory
NOAA
2300 Washtenaw Ave.
Ann Arbor, MI 48104

2. Principal Investigator: David S. White
Great Lakes Research Division and
School of Natural Resources
University of Michigan
Ann Arbor, MI 48109

3. Amount of 1983 Funds: $19.8 K

4. Total Amount of Project Funds to Date: $19.8 K

5. Title: Redistribution of Sediment-Bound Toxic Organics by Benthic Invertibrates

6. Project Summary: The objectives of the project are (1) to determine the movement of toxic organics through fine-grained sediments as mediated by aquatic oligochaete feeding. The first objective involves determination of both mixing and burial rates of sediments containing a range of concentrations of ^{14}C labeled 2,4,5,2',4',5'-hexachlorobiphenyl. These data will be of use in understanding long-term recovery in the Great Lakes. Objective (2) is to determine the effect of the toxicant itself on the sediment mixing and burial process. The first two objectives are met through radiometrically monitored laboratory microcosms, and it is hoped that the data will allow for (3) the monitoring system to act as a highly percise bioassay technique for determination of the effects of a wide range of toxicants which may accumulate in Great Lakes' sediments. Present studies focus on the dominant Great Lakes' aquatic oligochaete *Stylodrilus heringianus*, an oligotrophic indicator species, but will include some testing with a eutrophic species, *Limnodrilus hoffmeisteri*.

7. Status: Several activities have occurred. First has been an evaluation of two preliminary experiments using hexachlorobiphenyl. Objectives (1) and (2) above were tested using *Stylodrilus* with toxicant concentrations of 5.3 to 498 ppb and *Limnodrilus* with concentrations of 5.3 to 996 ppb. *Stylodrilus* selectively fed on and translocated organic particles (containing the toxicant) at a faster rate than inorganics resulting in toxicant transfer greater than that represented by total sediment reworking rates. A similar observation was made for *Limnodrilus*. At toxicant levels greater than 50 ppb, reworking rates for *Stylodrilus* decreased significantly after 300 hrs, but reworking rates for *Limnodrilus* did not decrease up to 1400 hrs even at 996 ppb.

Second, results of a preliminary 96 hr LC_{50} using Stylodrilus produced a value of approximately 100 ppm for hexachlorobiphenyl. These results are in agreement with studies by Chapman et al. (1982) who have shown Stylodrilus to be highly tolerant to a variety of pollutants. From their studies, Chapman et al. questioned the validity of listing Stylodrilus as an oligotrophic species. They showed also that Limnodrilus hoffmeisteri had a much lower LC_{50} for several toxicants than did Stylodrilus. Thus we are highly encouraged by our findings which indicate that, while an LC_{50} might be quite high, behavioral changes for Stylodrilus occur at fairly low concentrations, and the behavioral response may have been responsible for this species' elimination from areas of the Great Lakes with moderate to heavy inputs of pollution but lower than an LC_{50} level. Limnodrilus, while having a possible lower LC_{50}, may not initiate a behavioral response until concentrations reach a much higher value. The differences between the behavioral effect concentration and the LC_{50} for Stylodrilus favor the use of the microcosm system as a highly percise bioassay technique.

Third, the above results have allowed us to produce designs for a series of more closely controlled experiments on redistribution, net accumulation and uptake kinetics of hexachlorobiphenyl by both species, primarily Stylodrilus. This includes examination of possible endpoints which will be needed if the system is to be used as a bioassay. One experiment has been run using Stylodrilus and a much broader range of toxicant concentrations. The sediments used in this experiment differed considerably from those used in past runs by having a much higher percentage of fine sand and floccuent organics. Results are still being analyzed, but it appears that compaction is prevented in this sediment type as compared with the control without worms. This type of sediment occurs commonly off the mouths of rivers which may act as a source of toxicants to the Great Lakes.

Fourth, a typical experiment must run from 1400 to 1600 hrs with monitoring taking 4-5 hrs every 2 to 3 days. We are presently considering ways of automating the system to consume less manpower. This will allow more frequent measurements and more precisely determine reworking rates. All microcosms have been redesigned and rebuilt specifically for toxic studies, and fresh collections of sediments and oligochaetes will occur in late September or early October.

8. References:

Chapman, P. M., Farrell, M. A., and Brinkhurst, R. O. 1982. Relative tolerances of selected aquatic oligochaetes to combinations of pollutants and environmental factors. Aquatic Toxicol. 2: 69-78.

9. Products:

White, D. S., and P. C. Klahr. Effect of PCBs on the rate of sediment reworking by Stylodrilus heringianus. 30th Annual Meeting of the North American Benthological Society, Ann Arbor, Michigan, May 18-21, 1982.

Redistribution of sediments containing hexachlorobiphenly by the

freshwater oligochaete, *Stylodrilus heringianus*. Manuscript in preparation (revised summer 1983).

Keilty, T. J. 1983. Redistribution and uptake of PCBs by aquatic oligochaetes in Great Lakes sediments. Doctoral proposal submitted to the School of Natural Resources, University of Michigan.

Organization: Pesticide Research Center
Michigan State University
East Lansing, MI 48824-1311

Principle Investigator: John P. Giesy

Amount of 1983 Funds: $17,484

Total Project Funds to Date: $17,484

Title: Changes in the Free Amino Acid Pool of Lake Michigan Benthic Invertebrates as a Sublethal Toxic Response to Xenobiotic Residues.

Project Summary

The overall objective is to determine if changes in the free amino acid (FAA) pool profile of specific benthic invertebrates can be used as a sublethal indicator of an organisms' exposure to stressful environmental conditions. Specifically, we are investigating changes in the FAA pool, glycogen, lipid and protein content of Stylodrilus heringianus (oligochaetea) and Gammarus pseudolimneaus (Amphipoda) during laboratory exposure to pentachlorophenol (PCP) and field exposure in contaminated areas. The experimental strategy for this study includes four phases; I) development and validation of analytical techniques, II) development and validation of toxicity test protocols, III) laboratory quantification of the effect of PCP on FAA pool, glycogen, lipid and protein concentrations and on the growth and/or reproductive success of the test organism and IV) field application of the stress indices.

Status

Significant progress has been made during the initial year of this project. Complete analytical methodologies have been developed for free amino acids, glycogen, lipids and proteins. The entire extraction procedure is presented in figure 1. Exclusive of glycogen, this analytical scheme is sensitive enough to analyze a single organism (1-2 mg dry weight). The FAA pool, after extraction into methanol, is derivatized with 0-phthalaldehyde and analyzed by reverse phase high performance liquid chromatography using fluorescence detection. The precipitated glycogen fraction is cleaved to glucose by

α-amyloglucosidase and the resulting glucose analyzed by the glucose peroxidase method. Total lipids are determined by the charring method of Marsh and Weinstern (1966), unsaturated lipids by the sulfophosphovanillin method and saturated lipids calculated by the difference. Protein is measured by the method of Peterson (1977). Methodology for the analysis of PCP in water was also finalized. The method, developed by Carr et al. (1982), involves liquid-liquid extraction into chloroform, repartitioning into 0.2M NaOH and spectrophotometric detection at 320 nm.

Generation of an extensive data base is essential to the development of any biochemical indicator of stress. Tables 1 and 2 contain representative data for Gammarus pseudolimneaus and Stylodrilus heringianus. Also included in these tables are statistics showing biological variability of the test parameters.

With analytical methodology developed, the next phase of the project has been initiated. The second phase involves a variety of peripheral but essential objectives. First, knowledge of seasonal fluctuations in test parameters (i.e., FAA pool) is essential for effective data interpretation and subsequent use of any biochemical indicator of stress. Monitoring of seasonal variation has been ongoing since July, 1983. The effect of transport and laboratory holding conditions on test parameters is presently being investigated, as is the development of chronic toxicity test methodology. Gammarus, collected in late July, 1983, are presently being held under various laboratory conditions to determine the least stressful conditions (as determined by periodically monitoring the parameters of interest). This is being done in conjunction with the development of culturing procedures and life cycle toxicity tests.

Fig. 1 Extraction Procedure

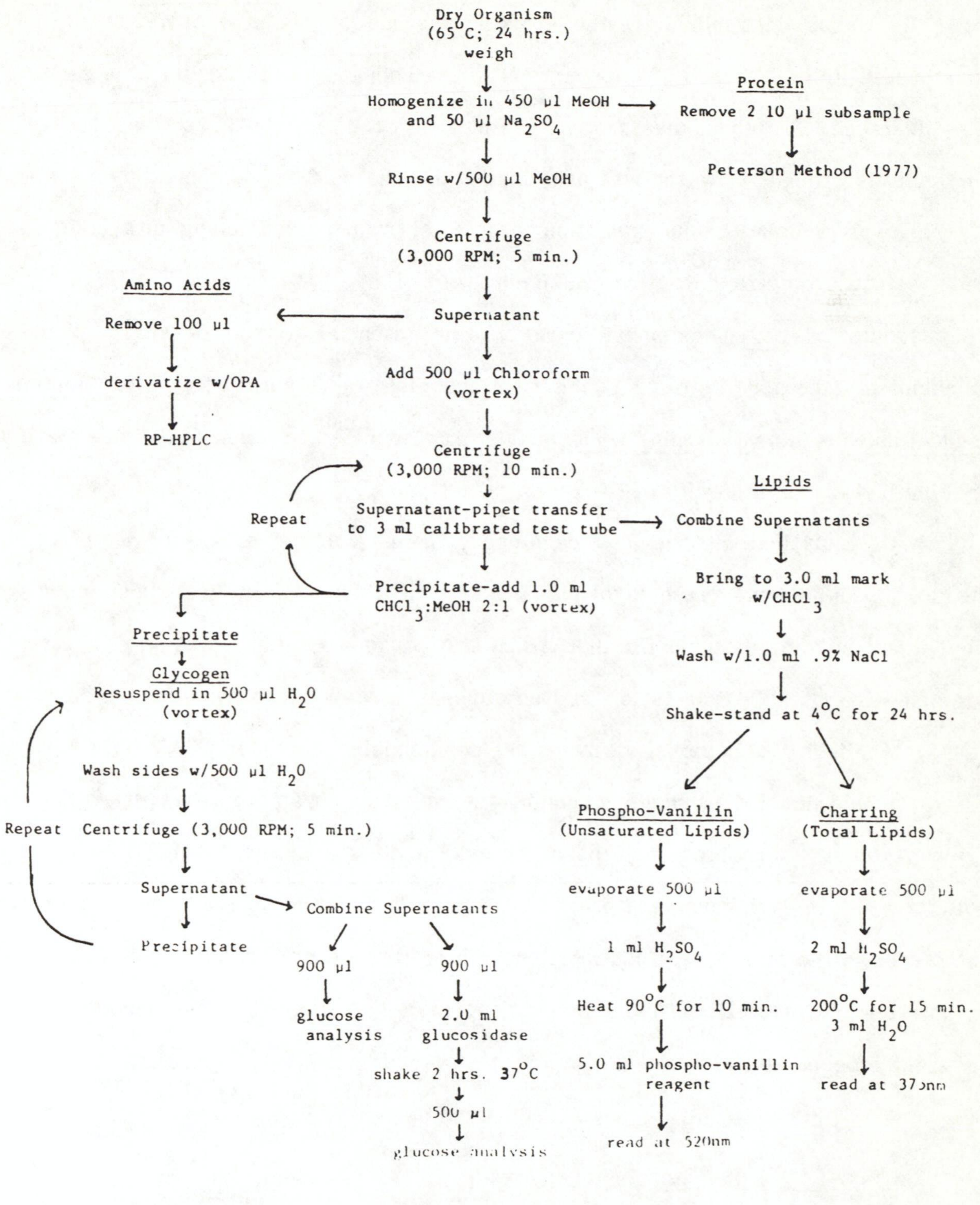


Table 1. Amino acid, glycogen, lipid and protein content of *Gammarus pseudolimneaus*

Amino Acid	nm/mg[b] (avg. n=6)	C.V.[a]	Amino Acid	nm/mg (avg. n=6)	C.V.[a]
Aspartic Acid	2.12	33.5%	Alanine	24.36	9.30%
Glutamic Acid	6.89	28.5%	Tyrosine	5.98	26.50%
Asparagine	1.94	35.2%	Tryptophan	1.90	35.20%
Serine	3.42	38.6%	Methionine	5.22	29.65%
Glutamine	16.04	23.2%	Valine	12.17	27.75%
Histidine	7.92	13.6%	Phenylalanine	7.00	33.50%
Glycine	5.28	32.6%	Isoleucine	7.56	35.96%
Threonine	4.12	21.5%	Leucine	15.91	24.90%
Arginine	26.68	18.2%	total	154.51	

Glycogen	µg/mg[b]	C.V.[a]
Mean (n=5) =	6.18	14.9%

Lipids	µg/mg[b]	C.V.[a]
Total (n=6)	21.8	12.2%
Unsaturated (n=7)	7.37	9.75%
Saturated	14.43	

Protein	µg/mg[b]	C.V.[a]
Mean (n=6)	104.2	10.9%

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[a] Coefficient of variation among the population of organisms analyzed

[b] Wet Weight

Table 2. Amino Acid, glycogen, lipid and protein content of *Stylodrilus heringianus*

Amino Acids	nm/mg[b] (avg. n=3)	Amino Acid	nm/mg[b] (avg. n=3)
Aspartic Acid	1.26	Alanine	11.68
Glutamic Acid	2.98	Tyrosine	2.04
Asparagine	1.32	Methionine	3.19
Serine	3.58	Valine	3.78
Glutamine	2.38	Phenylalanime	4.21
Histidine	2.41	Isoleucine	1.21
Glycine	5.34	Leucine	7.84
Threonine	2.08	Arginine	.09
		total	55.39

Glycogen	µg/mg[c]	C.V.[a]
mean (n=4)	11.9	16.4%

Lipids	µg/mg[b]	C.V.[a]
Total (n=4)	166.6	19.5%
Unsaturated (n=4)	29.2	25.1%
Saturated	137.4	

Proteins	µg/mg[b]	C.V.[a]
mean (n=3)	85.7	13.8%

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[a] Coefficient of variation among the population of organisms analyzed

[b] Dry Weight

[c] Wet Weight

PROGRESS REPORT

September 1983

1. Organization: Great Lakes Environmental Research Laboratory/NOAA
2300 Washtenaw Avenue
Ann Arbor, MI. 48104

2. Principal Investigators: John R. Bennett and Anne H. Clites

3. Title: Modeling the Transport of Toxic Substances

4. Project Summary: The objective of this project is to develop methods to predict the temporal and spatial movement of toxics in the Great Lakes. A two-dimensional, vertically integrated model and a three-dimensional, thermally stratified model will be used to calculate currents in Lake Michigan. These currents will then drive a water quality model that will advect, diffuse, settle, and resuspend particles and dissolved substances.

5. Status: In order to simulate the movement of dissolved and particulate-bound materials in the Great Lakes, we must first model the currents. The vertically-integrated circulation model used to generate wind stress and current fields was developed by Schwab, Bennett, and Jessup (1981) for other GLERL studies. The program used to calculate advective motion, settling, resuspension, and diffusion is documented in Bennett, Clites, and Schwab (1983). The accuracy of this model has been thoroughly tested in Bennett, Campbell, and Clites (1983). At this point, we are using the model to test and calibrate these physical parameters, derived from sediment trap profiles, in idealized cases. Eventually, we will attempt to simulate the zones of sediment deposition and erosion in southern Lake Michigan, using radionuclide data for verification.

The three-dimensional effects of Ekman drift were incorporated into our vertically integrated two-dimensional model by some mathematical manipulations. According to the physics of this bottom layer, when the lake model has a mean cyclonic flow, Ekman layer transport causes high sedimentation in the center of the gyre; with anti-cyclonic flow, the sedimentation occurs nearshore. The analytical solution for steady Ekman layer currents in deep water was combined with the steady solution for the vertical profile of suspended matter to calculate the relationship between the vertically averaged current vector and the sediment transport vector. This relationship enables the two-dimensional model to simulate a three-dimensional effect.

To test the importance of Ekman drift to the model, a circularly symmetric idealization of Lake Michigan's southern basin was developed. The model computes the sedimentation pattern for a wide range of values of the resuspension rate, source location, and lateral diffusion coefficient. Increasing either the resuspension rate (Figure 1) or the lateral diffusion coefficient causes more sedimentation to occur at the gyre center. For realistic ranges of these parameters, these coefficients are as important to the model results as is Ekman layer transport. Another surprising result of this study is that the sedimentation pattern appears not to be sensitive to the location of the source. Whether the load is uniformly distributed over the lake surface or only from the shorelines does not appear to be important to the model. (Figure 2).

Now that we are convinced of the soundness of both the model and the rate coefficients we have chosen, we will begin testing the model for different circulation patterns, using the idealized southern basin of Lake Michigan we developed. After testing for various combinations of theoretical circulation patterns, we will run the model using an actual simulation of Lake Michigan's current developed at GLERL in another study. Using these "real" currents, we hope to eventually simulate the observed sedimentation patterns in southern Lake Michigan with our model.

6. References:

Bennett, J. R., A. H. Clites, and D. J. Schwab. 1983. A two-dimensional lake circulation modeling system: Programs to compute particle trajectories and the motion of dissolved substances. NOAA Tech. Memo. ERL-GLERL-46. 51 pp.

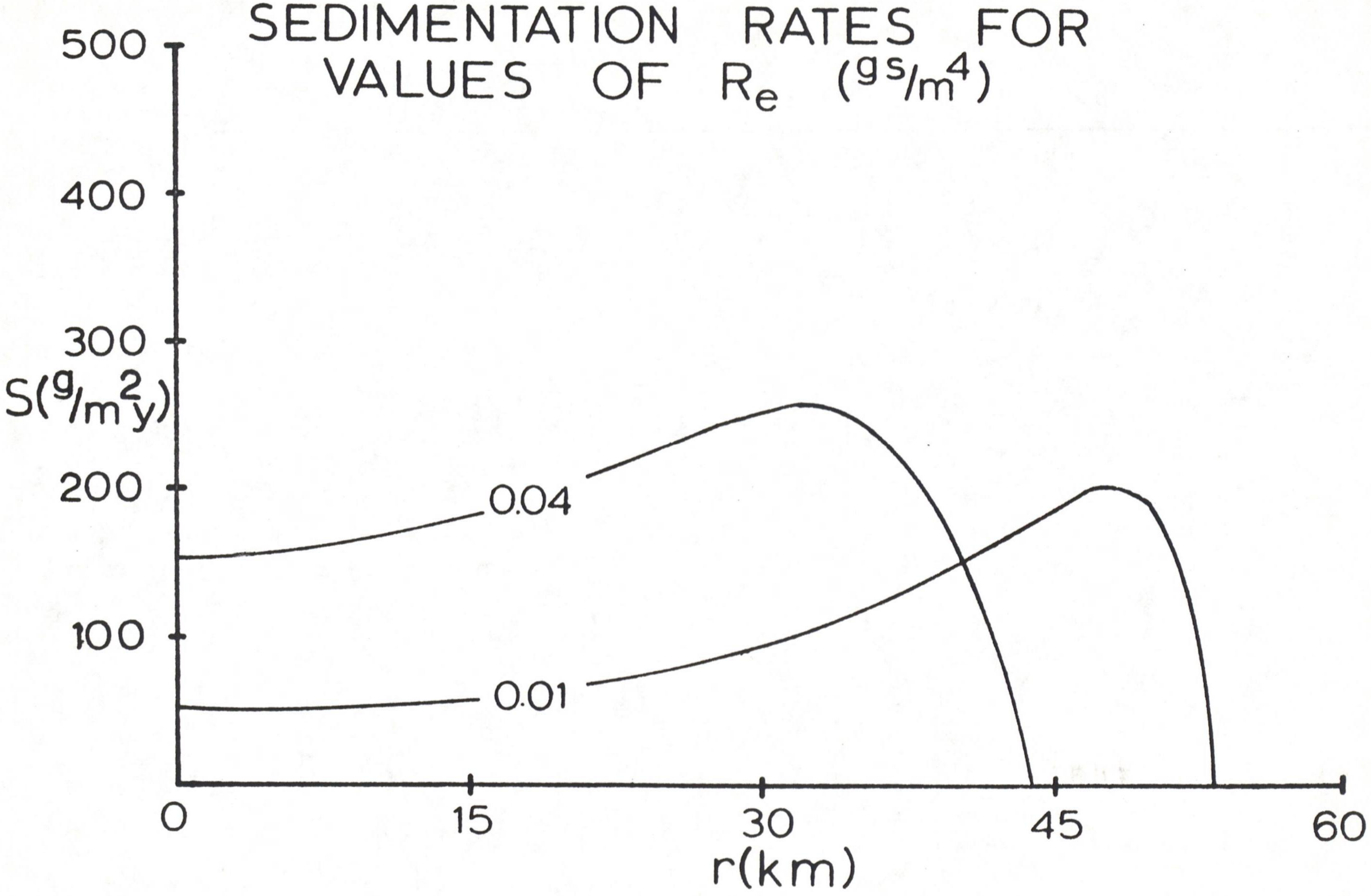
Bennett, J. R., J. E. Campbell, and A. H. Clites. 1983. Accuracy of a finite difference method for computing Eulerian and Lagrangian lake currents. American Geophysical Union. (In press).

Schwab, D. J., J. R. Bennett, and A. T. Jessup. 1981. A two-dimensional lake circulation modeling system. NOAA Tech. Memo. ERL-GLERL-38. 79 pp.

7. Products:

Bennett, J. R., A. J. Clites, and D. J. Schwab. 1983. A two-dimensional lake circulation modeling system: Programs to compute particle trajectories and the motion of dissolved substances. NOAA Tech. Memo. ERL-GLERL-46. 51 pp.

Bennett, J. R., J. E. Campbell, and A. H. Clites. 1983. Accuracy of a finite difference method for computing Eulerian and Lagrangian lake currents. American Geophysical Union. (In press).



SEDIMENTATION RATES FOR VALUES OF R_e ($^{gs}/_{m^4}$)
500
400
300
200
100
S($^g/_{m^2 y}$)
0.04
0.01
0
15
30
45
60
r(km)

Figure 1

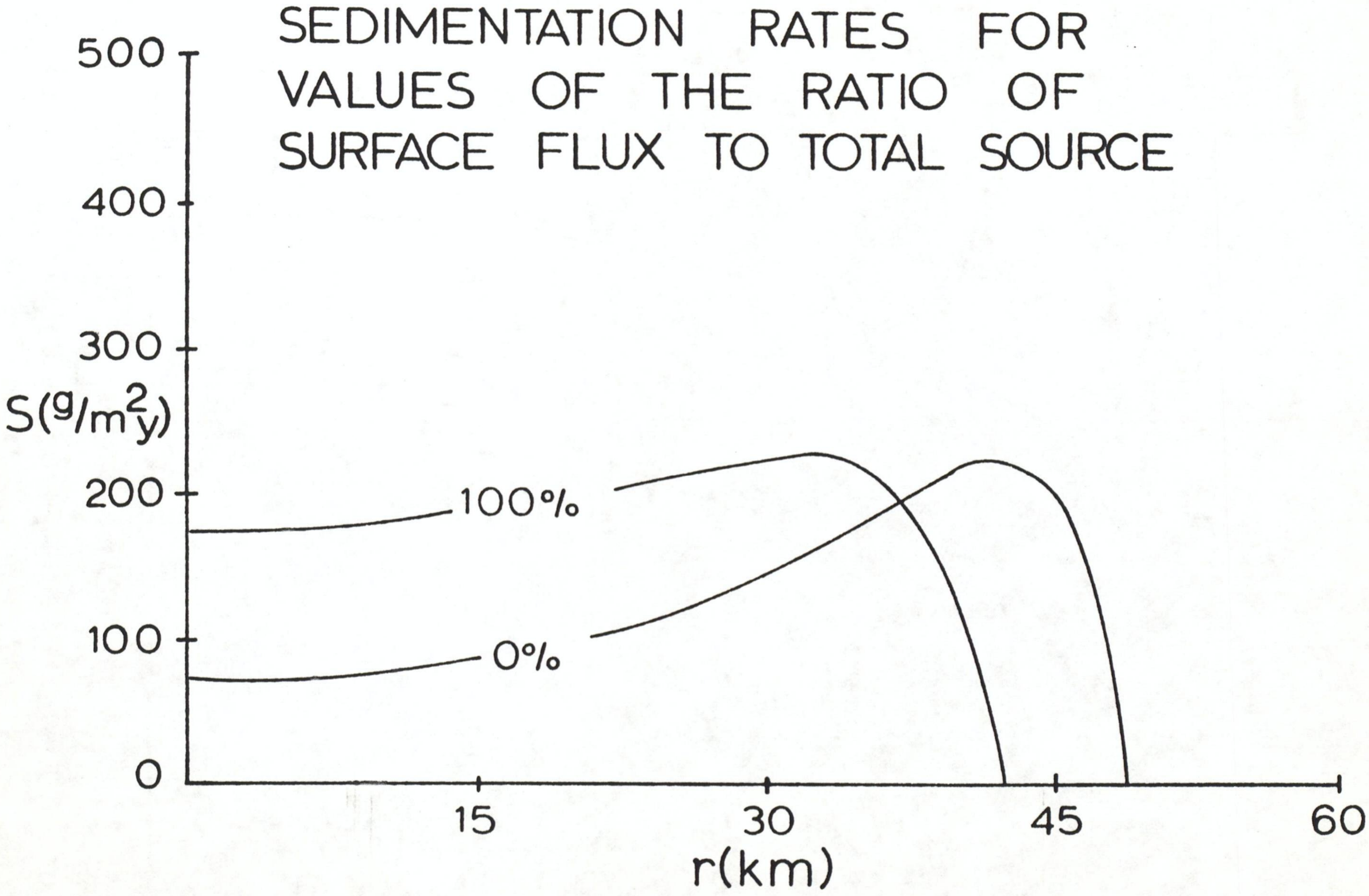

SEDIMENTATION RATES FOR VALUES OF THE RATIO OF SURFACE FLUX TO TOTAL SOURCE
500
400
300
S(g/m2y)
200
100
0
100%
0%
15
30
45
60
r(km)

Figure 2

PROGRESS REPORT

September, 1983

1. Organization: Great Lakes Environmental Research Laboratory
NOAA
2300 Washtenaw Avenue
Ann Arbor, MI 48104

2. Principal Investigator: Michael J. McCormick

3. Title: Vertical Dynamics of Toxic Organics in the Great Lakes

4. Project Summary: The objectives of this project are twofold: (1) to quantitatively describe the decomposition pathways of persistent contaminants, and (2) to improve such models by identifying and then minimizing the major sources of prediction errors. A one-dimensional model has been completed and used to investigate the Mirex problem in Lake Ontario. Current efforts are focused on improving the predictability of submodels detailing vertical mixing. Also, field work is being conducted on horizontal transport problems.

5. Status: Progress has been made on process parameterizations, error analyses, and in initiating a field program dealing with horizontal transport. In particular, a global radiation model (Atwater and Brown, 1974) using cloud information from coastal meteorological stations on Lake Michigan has been programmed and is currently being compared against measured solar radiation data from Madison, Wisconsin. This model will be used to improve estimates of both photodecomposition losses and the intensity of vertical mixing. Both processes are strongly dependent upon knowing the irradiance which, in general, must be modeled due to the sparse radiation gathering network in the Great Lakes region.

   Error analyses have been performed on two models to examine transport uncertainty on prediction estimates. A preliminary error analysis dealt with leakage of Mirex from the sediments of Lake Ontario into the water column and its vertical transport therein. The results suggest gross uncertainty in particle associated concentrations of Mirex in surface waters, during winter, and suggests that vertical eddy diffusion is a major error source. The other model dealt with uncertainty in nutrient regeneration rates in Lake Michigan. In this case horizontal advection was a major error source. Comparison of vertically to horizontally associated errors indicates an error dominance due to horizontal variability. Therefore, guidelines are being developed to provide minimum estimates of error bounds for different applications of horizontal averaged one-dimensional models.

   Error analyses have motivated additional work on vertical mixing. Comparisons have been made between eddy diffusion models of McCormick and Scavia (1981) and Henderson-Sellers (1980). The results indicate similarities under three conditions: (1) constant current shear, (2) high Richardson number, and (3) low wind speed. Differences occur in treatment of low diffusion situations which may significantly affect rate loss estimates in the toxic's model. Resolving discrepancies in the two approaches is an ongoing problem with alternative methods being addressed. The most hopeful approach involves an integral type model (Pollard *et al.* 1973) to estimate vertical mixing.

A manuscript is in preparation summarizing the one-dimensional toxics modeling.

Future efforts are being focused on horizontal transport problems. Dye experiments are being conducted in Lake Michigan for two purposes: first, to estimate the horizontal eddy diffusivities and secondly, to estimate the wind slippage of satellite tracked current drifters. Knowledge of the eddy diffusivity and its scale dependence is critical to predicting pollutant dispersal. Equally important to toxicant transport is determining how well current drifters are able to track a given water mass. Both problems are being addressed by monitoring dye dispersion relative to time and several current drifters.

6. References:

Atwater, M. A. and P. S. Brown, Jr. (1974). Numerical Computations of the Latitudial Variations of Solar Radiation for an Atmosphere of Varying Opacity. *J. Appl. Met.* 13:(2), 289-297.

Henderson-Sellers, B. (1980). Limnological Modelling: Simulation of Vertical Profiles to Temperature, Dissolved Oxygen and Nutrients. I. Theory. *J. Limnol. Soc. Sth. Afr.*, 6, 49-54.

McCormick, M. J. and D. Scavia (1981). Calculation of Vertical Profiles of Lake-Averaged Temperature and Diffusivity in Lakes Ontario and Washington. *Water. Resour. Res.* 17:(2), 305-310.

Pollard, R. T., P. B. Rhines and R. O. R. Y. Thompson (1973). The Deepening of the Wind-Mixed Layer. *J. Geophys. Fluid Dyn.*, 3, 381-404.

7. Products:

Henderson-Sellers, B., M. J. McCormick and D. Scavia (1983). A Comparison of the Formulation for Eddy Diffusion in Two One-Dimensional Stratification Models. *Appl. Math. Mod.* 7, 212-215.

Henderson-Sellers, B. and M. J. McCormick (1983). Vertical Eddy Diffusion Formulations in One-Dimensional Thermal Stratification Models for Lakes and Reservoirs. To be presented at *Fourth Inter. Conf. on Math. Mod.*, Zurich, Switzerland, 15 August.

McCormick, M. J. and S. J. Tarapchak (1983). Uncertainty Analysis of Calculated Nutrient Regeneration Rates in Lake Michigan. *Can. J. Fish. Aquat. Sci.* (In Press).

Progress Report

September 1983

1. Principal Investigator: Mila S. Simmons

2. Affiliation: Department of Environmental and Industrial Health
   The University of Michigan

3. Amount of 1983 Sponsored Funds: $ 21,857

4. Total Amount of Project Funds through 1983: $ 148,657

5. Title: Photochemical Degradation and Transformation Studies of Toxic Organics in the Great Lakes

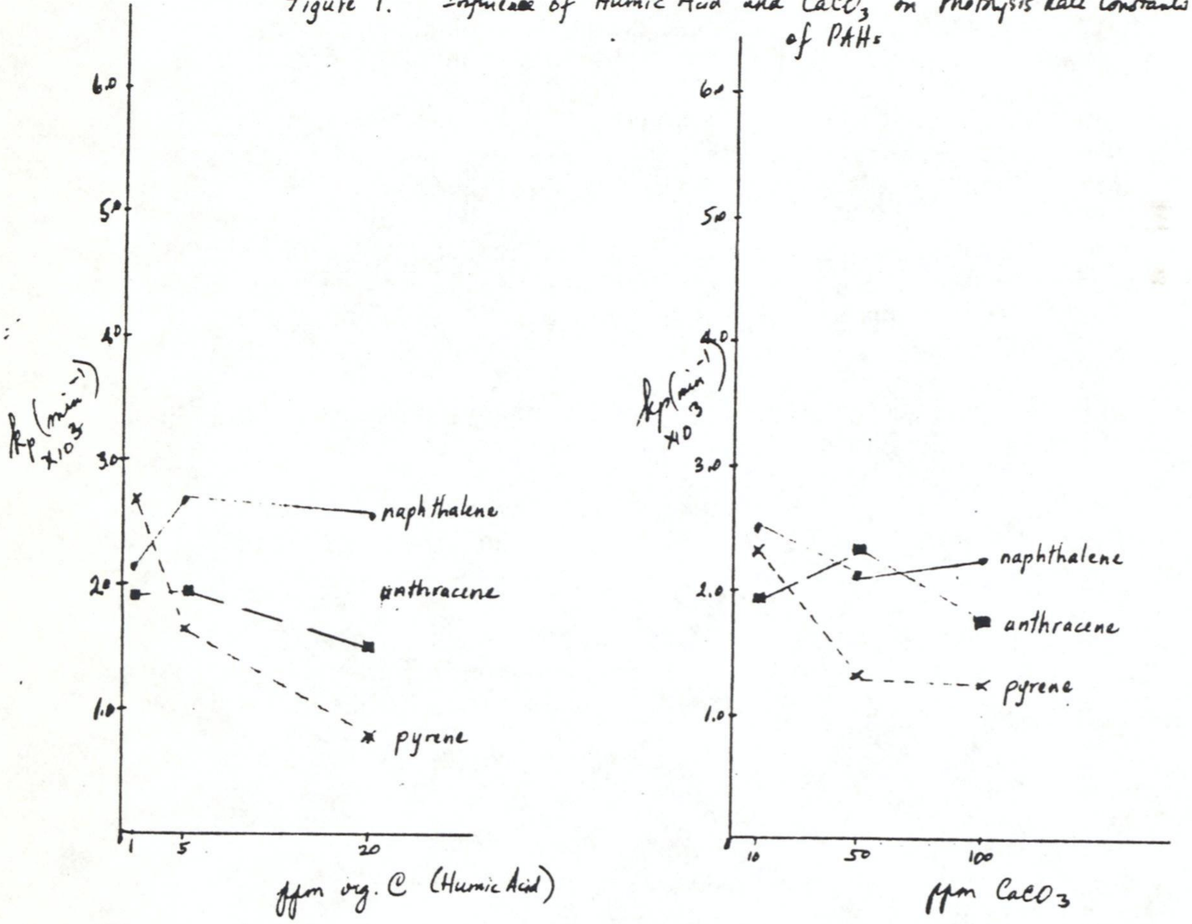
6. Project Summary: The overall objective of this research project is to conduct studies on the photochemical degradation of toxic organics. Photolysis rate constants for PCBs and PAHs in lakewater under natural and artificial sunlight are measured to be incorporated in a model which will describe the cycling, transport and fate of toxic organics in the Great Lakes. The influence and the role of humic acids, particulates and algae present in the lakewater on the photolytic process and the magnitude of these effects on the rate constant is also investigated.

7. Status: Work has been completed on the studies on pyrene and anthracene and the effect of microlayer constituents, humic acids, $CaCO_3$ and algae on their photodegradation. The pyrene studies show a two-fold enhancement of the photolysis rate constant in Lake Michigan water and Lake Michigan microlayer compared to that of distilled water. Light attenuation effects for these waters were measured and were found to be negligible. The presence of algae in the reaction mixture enhances the photolysis rate 3.5 times. This type of enhancement was also observed by Zepp and Schlotzhauer (EST 17,462-468 (1983)) for several PAHs. The photolysis rates of anthracene were enhanced tenfold both in lakewater and lake microlayer but no significant effects were observed by algae.

   Humic acids and $CaCO_3$ also affected the photolysis rates of pyrene and anthracene differently. The photolysis rate constant of anthracene appears to be unaffected by the constituents added to the reaction mixture while their effect on the photolysis of pyrene show a decrease with increasing concentration of the constituents. Figure 1 also shows that naphthalene behaves differently than pyrene and anthracene when exposed to similar conditions. These conditions have not been corrected for light attenuation effects. It is possible that different mechanistic pathways are involved in these photoreactions.

   Current work in progress deals with the investigation of these mechanisms for the photolysis of selected PAHs. Photoproduct identification and analysis by GC/MS to further elucidate the mechanistic pathways for these photoreactions will also be conducted.

Figure 1. Influence of Humic Acid and $CaCO_3$ on Photolysis Rate Constants of PAHs



This is the last phase of this project and a compilation of all existing photochemical data on PCBs and PAH are being assembled so as to compare rate constants generated by several investigators for these toxic organics. We can calculate direct photolysis rate constants using laboratory-generated quantum yield and extinction coefficient values. It appears, however that the rate constants measured in distilled water will only estimate the minimum value for assessing degradation due to photolysis. Effects of other constituents such as organics in water, particulates and algae could enhance this rate immensely depending on the toxicant. Our study provided some insight on the magnitude of these enhancement effects in lake environments. Further studies on these effects and their mechanisms for other toxicants need to be addressed.

-Products:

1. Zadelis,D., Haubenstricker,M. and Simmons, M. Photolytic Decomposition of Chlorinated Biphenyls in Aquatic Media. Presented at the 1st Annual Meeting of the Society of Environmental Toxicology and Chemistry, Maryland/ Washington D.C., Nov. 24-26, 1980.

2. Haubenstricker,M., Zadelis, D. and Simmons, M.S. Photolytic Studies of Hexachlorobiphenyl Isomers in Aquatic Systems. Presented at the 3rd Midwest Water Chemistry Workshop. Ann Arbor, MI, Dec. 4-5,1980.

3. Zadelis,D. and Simmons, M. Polychlorinated Biphenyl Isomers: Photolysis in Aqueous Systems. Presented at the 10th International Conference on Photochemistry, Iraklion, Greece (Crete), Sept.6-12, 1981

4. Zadelis,D. and Simmons, M. Effects of Particulates on the Photolysis of Naphthalene. Presented at the 7th International Symposium on Polynuclear Aromatic Hydrocarbons. Battele Laboratories, Columbus, Ohio, October 26-28,1982

5. Zadelis,D and Simmons,M.S. Polychlorinated Biphenyl Isomers. Photolysis in Aqueous Systems. J. Photochem. 17,146 (1981)

6. Zadelis,D. Haubenstricker,M. and Simmons,M.S. Photolytic Decomposition of chelorinated Biphenyls in Aquatic Media. J. Soc. Environ. Toxicol. and Chem. Accepted with revision.

7. Zadelis, D. and Simmons,M.S. Effects of Particulates on the Photolysis of Naphthalene. Proceedings of the 7th International Symposium on Polynuclear Aromatic Hydrocarbons. Battele Laboratories, Columbus, Ohio, October 26-28, 1982. In press.

PROGRESS REPORT

OCTOBER, 1983

1. Organization: Oak Ridge National Laboratory
   P. O. Box X
   Oak Ridge, TN 37831

2. Principal Investigator: James E. Breck

3. Amount of 1983 Funds: $40 K

4. Total Project Funds to Date: $40 K

5. Title: Models for the Behavior and Fate of Long-lived Contaminants in the Upper Trophic Levels of the Great Lakes

6. Project Summary: The objective of this project is to develop and analyze models for simulating contaminant concentrations in Great Lakes fishes; this will include an evaluation of the relative contributions of direct uptake from water, pelagic food chain pathways, and benthic food chain pathways. Initial work has focused on simulating the accumulation of PCBs and dieldrin by alewives, the dominant forage fish in Lake Michigan, using a bioenergetics modeling approach.

7. Status: Progress has been made in several areas during the second six months of this project. First, a new estimate of direct uptake of contaminant from water has been obtained. The bioaccumulation model used in this project computes the direct uptake rate of contaminant as proportional to the uptake rate of oxygen. The proportionality factor now used in the model was determined experimentally by McKim and Goeden (1982), whereas the earlier factor was estimated by Weininger (1978) from relative diffusivity calculations. Use of the new factor results in a 4.6-fold increase in the simulated direct uptake rate from water. When a long-term elimination rate of 0.00120 per day (estimated from Guiney et al. 1977, 1979) is also included, then the simulated alewife PCBs coming from the water is increased from less than 20% to about 50% of the total alewife body burden (see the accompanying figure). The contribution from the food chain is correspondingly decreased. The benthic component of the food chain (Pontoporeia) is now estimated to contribute about 30% of the total alewife body burden of PCBs.

   Second, a data set for dieldrin bioaccumulation by alewives has been compiled, and preliminary simulations have been done. The results are encouraging. Using the same bioenergetics parameters, diet data, and temperature history as for the PCB simulations - changing only the contaminant concentrations in prey and water and the depuration rate - the simulated dieldrin concentration in alewives is within a factor of two of the observed. Because the depuration rate of dieldrin is faster than that of most PCBs, the dynamics of dieldrin bioaccumulation provides an interesting contrast to the dynamics of PCB bioaccumulation. As can be seen in the accompanying figures, dieldrin concentration in alewife is predicted to be nearly independent of fish age, whereas PCB concentration is expected to increase with fish age. Direct uptake from the water is predicted to be the major route of dieldrin bioaccumulation, responsible for about 60% of the body burden of dieldrin in alewives. While the food chain pathway is thus, somewhat less important for dieldrin than for PCB, the benthic food chain (Pontoporeia) is still responsible for about 25% of the body burden of dieldrin.

Third, J. E. Breck visited GLERL on June 6-7, 1983, and presented a seminar entitled "Modeling Contaminants in Lake Michigan Alewives." During this visit discussions about this research were held with GLERL staff members, several faculty and students at the University of Michigan, and researchers at the Great Lakes Fishery Laboratory.

Fourth, several improvements were made to the FORTRAN code for this bioaccumulation model. Some changes were necessary so that an error analysis of the model could be done. Other changes make the computer program easier to use, make it easier to fit observed fish growth data, and allow greater flexibility in specifying seasonal changes in diet proportions and contaminant concentrations in prey.

Future research will involve analysis and evaluation of the alewife bioaccumulation model, comparison of the behavior of different contaminants (e.g., PCBs, dieldrin, ^{137}Cs), and estimation of the contaminant flux through forage fish to their salmonid predators. Work has begun on an error analysis of the bioaccumulation model. Further evaluation of the model could utilize the extensive time series of ^{137}Cs concentrations in Lake Michigan. Work has also begun on estimating the contaminant flux along different pathways to the entire alewife population of Lake Michigan.

8. References:

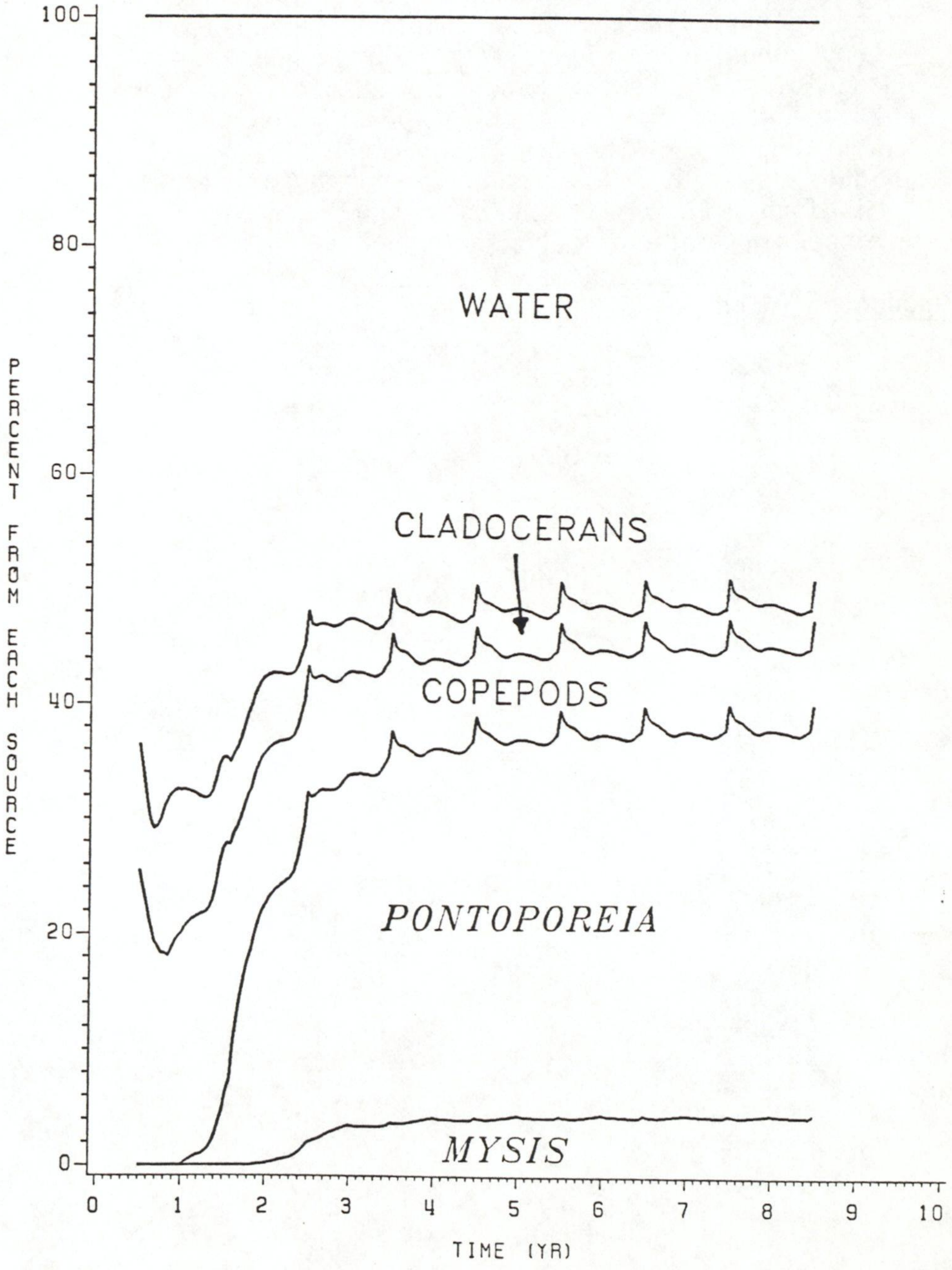
Guiney, P. D., R. E. Peterson, M. J. Melancon, Jr., and J. J. Lech. 1977. The distribution and elimination of 2, 5, 2', 5' - [^{14}C] tetrachlorobiphenyl in rainbow trout (Salmo gairdneri). Toxicol. Appl. Pharmacol. 39:329-338.

Guiney, P, D., M. J. Melancon, Jr., J. J. Lech, and R. E. Peterson. 1979. Effects of egg and sperm maturation and spawning on the distribution and elimination of a polychlorinated biphenyl in rainbow trout (*Salmo gairdneri*). Toxicol. Appl. Pharmacol. 47:261-272.

McKim, J. M., and H. M. Goeden. 1982. A direct measure of the uptake efficiency of a xenobiotic chemical across the gills of brook trout (*Salvelinus fontinalis*) under normoxic and hypoxic conditions. Comp. Biochem. Physiol. C Comp. Pharmacol. 72:65-74.

Weininger, D. 1978. Accumulation of PCBs in lake trout in Lake Michigan. Ph.D. dissertation (Water Chemistry), University of Wisconsin-Madison, Madison, Wisconsin. 232 pp.

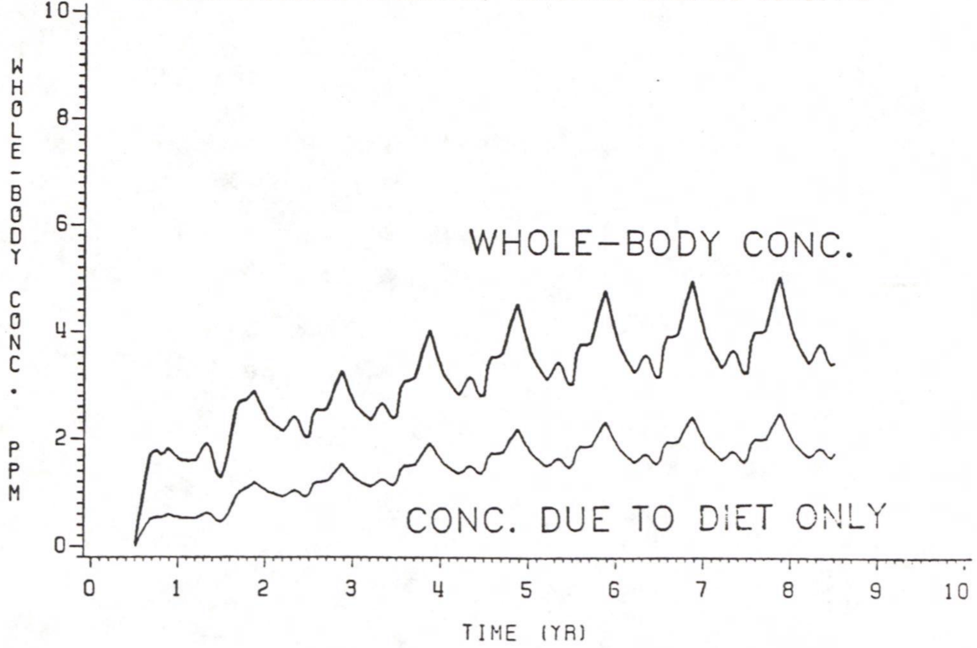
9. Products: None yet.



PERCENT OF ALEWIFE PCB
FROM WATER & EACH PREY TYPE.
SPAWNING LOSSES AND LONG-TERM ELIM. ARE INCLUDED

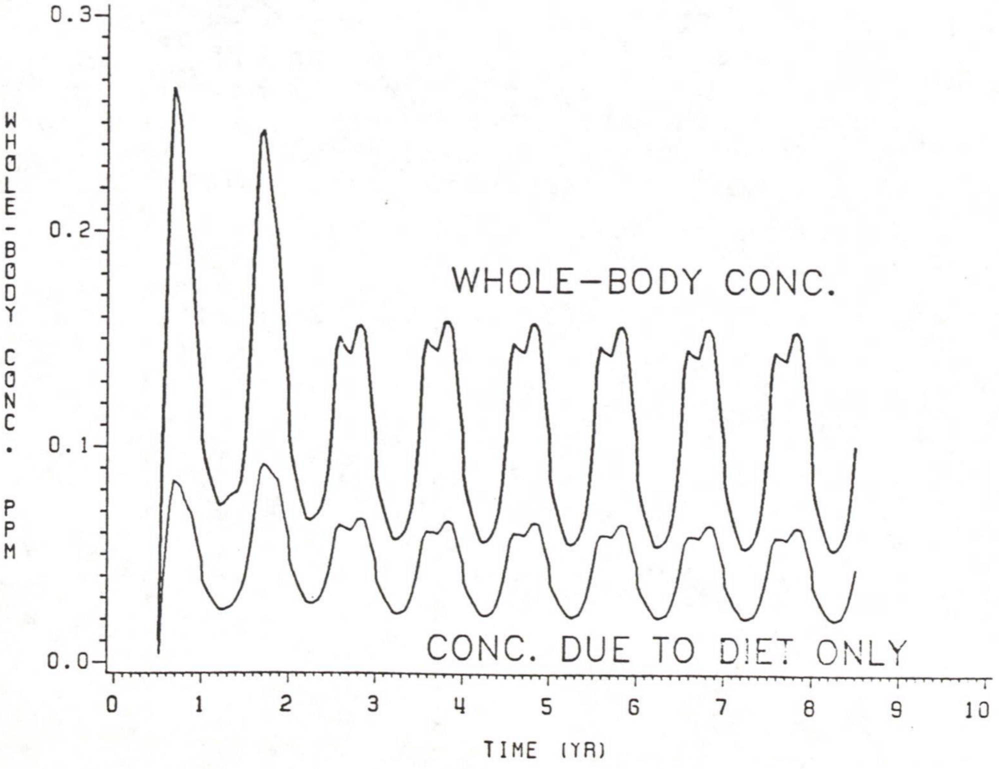
ALEWIFE PCB CONC.

TOTAL CONC. & CONC. DUE TO DIET ONLY
LONG-TERM ELIMINATION IS INCLUDED
SPAWNING LOSSES INCLUDED, SEASONAL CALORIC DENSITY.



ALEWIFE DIELDRIN CONC.

TOTAL CONC. & CONC. DUE TO DIET ONLY
INCLUDES LONG-TERM ELIMINATION
SPAWNING LOSSES INCLUDED, SEASONAL CALORIC DENSITY.



PROGRESS REPORT

September 1983

1. Organization: Great Lakes Research Division and
Department of Atmospheric and
Oceanic Sciences
The University of Michigan
Ann Arbor, Michigan 48109

2. Principal Investigators: Clifford P. Rice and
Philip A. Meyers

3. Amount of 1983 Funds: 60,000

4. Total Project Funds to Date: 60,000

5. Title: Partitioning and Cycling of Toxic Organics
in the Great Lakes Ecosystem.

6. Project Summary: The objective of this project is to study the role particle suspension plays in the continued recycling of toxic organic compounds in the Great Lake system. Emphasis will be placed on analyses of the suspended and settling particulate portions of the samples. Both selected toxic organics, e.g. pesticides (dieldrin, DDT, etc.), PCBs, phthalates, and chlorobenzenes, and nonselective GC/MS scans will be performed. Analyses of lipid biomarkers of samples will be performed in order to follow biogeochemical cycling at the sediment-water and epilimnion-hypolimnion interfaces and in other turbidity zones, such as river plumes and coastal locations.

7. Status: Results for PCB in sediment traps from the summer of 1980 and winter of 1980 and 1981 have been processed using a newly devised technique for PCB homologue identification. The homologue composition for the surface traps was predominantly 2 and 3 chlorine containing biphenyls which agrees with the relative composition of these groups in the air. Assuming that the PCB in the near surface trap samples were atmospherically derived, allows these trap data to be used for estimating atmospheric flux of PCB to Lake Michigan. These flux values agreed well with estimates made by other investigators using shore based rain and dryfall collectors.

Using the homologue identification technique described above we found that the PCB in samples collected from trap profiles showed increasing chlorine content with depth. This implies that the bottom traps have selectively lost the 2 and 3 chlorine containing homologues.

Foam pads which were submerged in Lake Michigan for extended periods of time are being tested as integrated collectors of hydrophobic pollutants. Pads which we analyzed for chlorinated organics had p,p'-DDE well above the blanks; however all of the other expected compounds (PCB, toxaphene, and DDT-residues) were obscured by blank comtamination problems.

Work on natural biomarker identifications in bottom material and settling particulates is proceeding. The enclosed figure is an example of the kind of variation of natural organic materials which is found in the water column. The upper figure represents the hydrocarbon mix from a sediment trap sample positioned just below the metalimnion in a Lake Michigan trap profile and the lower figure represents the same mix from the lowest trap just above the sediment-water interface. A complete discussion of the differences observed in these samples is presented in the manuscript listed below (Meyers et al. in press). Additional sediment trap samples and sediment core sections are presently being analyzed for saturated and unsaturated hydrocarbons, ketones and alkonol fractions. GC/MS structural identifications of PAH metabolites are planned for some of these samples.

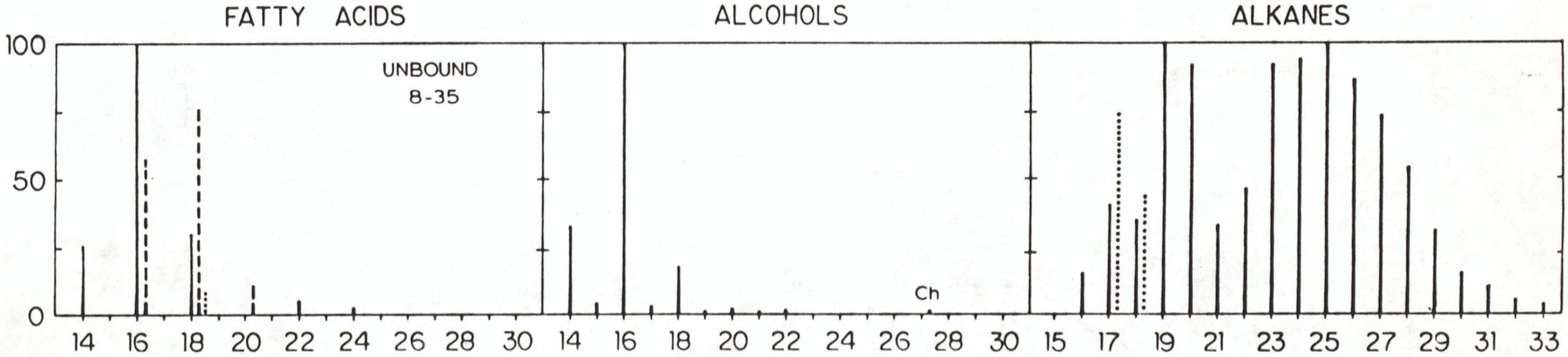
8. Products:

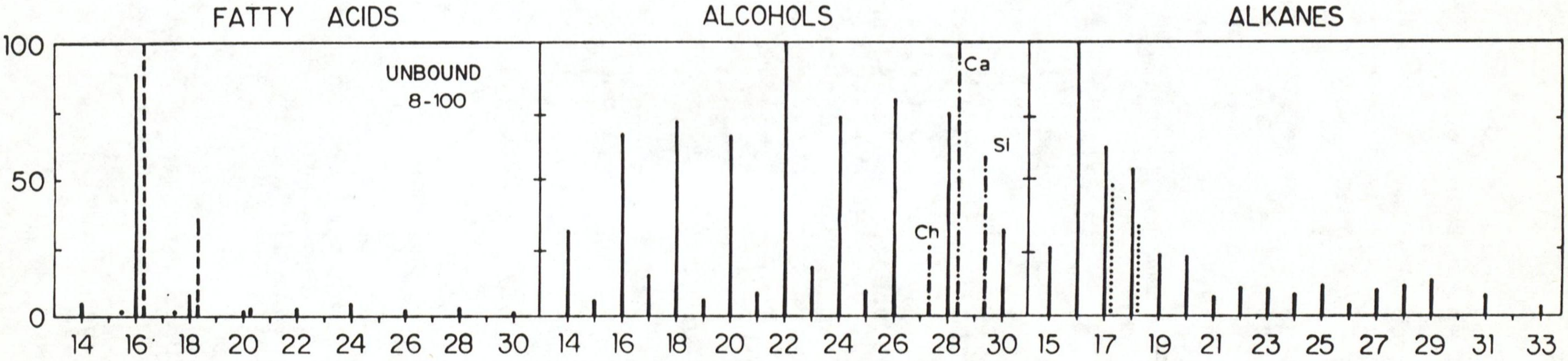
Meyers, P.A., M.J. Leenheer, B.J. Eadie and S.J. Maule. (in press). Organic geochemistry of suspended and settling particulate matter in Lake Michigan. Geochemica et Cosmochimica Acta.

Meyers, P.A., M.J. Leenheer, and B.J. Eadie. 1983. Organic matter alteration during sinking of sediment particles in Lake Michigan. North-Central Section of the Geological Society of America. Abstract with Programs, 15:238.

Dunham, K.W., P.A. Meyers and B.J. Eadie. 1983. Hydrocarbon geochemistry of sediments from Lakes Michigan, Huron, Erie, and Ontario. North-Central Section of the Geological Society of America. Abstracts with Programs, 15:238.

Rice, C.P., P.A. Meyers, B.J. Eadie and J.A. Robbins. 1983. Sources, transport, and degradation of organic matter components associated with sedimenting particles in Lake Michigan. Sixth International Symposiom on Environmental Biogeochemistry, Sante Fe, N.M.


FATTY ACIDS
ALCOHOLS
ALKANES
100
50
0
UNBOUND
8-35
Ch
14 16 18 20 22 24 26 28 30
14 16 18 20 22 24 26 28 30
15 17 19 21 23 25 27 29 31 33


FATTY ACIDS
ALCOHOLS
ALKANES
100
50
0
UNBOUND
8-100
Ca
Si
Ch
14 16 18 20 22 24 26 28 30
14 16 18 20 22 24 26 28 30
15 17 19 21 23 25 27 29 31 33

DATE	ISSUED TO