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THE CYCLING OF TOXIC ORGANICS IN THE
GREAT LAKES: A 3-YEAR STATUS REPORT

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This interim 3-year status report describes the results of GLERL's studies on the cycling of toxic organics in the Great Lakes. A hierarchy of models has been developed including 1) a lakescale equilibrium model, 2) a one-dimensional steady-state model, 3) one- and two-dimensional time dependent models, and 4) several individual process models. These modeling efforts have identified process research needs, some of which have been supported. Reported here are results of our work on: 1) air-water exchange; 2) photolysis; 3) sorption and partitioning; 4) particle settling and transport; 5) early diagenetic processes in lake sediments; 6) interaction of sediments, contaminants, and benthic organisms; and 7) simulation studies of organic contaminants.

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;

*GLERL Contribution No. 369.

- (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 (OMPA), 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 OMPA funding 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 (tumorous 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. Such an approach has enabled us to develop specific

Conceptualized Toxic System Model

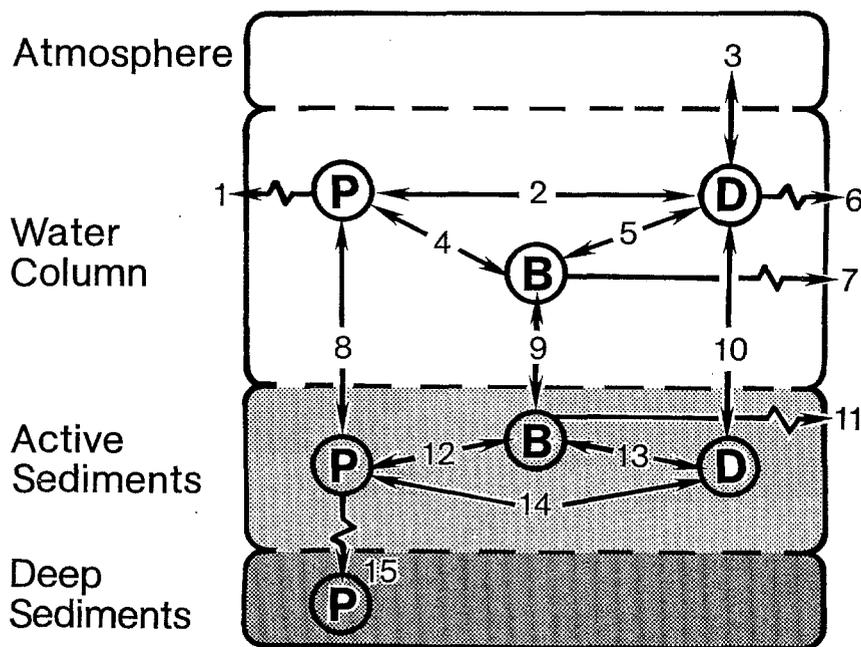


FIGURE 1.--Conceptualized toxic system model. P represents particle phase, D represents dissolved phase, and B is an abbreviated food web. The 15 process arrows are: photolysis (1 and 6), sorption (2 and 14), air-water exchange (3), grazing and fecal pellet generation (4), filtering (5), biological decomposition (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).

research objectives, in terms of questions or testable hypotheses, that focus on the common goal. In terms of the major identified processes, some of these are:

Processes 1 and 6 (Photolysis)

Photolytic decomposition rates of selected compounds are lower in Great Lakes waters (with their indigenous particulates and natural organics) than in models developed from published laboratory studies using distilled water or sea water.

Photolysis is a major removal mechanism for selected synthetic organic contaminants.

Processes 2 and 14 (Sorption)

Partitioning of selected synthetic organic contaminants measured in Great Lakes waters is proportional to compound solubility and can be represented as an equilibrium.

The equilibrium partition coefficient is inversely related to particle concentration.

Process 3 (Air-water exchange)

The partitioning of selected organic contaminants in the surface microlayer is different from that in bulk water samples.

It is necessary to explicitly model the microlayer in order to simulate the cycling of synthetic organic contaminants.

Process 4 (Grazing and fecal pellet generation)

Fecal pellet settling is the primary removal mechanism from the water column for selected contaminants.

Process 5 (Filtering)

Zooplankton, benthos, and fish acquire more than 50 percent of their body burden of selected contaminants by adsorption through their gills.

Processes 7 and 11 (Biological decomposition)

For selected toxic organics, decomposition rates in the water column or sediment are not significantly different from zero.

Process 8 (Particle settling and resuspension)

See process 4.

Particle residence times in the water column are less than 1 year.

Resuspension, during the stratified period, introduces significant (with respect to primary loading) contaminant into the epilimnion.

Resuspension, during the unstratified period, significantly increases contaminant half-life in the water column.

Process 9 (Food web dynamics)

A significant fraction of the body burden of top predator fish comes from benthic organisms.

The contaminant concentration in fish establishes a rapid equilibrium with the water column.

Process 10 (Advection and diffusive mixing)

Diffusive flux at the sediment water interface is small. It appears that the downslope movement of particle-bound contaminants is dominated by nepheloid layer processes.

The movement of particle-bound contaminants into sediment catchment basins is controlled by storms during the unstratified period.

Upwelling events introduce a significant amount of sediment-bound contaminants into the epilimnion.

Processes 12 and 13 (Benthos-sediment interactions)

Benthic organisms obtain a significant fraction of their body burden of selected organic contaminants directly from the sediment/pore water system.

Bioconcentration of selected contaminants by benthic organisms are greater than by fish.

Process 15 (Burial and bioturbation)

Bioturbation of recent sediments, combined with resuspension, significantly increases the residence time of selected organic contaminants in the water column.

Lake-wide averaged sediment mixed depths represent times of greater than 10 years.

Bioturbation depths are proportional to organism density.

Burial into deep sediments is a significant removal process for selected organic contaminants.

2.5 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.

2.6 Current State of Knowledge and Summary of Work Accomplished During FY 1980-82

There are nine major units of work which will be reported on here. These have been partially funded by the OMPA program. Other process research incorporated into our model, primarily biological and food web processes, have been totally supported by Great Lakes research funds and are not included in this document. Reports on the nine topics follow:

3. AIR-WATER EXCHANGE

There are three separable components of the air-water exchange process: precipitation, dry dustfall, and vapor phase exchange. Precipitation input is being measured throughout the Great Lakes and data are not yet fully analyzed.

Rain and snow samples analyzed by Murphy and Rzeszutko (1978) contained an average of approximately 200 mg polychlorinated biphenyls (PCB) L⁻¹ and constitute the major input of PCB to Lake Michigan (table 1). Information on precipitation from the National Weather Service will give some general time dependent loads. Improved information is currently being obtained from analysis of samples collected during 1979-81. This input estimate does not include vapor phase transport that Eisenreich (pers. comm.) and Rice (pers. comm.) both consider important. Further information on this latter process will be included as it becomes available. Estimates of volatilization and aerosol formation will be summarized below. The process appears to be well estimated by a first-order form

$$\frac{dC}{dt} = k \frac{C}{V} \quad (1)$$

where $k \frac{C}{V}$ = volatilization rate of the compound under investigation.

The work of several research efforts (Tsivoglou, 1965; MacKay, 1982) has been synthesized into the relationship of the form:

$$\frac{k_v^c}{k_v^o} = \frac{d^o}{d^c} \quad (2)$$

where k_v^o is the volatilization rate of oxygen;

d^o is the molecular diameter of oxygen, assuming a sphere (2.98/); and

d^c is the molecular diameter of the compound under investigation.

TABLE 1.--Inputs of PCB (kg yr⁻¹) to Lake Michigan

| Sources | Prior to | |
|--|----------|---------|
| | 1975 | 1977 |
| Major Industrial Discharge ¹ | (25,000) | -- |
| Precipitation ² | 4,800 | 4,800 |
| Streams and Waste Water Effluents ³ | 1,650 | 1,650 |
| Others ⁴ | (2,500) | (2,500) |
| Total | 33,950 | 8,950 |

¹This estimate is a lower limit. The actual amount may be several times larger.

²Murphy and Rzeszutko (1978).

³Hesse, J. L. (1976). Conference Proceedings. National Conference on Polychlorinated Biphenyls, Nov. 19-21, 1975, Chicago, Ill., EPA 560/6 75/004; NTIS, PB-253 248/9PSX; p. 127.

Kleinert, S. (1976). Conference Proceedings. National Conference on Polychlorinated Biphenyls, Nov. 19-21, 1975, Chicago, Ill., EPA 560/6 75-004; NTIS, PB-253 248/9PSX; p. 124; Personal communication.

Schact, R. A. (1974). Pesticides in the Illinois Waters of Lake Michigan. EPA 660/3-74-002, January 1974.

⁴An attempt to account for dry deposition of PCBs on the lake surface and to allow for small industrial discharges not yet identified.

A second formulation, the two film resistance model, is based on the work of Liss and Slater (1974) and Liss (1973) and the rate of the process under a given set of conditions is described as a simple first-order exponential decay with rate constant K_L per depth. K_L , the overall mass transfer coefficient, has units of distance per time (such as cm hr^{-1}) and can be expressed in terms of three components: k_g , k_l , and H , related by the expression

$$K_L = \frac{H k_g k_l}{H k_g + k_l} \quad (3)$$

where: H = the Henry's Law constant, a distribution coefficient representing the equilibrium distribution of a material between gaseous and liquid phases. Units used for H are molar concentration contaminant in air per molar concentration contaminant in water.

k_g = the gas phase exchange constant, a measure of the rate of transport of the material away from the interface in the air. Units are cm hr^{-1} .

k_l = the liquid phase exchange constant, a measure of the rate of transport of the material to the interface in the water. Units are cm hr^{-1} .

Both k_g and k_l are influenced by mixing within their respective phases, and to a lesser extent by mixing within the adjoining phase (Liss, 1973). The rate of volatilization of substance from a given water body will be determined by properties of the substance (H) and the environment (wind, water turbulence, and temperature). Temperature acts to influence H (Schwarz and Wasik, 1977), while k_l and k_g are primarily functions of wind and water turbulence, which vary to a lesser degree with temperature.

The gas phase mass transfer coefficients (k_g) are calculated at various wind velocities by multiplying the data of Liss (1973) for H_2O by

$$\left(\frac{\text{mol. wt. H}_2\text{O}}{\text{mol. wt. C}} \right)^{1/2} \quad (4)$$

Liquid phase mass transfer coefficients were calculated for various current velocities from stream reaeration coefficients (k_2) converted to metric units (Southworth, 1979).

$$k_2 = 0.2351 \frac{V^{0.969}}{R^{1.673}} (\text{hr}^{-1}) \quad (5)$$

where V is current velocity (m s^{-1}), and R is mean depth (m^{-1}).

The reaeration coefficient (a first order-rate constant) was converted to the mass transfer coefficient by multiplying by the depth. While the most direct effect of varying wind velocity is upon k_g and of current velocity is upon k_1 , each also affects the mass transfer coefficient of the adjoining phase.

Southworth (1979) fit the data of Liss (1973) to an exponential curve:

$$k_g = 1,137.5 (V_{\text{wind}} + V_{\text{current}}) \left(\frac{18}{\text{mol. wt.}} \right)^{1/2}; \quad (6)$$

for wind $< 1.9 \text{ m s}^{-1}$

$$k_1 = 23.51 \frac{V_{\text{current}}^{0.969}}{R^{0.673}} \left(\frac{32}{\text{mol. wt. C}} \right)^{1/2}; \quad (7)$$

for wind $> 1.9 \text{ m s}^{-1}$

$$k_1 = 23.52 \frac{V_{\text{current}}^{0.969}}{R^{0.673}} \left(\frac{32}{\text{mol. wt. C}} \right)^{1/2} \left(e^{0.526(V_{\text{wind}}^{-1.9})} \right) \quad (8)$$

V_{wind} = wind velocity (m s^{-1}), V_{current} = current velocity (m s^{-1}), R = stream depth (m), and units of k_1 and k_g are cm hr^{-1} .

For wind velocities below 1.9 m s^{-1} (<11 mph), the reaeration coefficients were assumed constant. This approximation was made because there were no data for wind velocities below 1.9 m s^{-1} .

O_2 reaeration values for large bodies of water are scarce. The EXAMS model uses the values reported in Metcalf and Eddy (1972) of 0.10–0.30 per day. For convenience they selected 0.24 per day,

$$k_v^c = \frac{0.24 \times 2.98}{d^c}, \quad (9)$$

Making k a constant for each substance under consideration.

For the dynamic calculations:

$k_1 = f(\text{currents, wind and depth})$ that are available;

$k_g = f(\text{wind and currents})$.

The two film model is theoretically more satisfactory and data for Henry's Law constants are becoming available for many compounds.

Laboratory estimates of Henry's Law coefficients (H) and estimates based upon the ratio of equilibrium vapor pressure to aqueous solubility are presented in table 2 from Southworth (1979). The trend toward decreasing H with increasing molecular weight within the PAH group is clear for either group of estimations. The relationship between H and molecular weight for the laboratory data is given by:

$$\log H = -0.01910 (\text{mol. wt.}) + 0.78540, R^2 = 0.996. \quad (10)$$

Except for anthracene, laboratory and literature values of H are in reasonable agreement, especially in view of the very low vapor pressures and solubilities which must be determined. There is a temperature effect in Henry's Law coefficients; however, over the 25°C range in the lakes (273° to 298°K), the effect is small with respect to measurement errors, which are probably a factor of two.

From our review work, the following formulations will be adapted initially:

$$K_L = 0.30 + 0.028 W^2 \quad (\text{M day}^{-1}) \quad W \equiv \text{wind speed (m s}^{-1} \text{ @ 10 M).}$$

$K_L =$ liquid transfer coefficient

Flux = $K_L (C_{\text{air}} - C_{\text{water}})$

$$k_g = 1,137.5 (W + V) \left(\frac{18}{\text{mol. wt. } C} \right)^{1/2}$$

$k_g =$ gas transfer coefficient

V = current velocity (assumed zero)

$$K_T = \frac{H K_L K_g}{H K_g + K_L}$$

where H is Henry's Law coefficient.

Research on air-water exchange is being conducted in many places. Our work focuses on the question of whether the surface microlayer plays an important role in the cycling of selected organic contaminants.

TABLE 2.--Estimations of Henry's Law constants for PAH in water at 25°C, S.E. of regression coefficient. Units of H are molar concentration of PAH in each phase. Exponent (10-n) applies to both columns (from Southworth, 1979)

| | Experimental | Literature |
|--------------------|----------------------|------------------------------|
| Naphthalene | 2.26 ± 0.03 | 1.9 × 10 ⁻² (a) |
| Anthracene | 2.66 ± 0.07 | 12 × 10 ⁻³ (b,d) |
| Phenanthrene | 2.24 ± 0.05 | 2.0 × 10 ⁻³ (c,e) |
| Pyrene | 7.64 ± 0.26 | 4.3 × 10 ⁻⁴ (b,f) |
| Benzo(a)anthracene | 3.28 ± 0.46 | 1.0 × 10 ⁻⁴ (c,f) |
| Benzo(a)pyrene | 1 × 10 ⁻⁴ | 2.1 × 10 ⁻⁵ (b,f) |

(a) Schwarz and Wasik, 1977.

(b) Solubility from Schwarz and Wasik (1976).

(c) Solubility from Davis *et al.* (1942).

(d) Vapor pressure extrapolated from Handbook of Chemistry and Physics, 46th Edition.

(e) Vapor pressure extrapolated from Osborn and Douslin (1975).

(f) Vapor pressure from Pupp and Lad (1974).

There is little question today that atmospheric transport is an important route of delivery of pollutants to the Great Lakes. Some recent evidence for this comes from the discovery of toxaphene, an insecticide used mostly in the south, in Great Lakes fish. Details of the processes that deliver these materials to the lake surfaces are largely unknown.

Recently, interest has been growing in trying to explain cycling between major reservoirs, and in describing exchange processes and defining new compartments. One of these compartments of interest in the Great Lakes is the surface microlayer. Because of its extreme thinness (0.001 to 200 μm, Liss, 1975), this compartment is not important as a major reservoir for contaminants. However, its roles as a biologically active zone for neustonic pollutant cycling and as a collector and recycler of both natural and anthropogenic hydrophobic compounds have only recently been appreciated.

Critical to determining the importance of the microlayer to PCB transfer are precise measurements of PCB concentrations in the surface microlayer and determination of residence times for PCBs in this region. A number of measurements of PCBs and related toxicants in microlayers from the marine environment can be found in the literature; however, few data are available for freshwater environments. Andren *et al.* (1976) and Eisenreich *et al.* (1978) reported DDT enrichments in the surface microlayer of Lake Mendota, Wis., and Elzerman (1976) and Rice *et al.* (1982a) reported significant enrichments of PCB in surface microlayers of Lake Michigan.

Despite the many measurements of PCBs in surface microlayers, there have been no studies to determine residence times at the air-water interface. Modelers of air-water transfer of PCBs have generally considered the microlayer as unimportant. Slinn *et al.* (1978) stated that, without the water surface being constantly covered by a surface film, it is difficult to see how it could be important to transport. MacKay (1982) and Liss (1975) have stated that, from a theoretical standpoint, the microlayer would seem to offer at most only a mildly increased resistance to transfer at the air-water interface. Both of these suppositions, however, are based more on conjectural rather than on empirical foundations and neither consider the implications of photodegradation. The extent of coverage of the water surface by microlayer is not well known, and theoretical estimates are far from precise in terms of modeling air-water exchange of PCBs. Air-water exchange coefficients presently in use have been based on laboratory experiments that only partially reproduce the real system. For example, the particulate-to-dissolved associations of PCBs in the microlayer have not been considered, biological involvements in this transfer process have been largely ignored, and the actual chemical composition of the lipophilic materials in this region is only poorly understood.

PCBs, because of their high affinity to surfaces (Haque and Schmedding, 1976), would seem to be readily transported by particle and bubble transport. Recent research has disclosed that bubbles and particles may function as important vehicles of transport of materials contained in microlayers. Sodergren (1979) presented evidence from a laboratory study which shows that bubbles discharging through the microlayer surface can remove significant portions of lipid components of the microlayer. Johnson and Cooke (1980) studied the rate of bubble dissolution in the formation of aggregates and particles. Many of the processes described by Johnson and Cooke (1980) as "below-surface phenomena" may actually be taking place at the sea surface as this surface film can be loosely construed as a large bubble surface separating the air from the lake. Wheeler (1975) demonstrated that particles could be produced by compressing surface films. Thus particle generation by and in surface films may be an important mechanism leading to transfer of substances from this zone. A net result of this process would be a downward flux of sedimenting particles with their associated organic contaminants.

Data are presented here on the concentration of PCB as Aroclor® 1242 and Aroclor® 1254 in the surface microlayer, near-surface water, and air over Lake Michigan. The data are further detailed to describe these PCB distributions as either absorbed to particles or free as a solution or gas. The premise is that knowing the particulate phase distribution should offer insight into transport pathways.

3.1 Methods

Samples for this study were collected from Lake Michigan during cruises in 1979 and 1980. The stations occupied are shown in figure 2. On each of these cruises, samples of air were collected while underway and samples of surface microlayer and subsurface water were collected while on the designated stations. The air was sampled by drawing air first through a precleaned glass fiber filter for particulate removal followed by series of pre-extracted polyurethane foam plugs for vapor phase removal of high molecular weight chlorinated hydrocarbons (Billings and Bidleman, 1980). Some of the samples were collected near shore in the vicinity of the Grand River (inset in figure 2). The details of sampling are described in Rice *et al.* (1982b). Surface film collection was done primarily with a screen sampler of the type first described by Garrett (1965). Film thicknesses collected by this method were calculated to be about $385 \mu\text{m} \pm 55$. The material collected by the microlayer samplers was drained into glass bottles. For subsurface water collection, a 10-L stoppered bottle was submerged to a depth of approximately 1 m before being opened. After collection, each of the samples was immediately filtered through precombusted Gelman glass fiber filters which were stored frozen for subsequent extraction. The dissolved fractions were extracted by mixing with pesticide grade methylene chloride.

To address the question of possible shipboard contamination, some microlayer samples were collected at a distance from the ship with a small fiberglass boat. Care was taken to position the boat upwind of the ship and at a distance no closer than 30 m. There was no significant difference in samples collected from the ship versus those collected from the small boat.

Organic carbon concentrations of the dissolved and particulate phases were determined. Each of the sample fractions--microlayer particulate and dissolved, and subsurface particulate and dissolved--was analyzed for PCBs. This involved solvent extraction of the dissolved material with methylene chloride and Soxhlet extraction of the filters with a 1:1 mixture of acetone:hexane. For preparation of the samples for electron capture gas chromatograph (EC/GC) analysis, each of the separate particulate and dissolved fractions was cleaned of contaminants by alumina chromatography (Christensen *et al.*, 1979) and then these extracts were separated by silicic acid column chromatography (Bidleman *et al.*, 1978) into their various organochlorine classes. Suspended solids determinations were carried out for the 1980 collections.

3.2 Results and Discussion

To compile a total PCB concentration, each particulate phase concentration has been combined with its dissolved complement and the Aroclor® levels added together. The total PCBs in each region--surface microlayer or subsurface water--for each sampling period in 1979 and 1980 are summarized in table 3. Air collected in 1979 averaged 2.8 ng m^{-1} and ranged from 0.84 to 4.6 ng m^{-1} PCB. Less than 5 percent of the total was collected on the prefilter and the total PCB in these samples was 70 percent Aroclor® 1242 and 30 percent Aroclor® 1254. The various water and microlayer collections were compared statistically. The test of variance on the totals for each of the four

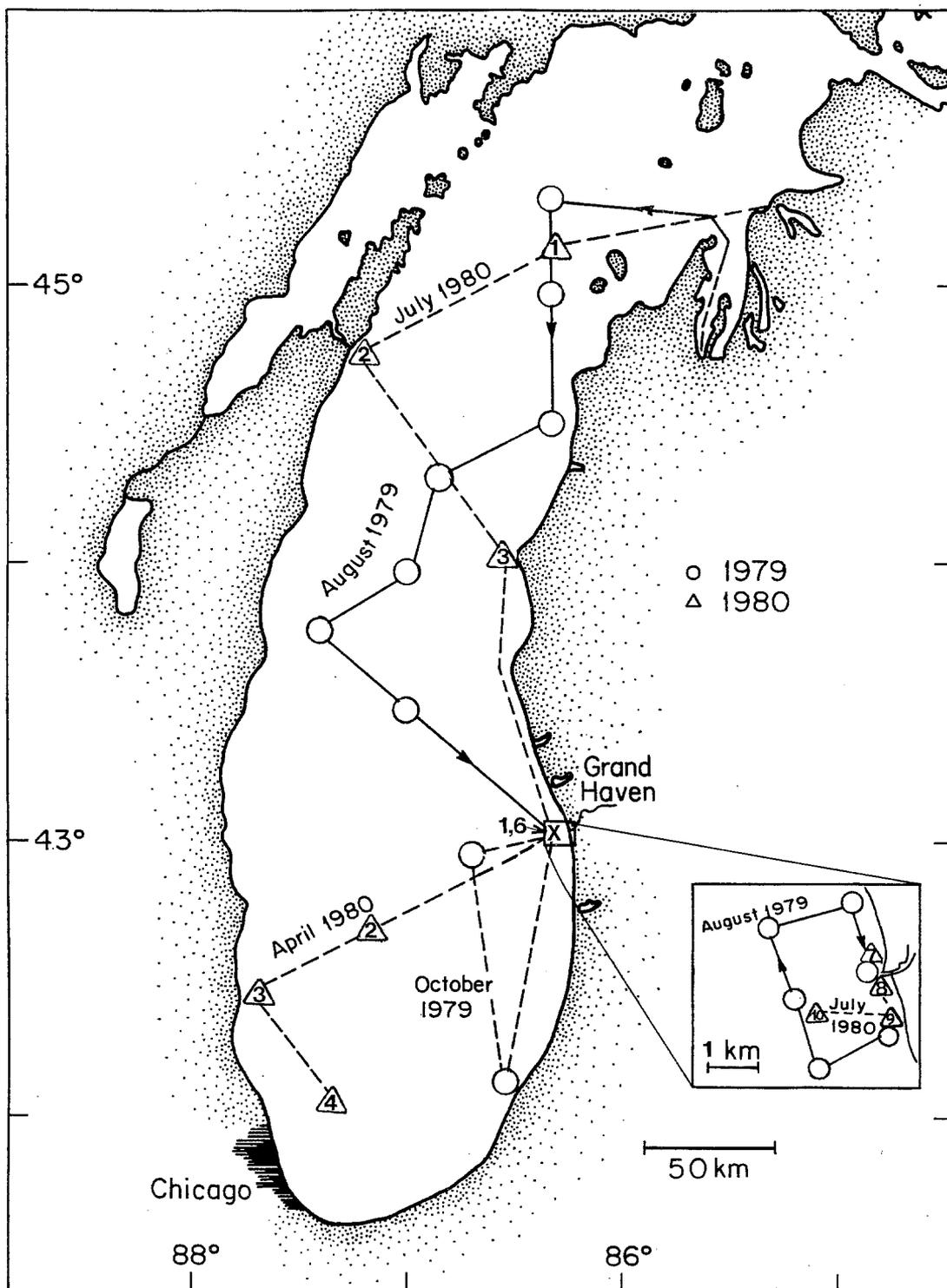


FIGURE 2.--Cruise tracks and sampling stations occupied in 1979 and 1980 for collection of microlayer and subsurface water from Lake Michigan. The solid arrows connecting the circles indicate that air sampling results are available for this cruise. The numbered stations refer to figures 3-5.

TABLE 3.--Average concentration of total PCB in Lake Michigan surface microlayer and subsurface water (1979-80)

| | Number of Samples | Mean Values | |
|---------------------------|-------------------|------------------------------|-------------|
| | | (ng/L) | s.d. (ng/L) |
| Surface Microlayer | | | |
| August 1979 | 12 | 15.70 | 12.28 |
| October 1979 | 5 | 21.38 | 17.02 |
| April 1980 | 11 | 22.03 | 8.91 |
| July 1980 | 10 | 17.63 | 3.71 |
| Subsurface Water | | | |
| August 1979 | 9 | 4.79 | 6.56 |
| August 1979 (qualified)* | 8 | 2.88 | 3.37 |
| October 1979 | | ----- no samples taken ----- | |
| April 1980 | 4 | 5.66 | 1.12 |
| July 1980 | 7 | 6.36 | 1.30 |

*See text.

periods indicated that there was no significant difference between them. For the subsurface values in August 1979, it was difficult to do any statistical treatment due to apparent outliers in the data set. By discarding one suspicious nearshore result, an average value of 2.88 ng L⁻¹ was calculated. Using the qualified value of 2.88 ng L⁻¹, it appears that there might have been a higher concentration of PCB in 1980 subsurface waters than in 1979.

The April and July collections from 1980 offer the most complete data sets for statistical processing. Figure 3 illustrates the particle and dissolved distribution of total PCBs in the microlayer and in the subsurface water in these samples. It can be seen in this figure that the proportion of PCBs carried on particles is always higher in microlayer than in subsurface samples. Also, the relative amount of PCBs on particles was higher in the microlayer and subsurface samples in July than in April. An explanation for this preferential partitioning onto particles in July might be related to a probable higher abundance of organic-containing particles in July as compared to April (Wetzel, 1975). In addition, elevated temperatures at this time resulted in higher rates of turnover (Paerl, 1978). Although this explanation is reasonable, organic carbon measurements were not carried out in April, and

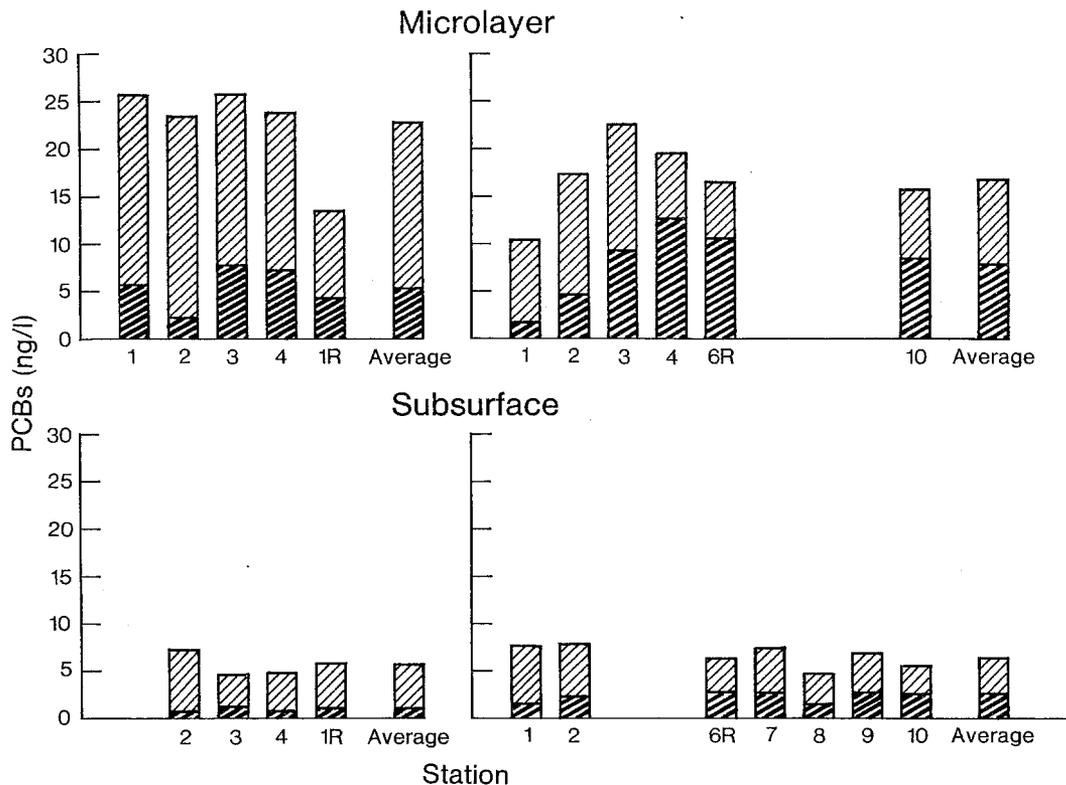


FIGURE 3.--The particulate and dissolved distributions of total PCB in samples of surface microlayer and subsurface water from Lake Michigan. The station numbers refer to the stations identified in figure 2.

so we were unable to test this supposition. Another reasonable possibility is the existence of a greater amount of suspended particulate material in Lake Michigan waters in July than in April. However, our measurements show that for July the suspended solids averaged 1.66 mg L^{-1} in the microlayer and 1.57 mg L^{-1} in subsurface samples, whereas for April these values were 2.95 and 2.01 mg L^{-1} , respectively. Therefore, a greater particle density did not correlate with the higher particulate partitioning, suggesting that the quality of the particles seems to be more important than their quantity.

Some qualitative observations were made on the particles in the microlayer from these two periods. Scanning electron microscopy was performed on the particles in the microlayer. In both April and July, bacteria were the dominant organisms in the microlayer. There was little variation in actual bacterial numbers (cell mL^{-1}) between the sets of samples. However, there was a difference in the mean percent composition. Bacteria represented from 76 to 90 percent of the total composition in April, whereas in July, 65 to 84 percent were bacteria. Algae represented a higher percentage of the total composition in the April microlayer, while in July, a higher percentage of miscellaneous particles was present. This trend was also apparent when samples collected at the same station in April and July were compared.

Comparison of the samples collected on 0.2 μm and 0.8 μm filters showed little variation of the contents and bacterial numbers were quite similar.

Careful examination of the peaks produced by the packed column analysis of the samples showed that various blends of Aroclor® 1242 and Aroclor® 1254 could best account for most of the GC peaks resolved in our analyses. Thus, each sample subset is initially reported in terms of these mixtures. For 1980 microlayer samples, it appears that the relative amount of Aroclor® 1242 on the particles is significantly correlated with the percentage of particulate-associated PCBs for both April and July sampling times (figure 4). In contrast, there appears to be a negative correlation on the percentage of particulate-associated PCBs with the proportion of Aroclor® 1242 on the subsurface particles (figure 5). For the subsurface region, this agrees with

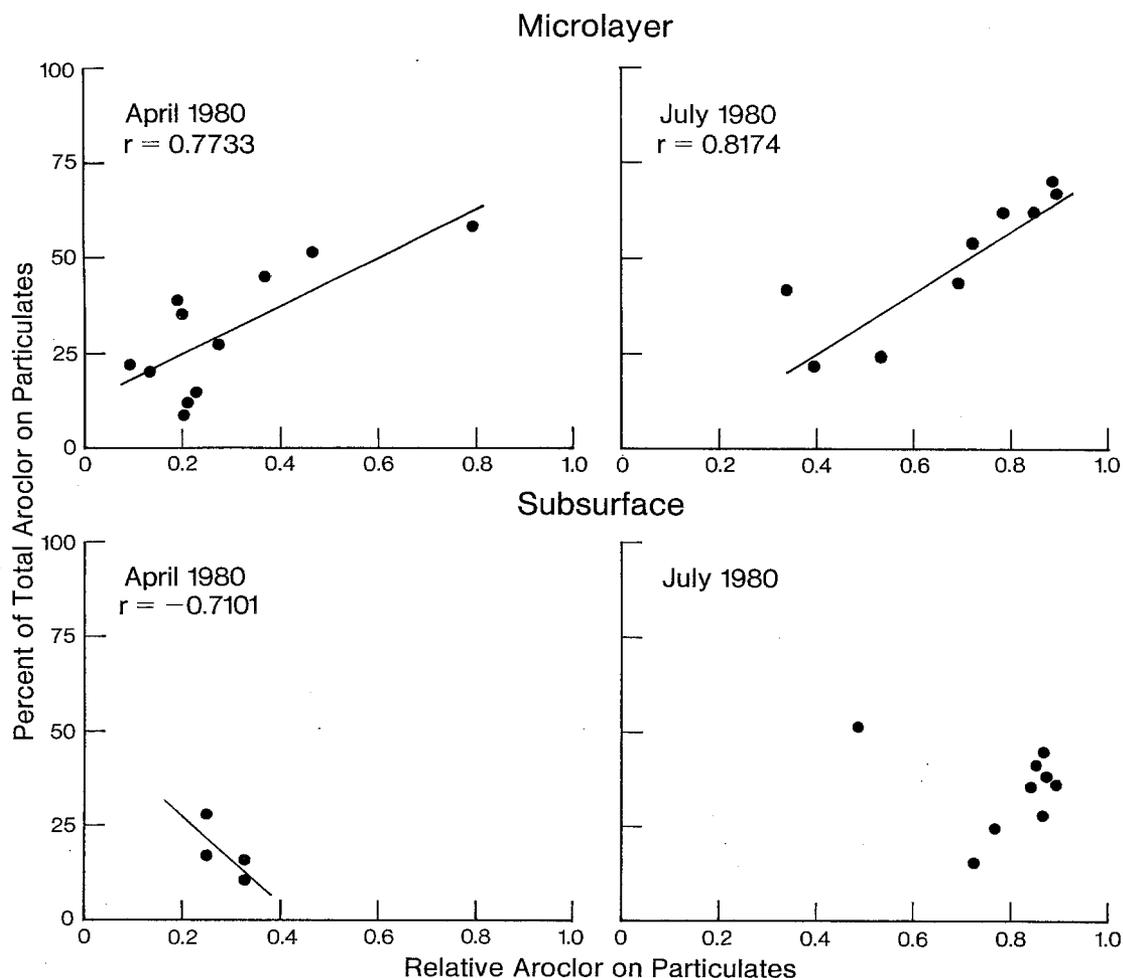


FIGURE 4.--Correlation between the amount of total PCB associated with the particulates in the microlayer samples from April 1980 and July 1980 versus the percentage of the total amount of the PCB on the particles that was measured as Aroclor® 1242.

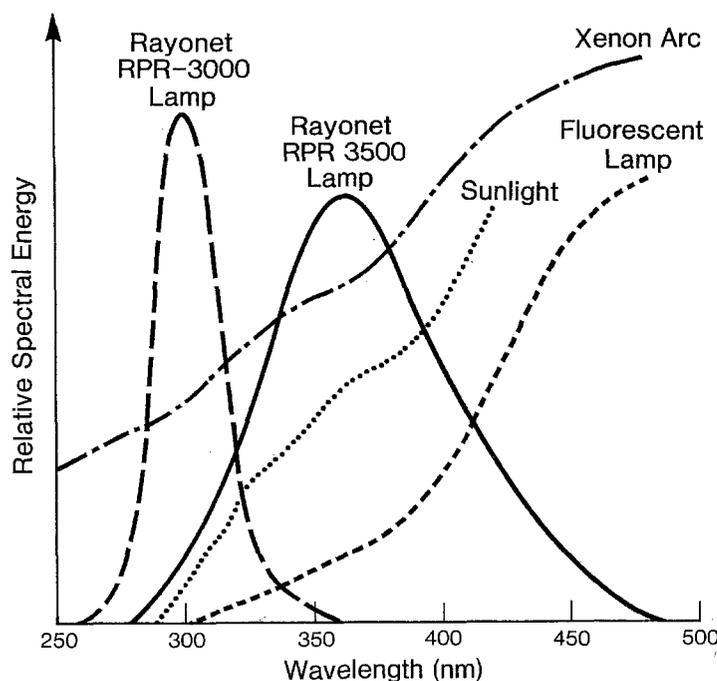


FIGURE 5.--Emission spectra of light sources: (a) fluorescent sunlamp, (b) transmission of borosilicate glass, (c) normal sunlight, and (d) daylight fluorescent.

predicted partitioning behavior of PCBs, because the less-water-soluble Aroclor® 1254 should associate more readily with particles than would Aroclor® 1242.

A useful way to express partitioning behavior is to calculate a partition coefficient (K_p) for the PCBs in each of the phases. For calculation of K_p 's, the usual procedure is to divide the concentration of the material on the particles by the concentration of the substance dissolved in the solution; therefore, this number adjusts for the concentration of suspended solids. In samples from July 1980, we were able to normalize these values to organic carbon content as suggested by Karickhoff *et al.* (1979). Partition coefficients calculated for 1980 samples ranged from 1.4×10^5 to 9.4×10^5 . A test of difference was performed using a Student's *t* test. None of the values was statistically different. After applying the Karickhoff organic carbon correction to the July values, the mean K_p 's were 4.5×10^6 and 1.5×10^6 , respectively, for the microlayer and subsurface samples. The greater K_p value in the microlayer was found for both the non-organic and organic corrected result. This finding is surprising as it would seem that the natural organic components that constitute the microlayer would reduce the difference in partitioning and that the surface K_p 's would be lower than those in the subsurface. For instance, the greater level of dissolves lipophilic materials generally present in microlayers (Meyers and Kawka, 1982) might keep hydrophobic materials in solution and therefore produce lower K_p 's in the surface

microlayer. Furthermore, there was no difference in particulate organic carbon concentrations in these surface and subsurface samples. The average organic carbon content of particulates in microlayer samples collected in July was 25.2 percent as compared to 25.3 percent for subsurface samples. Although some unmeasured difference in the biochemical composition of the particles may be responsible for this unexpected observation, differences in organic matter content of the surface microlayer and of subsurface waters do not seem to be responsible.

Partition coefficients for the subsurface PCBs were calculated by Aroclor® type and the relative values compared. Solubility differences would predict a stronger tendency for Aroclor® 1254 to be associated with the particles than Aroclor® 1242 (Haque and Schmedding, 1976). However, in general there was little difference in K_p 's for the two Aroclor® mixtures. Others have also observed this same lack of difference for the Aroclor® mixtures occurring on particles in Lake Superior water (Eisenreich *et al.*, 1981).

The correlation of percent particulate sorption of total PCBs with the percent Aroclor® 1242 content of the particulates has some interesting implications (figures 4 and 5). It suggests that, when the amount of PCB in the microlayers is more highly associated with particulates, the relative concentration of Aroclor® 1242 is higher. This is contrary to what solubility rules would dictate, as K_p 's are reported to decrease with increasing solid concentrations (O'Connor and Connolly, 1980). However, as the amount of Aroclor® 1242 increases disproportionately to the Aroclor® 1254, this correlation appears to relate to disequilibrium in the microlayer, perhaps from a recent input phenomenon. The likeliest source of higher than typical ratios of Aroclor® 1242 to Aroclor® 1254 is the atmosphere (recall from the atmospheric data that 70 percent of the total PCB was Aroclor® 1242). Both the microlayer and subsurface K_p 's could be influenced by a direct source input of particles from the atmosphere. In this case, partitioning has occurred through vapor phase onto a solid surface (i.e., the airborne particle). Therefore, it appears that the highly correlated particle association of Aroclor® 1242 to microlayer content of particulate PCBs has a direct link to an atmospheric input loading of this material. Murphy and Rzeszutko (1977) reported particles in rain to contain more Aroclor® 1254 and 1260 than Aroclor® 1242; therefore, rainout of particles is not a likely source of the Lake Michigan PCBs. A more plausible source of microlayer particulates would be the dryfall of particulates. A further implication of these results is that the particles, once in the microlayer, may play an important role in downward PCB transfer. Processes have been reported which might create particulate flux out of the microlayer (Wheeler, 1975) and lead to downward transport of PCBs and similar hydrophobic organochloride materials into deeper portions of the water column.

3.3 Summary and Conclusions

The results of this 2-year period of study of PCBs in the air-water interface of Lake Michigan provide new information about the probable significance of surface microlayers to the cycling and transport of contaminants. This information can be summarized as:

1. Concentrations of total PCBs are three times greater in the surface microlayer than in waters 1 m below the surface. Although considerable spatial and temporal variability exists in these concentrations, subsurface concentrations appear to be greater in samples collected in 1980 than in 1979 samples.

2. A greater proportion of total PCBs is in the particulate phase in the surface microlayer than in subsurface waters. This behavior does not correlate with organic matter nor with particulate matter concentrations.

3. Aroclor® 1242 and Aroclor® 1254 are the major PCB types present in Lake Michigan waters. The amount of Aroclor® 1242 with the particulates of the microlayer correlates positively with the proportion of total PCBs associated with particles. In subsurface samples, there is a negative correlation.

4. Particulate-dissolved partitioning coefficients (K_p 's) of total PCBs are greater in the microlayer than in subsurface water, although organic matter contents of particulates in both regions are the same. K_p 's of Aroclor® 1242 and of Aroclor® 1254 are not significantly different despite the possible effect of solubility differences.

These observations indicate that there is a significant enhancement of particulate-phase PCBs in the surface microlayer of Lake Michigan. The most probable origin of this phenomenon is dryfall input of airborne particles that contain PCBs and their transitory accumulation in the air-water surface. These particles have the potential of becoming sufficiently aggregated to sink into deeper parts of this lake.

We are currently attempting to incorporate this information into our model structures and determine whether we need to explicitly model a microlayer zone in order to simulate organic contaminant behavior.

4. PHOTOCHEMICAL DEGRADATION AND TRANSFORMATION STUDIES OF TOXIC ORGANICS IN THE GREAT LAKES

The overall objective of this research investigation is to conduct studies on the photochemical degradation of toxic organic compounds and to determine the role of this process in their transformation and fate in the Great Lakes. Laboratory simulation experiments using both natural and artificial light sources were conducted for PCBs and polynuclear aromatic hydrocarbons (PAH). The effects of varying conditions on the photodecomposition process, expressed as photolytic rates, can describe the cycling, transport, and fate of toxic compounds in the Great Lakes when incorporated in a model.

In the aquatic environment, PCBs and PAHs are relatively stable and resistant to breakdown. This persistent nature can be attributed to their chemical and physical properties, such as low water solubility, low vapor pressure, high dielectric constant, and resistance to chemical, heat, and biological degradation. Concentrations in the water column are much lower than concentrations in the sediments and in aquatic organisms such as fishes

(U.S. EPA, 1976; WHO, 1976; Andelman and Snodgrass, 1974; Nisbet and Sarofim, 1972).

A comparison of analytical data shows that the Great Lakes contain the highest concentration of these compounds (Peakall, 1975; Nisbet and Sarofim, 1972). Effluents from wastewater treatment plants serving industrialized communities have been found to be highly contaminated (Berg *et al.*, 1974). It appears that these compounds continue to be discharged into the Great Lakes from many small but diffuse sources, including atmospheric fallout (Delfino, 1976).

For some compounds, it may take several years before their concentration begins to decrease substantially in the environment. Transformation processes include photochemical and microbial pathways. Although these may degrade these pollutants, they may also be responsible for the production of more toxic substances. For example, chlorobiphenyls have been found to undergo photochemical degradation to produce not only the lower chlorinated products (less toxic) but also the more toxic dibenzofuran and chlorobiphenyl products (Safe *et al.*, 1976).

For many of these compounds, photochemical decomposition may be a major pathway of degradation. PCBs absorb strongly in the ultraviolet region. PAHs absorb both in the UV-A (320 to 400 nm) and UV-B (280 to 320 nm) regions. Differences in the absorbance of these compounds, as well as the intensities in the water column at certain wavelengths, will strongly influence the photochemical fate of these compounds. Because of the hydrophobic nature of PCBs and PAHs, they are expected to occur mostly in the lipid phases of organic films (Elzerman, 1976), in micelles (Ehrhardt, 1977), or adsorbed on particulate matter (Karickhoff *et al.*, 1979). Thus, sensitized photochemical processes are possible.

A common parameterization of the photochemical process assumes the reaction to be first-order where the net rate, K_p , is defined as

$$K_p = K_d + K_I \quad (11)$$

where K_d = direct photolysis rate, and

K_I = indirect photolysis rate.

Chemical transformations due to direct photolysis are caused by direct exposure to radiation, while indirect photodecomposition occurs only in the presence of a photosensitizer. The two rate processes are calculated for any depth in the water column according to equations (1) and (2).

$$K_d(Z) = \phi \int I(\lambda, Z) \epsilon(\lambda) d\lambda \quad (12)$$

$$K_I(Z) = S\phi_s \int I(\lambda, Z) \epsilon(\lambda, S) d\lambda \quad (13)$$

where $I(\lambda, Z)$ = irradiance at wavelength λ at depth Z ,

$\epsilon(\lambda)$ = molar absorptivity at λ ,

$\epsilon(\lambda, S)$ = molar absorptivity of sensitizer,

S = concentration of sensitizer,

ϕ = quantum yield, and

ϕ_S = quantum yield per unit concentration of sensitizer.

The results of this study provide information on the photolysis rates of selected contaminants found in the Great Lakes.

4.1 Experimental Methods

Sources of ultraviolet light for the irradiation experiments include the following:

- (a) Natural sunlight,
- (b) Sunlamp in an enclosure, General Electric 275W "Sunlamp-UV enhanced,"
- (c) Blacklight (four General Electric F40 BL fluorescent lamps mounted with reflective backing),
- (d) Rayonnet photochemical reactor (merry-go-round type equipped with the RPR 2537 Å, RPR-300 Å, and RPR 3500 Å lamps), and
- (e) Xenon arc lamp (150 w, Canrad-Hanovia, using Pyrex glass as filter).

The emission spectra of these light sources are shown in figure 5. Light intensities for the light sources in the Rayonnet are as follows: for 2537 Å, 1.05×10^{16} quanta $s^{-1} mL^{-1}$; 3000 Å, 3.53×10^{16} quanta $s^{-1} mL^{-1}$; 3500 Å, 1.29×10^{16} quanta $s^{-1} mL^{-1}$.

Midday, midsummer values for sunlight intensities at 40°N latitude in natural waters at shallow depths are: 0.24×10^{13} photons $cm^{-2} s^{-1} 2.5 nm^{-1}$ for 3000 Å and 0.102×10^{16} photons $cm^{-2} s^{-1} 10 nm^{-1}$ at 3500 Å (Zepp and Cline, 1977).

Pure compounds have been used in the studies from commercially available sources. Experimental media included Lake Michigan water at 1- and 10-m Lake Michigan microlayer, distilled water, and laboratory grown phytoplankton.

A Varian 3700 gas chromatograph equipped with a 6 ft by 0.318 cm ID column packed with 3 percent OV-101 on Gass-Chrom Q100/120 and a nichel-63 electron capture detector, as well as an SE-54 silica capillary column and a flame ionization detector were used.

Aliquots of the irradiated and control solutions were extracted with solvents. Internal standards were used in each case. The corrected peak heights or areas were averaged for the triplicate samples and the rates of decomposition calculation.

4.2 Results and Discussion

Preliminary experiments using Aroclor® 1254 (PCB) in water, irradiated under General Electric sunlamps were conducted. The results show that, without stirring, disappearance with time of the higher isomers was more pronounced than that of the lower isomers. With stirring, the lower isomers disappeared at a faster rate. In both cases a marked difference in the disappearance rate of the PCB in the light flask versus that in the dark flask (wrapped in foil) was observed. Figure 6 shows a chromatogram of PCB indicating where the major changes occurred. These peaks corresponded to the hexachlorobiphenyl (HCB) and higher chlorinated isomers of PCB (Stalling *et al.*, 1980).

Further experiments using fluorescent lights showed no significant change in the PCB 1254 concentration even after 48 hours of exposure. Sealed quartz tubes containing $60 \mu\text{g L}^{-1}$ of PCB 1254 were irradiated under natural sunlight. At the end of 5 days, most of the peaks disappeared, except for the HCBs. No appreciable change in the concentration of 2,4,5,2',4',5'-HCB occurred in 21 days, but a change was observed for ,3,6,2',3',6'-HCB after 10 days.

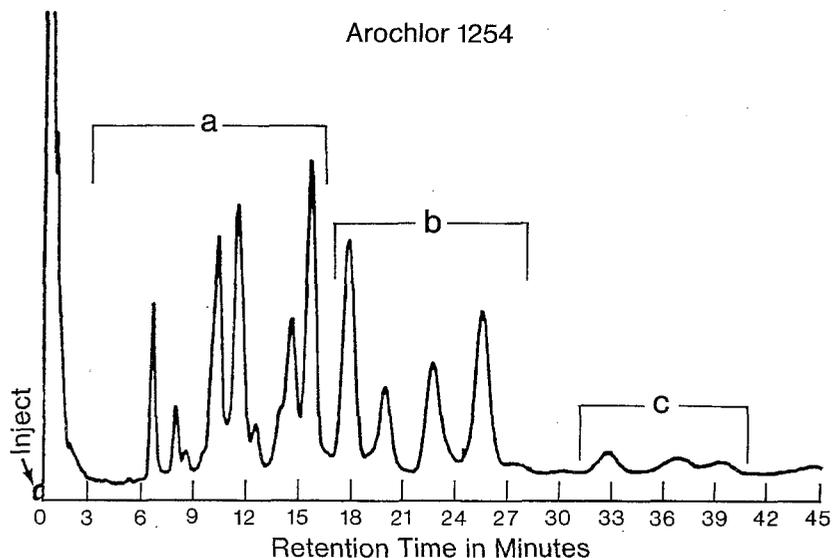


FIGURE 6.--PCB chromatogram: "a" peaks remained unchanged, "b" peaks decreased with time, and "c" peaks disappeared completely after 30 min.

4.3 Photolysis Studies of Pure Isomers

Commercially available pure isomers that have been previously identified to be components of PCB 1254 were selected and obtained to be used in a series of experiments.

Figure 7 shows a typical pattern of photodecomposition using the Rayonet reactor with 2537 Å, 3000 Å, 3500 Å, and a combination of 3000 Å + 3500 Å light sources. The 2,3,6,2',3',6'-HCB solution shows no appreciable degradation with the 3500 Å light source. The combination of 3000 Å + 3500 Å shows a rate intermediate of the individual lamps. And the 2537 Å shows the fastest rate. Because of the cut-off of sunlight irradiation at sea level at around 2950 Å, the choice was made to study the isomers using the 3000 Å light sources.

The photodecomposition rates of the isomers irradiated in the Rayonet system with a 3000 Å lamp are shown in table 4. The experiments using one-half the intensity of the light sources showed decreased degradation rates in

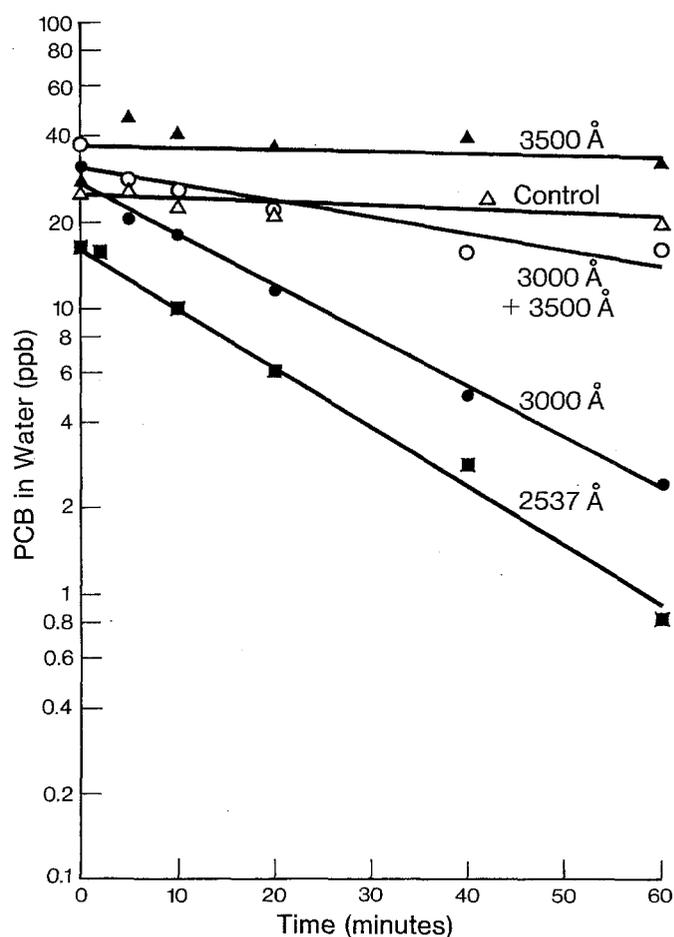


FIGURE 7.--Photodecomposition pattern for HCB resulting from exposure to several different light sources.

TABLE 4.--PCB isomers selected for this study

| PCB Isomers | Mol. Wt. | Solubility | | Total Surface Area | Photolysis** |
|---------------------|----------|-------------------|--|--------------------|----------------------------|
| | | mg/m ³ | | | Half-life (hr) (Summer) |
| 2,4 Dichloro | 223.10 | 1325 | | 226.01 | 3.42 |
| 2,4,4' Trichloro | 257.54 | 266 | | 243.58 | 48.21 |
| 2,5,4' Trichloro | 257.54 | ----- | | ----- | 93.43 |
| 2,3,2',3' Tetra | 291.99 | 26.2 | | 255.61 | 34.29 |
| 2,3,2',5' Tetra | 291.99 | ----- | | ----- | 72.05 |
| 2,4,3,4' Tetra | 291.99 | 16.8 | | 259.15 | 9.36 |
| 2,3,4,5,6 Penta | 326.43 | 9.04 | | 269.22 | 439.21 |
| 2,4,5,2',4',5 Hexa | 360.88 | 2.78 | | 290.78 | 167.74 |
| 2,3,4,2',3',4' Hexa | 360.88 | ----- | | ----- | 43.93 |

*Mackay, D., R. Mascarenhas and W.Y. Shiu. "Aqueous Solubility of Polychlorinated Biphenyls" *Chemosphere*, Vol. 9, pp. 257-264, 1980.

**Our studies

all cases (both for the two isomers at all wavelengths). Their quantum yields were calculated according to the Zepp (1978). From these data typical half-lives of PCB isomers were calculated (Zepp and Cline, 1977), and are shown in figure 8.

Structure activity relationship between the photolytic degradation rate, photolysis half-lives of PCBs, and their physico-chemical properties were investigated. The results of these studies are shown in table 5, indicating that the photolytic degradation rate strongly correlated to the total molecular surface area, the solubility, and fugacity ratio.

Continuing studies using HCB isomers were conducted. 2,3,6,2',3',6'-HCB and 2,4,5,2',4',5'-HCB were compared in terms of their photolytic behavior in the presence of lake water, calcium carbonate (CaCO₃), humic acid, and algae.

Using the sunlamp set-up, unfiltered lake water was found to have a much lower rate for both isomers (table 6). A decrease in the decomposition rate

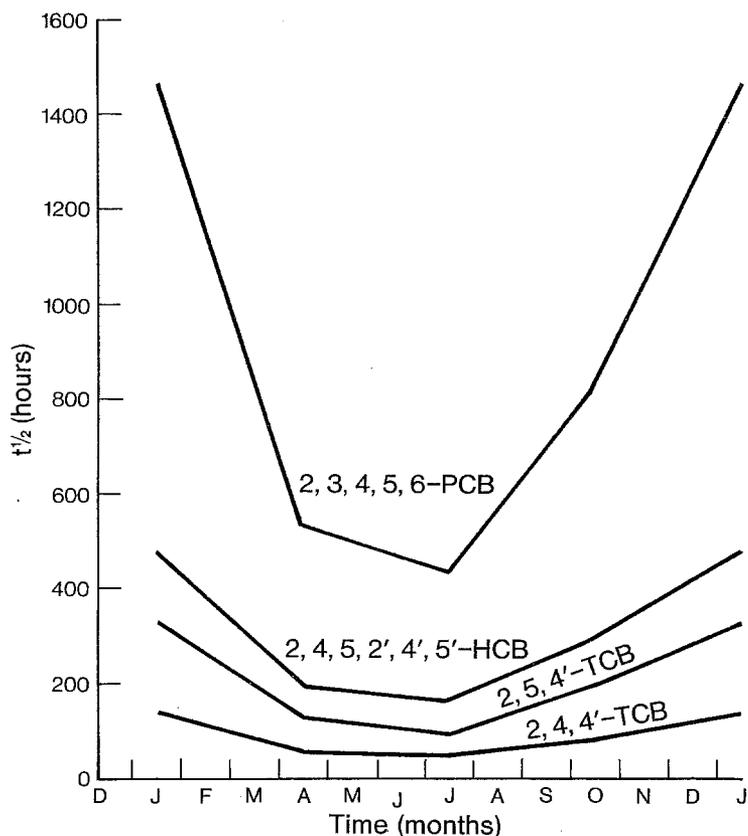


FIGURE 8.--Typical half-lives for four PCB isomers as a function of season.

was observed when 3.5 ppm CaCO_3 was added in solution. Filtered lake water exhibited a rate lower than the distilled water but higher than the unfiltered lake water. These results indicate the effect of shielding of light derived from the presence of particulate matter.

The same isomers showed the same behavior with filtered lake water using the Rayonet and the 3000 Å lamps (table 7). However, quite different results were obtained when algae were added to solution. The presence of algae suspensions (*Cyclotella meneghiana*) resulted in a marked increase in the decomposition rates for both isomers. These findings are in agreement with those of Zepp and Baughman (1978) using *Chlorella* and malathion, but no explanation has yet been found.

Current work in progress includes the effects of microlayer, humic acids, and CaCO_3 particulates on the photolytic degradation of PAH in aquatic systems. Lake Michigan microlayer and water samples were taken (on May 20, 1981; June 5, 1981; June 24, 1981; and August 3-5, 1981) at depths 1 and 10 m. Characterization of the microlayer by GC/MS (with capillary column) revealed the presence of the high molecular weight long-chain and aromatic hydrocarbons, which were practically eliminated when the samples were irradiated with a 5-Mrad dose of gamma rays. The radiation exposure was conducted to kill

TABLE 5.--Correlation coefficients

| | k degradation rate ⁽¹⁾ | ϕ_{300} Quantum Yield ⁽²⁾ |
|--|-----------------------------------|---|
| Mol. Wt. | 0.7027 (-) | 0.87252 (-) |
| γ activity Coeff. | 0.45741 (+) | 0.52918 (-) |
| Tot. Mol. Surf. Area | 0.90615 (-) | 0.82278 (-) |
| Solubility (mg/m ³) | 0.90668 (+) | 0.95335 (+) |
| Solubility (mol. f x 10 ⁹) | 0.89967 (+) | 0.95151 (+) |
| Fugacity Ratio | 0.92419 (+) | 0.88176 (+) |
| M.P. | 0.86065 (-) | 0.81945 (-) |

(1) For 2, 4' Dichloro-; 2, 4, 4' Trichloro-; 2, 3, 8', 3' Tetrachloro-; 2, 4, 3', 4' Tetra-chloro-; 2, 3, 4, 5, 6 Pentachloro-; 2, 4, 5, 2', 4', 5'; Hexachloro- 2, 3, 4, 2', 3', 4'; Hexachloro- Biphenyl.

(2) For 2, 4, 4' Trichloro-; 2, 3, 2', 3' Tetrachloro-; 2, 4, 3', 4' Tetrachloro-; 2, 3, 4, 5, 6 Pentachloro-; 2, 4, 5, 2', 4', 5', Hexachloro-Biphenyl.

TABLE 6.--Laboratory first-order decomposition rates using the sunlamp

| Medium | K(h ⁻¹) | |
|---|--|--|
| | 2,3,6,2',3',6'-HCB | 2,4,5,2',4',5'-HCB |
| Distilled Water | 0.00825 ¹ | 0.00722 ³ |
| Distilled Water +(3.5 mg L ⁻¹) CaCO ₃ | 0.00432 ² 0.00345 ⁵ | 0.00515 ⁴ 0.00212 ⁵ |
| Filtered Lake Water | 0.00566 | 0.0038 |
| Unfiltered Lake Water | 0.00365 | 0.0029 |

¹0 to 21 h. ²21 to 115 h. ³0.45 h. ⁴45 to 100 h. ⁵13 days.

TABLE 7.--Laboratory first-order decomposition rates using
Rayonet and 3000 Å lamps

| Medium | K(min ⁻¹)* | |
|--|------------------------|--------------------|
| | 2,3,6,2',3',6'-HCB | 2,4,5,2',4',5'-HBC |
| Distilled Water | 0.038 | 0.048 |
| In Filtered Lake Water | 0.029 | 0.046 |
| With Humic Acids 2.5 mg L ⁻¹ TOC | 0.037 | 0.042 |
| With Humic Acids 20 mg L ⁻¹ TOC | 0.034 | 0.034 |
| With Algal Suspension (1 x 10 ⁶ cells mL ⁻¹) | 0.557 (**) | 0.512 (**) |

*Average of triplicate runs.

**From 0 to 10 min.

bacteria and planktonic materials that might change the microlayer composition and affect the photolysis rates of the PCBs and PAHs. Work comparing irradiated vs. non-irradiated microlayer effects on the photodegradation process are in progress.

A method for introducing the toxic organics (PCB, PAH) into the lake water medium was also devised. This consists of exposing the solid or liquid pure compound through sublimation to 5 L of lake water contained in a closed system (vacuum desiccator) as follows. The compound is placed inside a weighing vial, which is supported above the water surface by a glass pedestal made of a three-legged Pyrex petri dish. Exposure is continued until the lake water medium is saturated with the compound. The solution mixture is then transferred to the reactor flasks and irradiated under sunlight along with the p-nitroacetophenone + pyridine and p-nitroanisole + pyridine actinometers (Dulin and Mill, 1982). Dark control flasks are also set up along with the reactor flasks.

Sunlight experiments using naphthalene at two concentrations showed a decrease of the degradation rate in Lake Michigan water compared to distilled water. Two concentrations of naphthalene in Lake Michigan microlayer showed a further decrease by a factor of two of the photolytic rate compared with deeper waters (table 8). Further studies of naphthalene with Lake Michigan water and 10, 50, and 100 ppm CaCO₃ showed an increase in the observed rates.

TABLE 8.--Sunlight experiments--
photodecomposition of naphthalene

| | |
|--|--------|
| Distilled Water $C_0 = 27.58$ ppm | 0.0291 |
| Lake Michigan Water $C_0 = 2.80$ ppm | 0.0112 |
| Lake Michigan Water $C_0 = 6.77$ ppm | 0.0130 |
| Lake Michigan Microlayer $C_0 = 3.57$ ppm | 0.0059 |
| Lake Michigan Microlayer $C_0 = 5.82$ ppm | 0.0064 |
| PNAP + PYR | 0.0352 |
| PNA + PYR | 0.0385 |

On the contrary, addition of 1, 5, and 20 ppm humic acid to Lake Michigan water showed a slight decrease in the rates.

We investigated the effect that algae (*Scenedemus*) grown in our laboratory might have in the photolytic rate of naphthalene. A marked increase in the photodecomposition rate of naphthalene in the presence of *Cyclotella* vs. Lake Michigan water was observed and further pursued. Growth medium only exhibited a decomposition rate for naphthalene comparable to that observed in Lake Michigan water. The addition of non-living *Cyclotella* to the growth medium showed a marginally increased rate compared to the growth medium alone. Thus it appears that algal exudates must exhibit only a marginal effect on the photolytic processes. Instead, the mechanism appears interconnected with the photosynthetic capacity of the cells. In any case, the importance of this process in natural systems is most important as an efficient degradation pathway of toxic organic compounds.

4.4 Conclusions

In conclusion, the following three points can be made:

(1) Photodecomposition rates for PCB are inversely related to their degree of chlorination. Higher chlorinated biphenyls have slower decomposition rates than less chlorinated ones.

(2) In general, the photodecomposition rate of PCB is slower in lake water than in distilled water. This is true for both filtered and unfiltered lake water.

(3) The presence of humic acids has no effect on photodecomposition rates for PCB, while algal suspensions markedly enhance the decomposition rate.

5. SORPTION

Sorption is probably the single most important process in the transport and fate of toxic organic compounds. This process affects all other subsequent removal mechanisms, the transport, and even the toxicity of these materials. For the neutral (nonionic), highly insoluble compounds that we are considering, the following equilibrium expression can describe the partitioning of material between liquid and solid phases:

$$K_p = [C]_s/[C]_w \quad (14)$$

where K_p = partition coefficient,

$[C]_s$ = concentration in substrate, and

$[C]_w$ = concentration in water.

Baughman and Lassiter (1978) state some generalities related to the sorption process based on their review of the field. They are:

- Sorption of highly insoluble organics by sediments and micro-organisms are rapid (time scale of hours);
- Sorption is rapidly reversible (time scale of days);
- Sorption by sediments is strongest with finer particles; and
- The most insoluble compounds are the most strongly sorbed (i.e., have the highest K_p).

The sorption of organic materials by sediments and soils is dependent on the nature of the adsorber and the adsorbate.

A number of soil/sediment parameters have been related to the sorption of organics. These include: organic matter, clay mineral content, clay mineral texture, pH, and amorphous and crystalline iron and aluminium hydrous oxide content. Organic matter and clay mineral content are the most active sorptive fractions of sediments. The nature of the organic molecule, whether it is a cation, anion or neutral molecule, its water solubility, its polarizability, its effective chain length, and molecular configuration are a few of the properties of the adsorbate that interact with the adsorber to influence the amount of adsorption.

Neutral molecules are generally not adsorbed to nonswelling-type clays, such as kaolinite, since only external surfaces are involved. Adsorption of neutral organic molecules by swelling-type clays is dependent on the polarizability of the molecule in the clay interlayer. Adsorption of neutral molecules may or may not result in a corresponding release of exchangeable inorganic ions.

Although clay minerals and to a certain extent hydrous oxides of iron and aluminium may be the most influential in adsorbing organic cations and some polarizable neutral molecules, sediment organic matter is undoubtedly of much more general importance in controlling neutral organic adsorption. Bailey and White (1970) gave the affinity of soil components for pesticides adsorption in this order: organic matter > vermiculite > montmorillonite > illite > chlorite > kaolinite.

Adsorption measurements of organic materials by soil and soil constituents generally have been expressed as adsorption isotherms. One of the most commonly used methods for describing the adsorption isotherms is the Freundlich equation.

The Freundlich adsorption isotherm is generally written as:

$$\frac{x}{m} = K C_o^{1/n} \quad (15)$$

where $\frac{x}{m}$ = the amount of material adsorbed per gram of adsorber,

C_o = the equilibrium concentration of the adsorbate left in solution,

K and n = constants.

An alternate form of the Freundlich isotherm can be written as:

$$C_s^n = K' C_w \quad (16)$$

or

$$K' = \frac{C_s^n}{C_w} \quad (17)$$

where C_s (the concentration of the adsorbate on the solid phase) = x/m

$$C_w = C_o \quad (18)$$

$$K^1 = K^n \quad (19)$$

The Freundlich isotherm is an empirical equation that has the disadvantage of predicting that adsorption can continue infinitely.

Karickhoff and co-workers (1978) have demonstrated that the adsorption of hydrophobic organics can be related substantially to the organic carbon content of sediments and sediment fractions. They also state that linear partition coefficients (K_p) are relatively independent of sediment concentration, and mixtures of hydrophobic substances are sorbed independently. Further, they determined that partition coefficients (K_p) that have been normalized on an organic carbon basis (K_{oc}) can be estimated from octanol/water partition coefficients. The relationships they suggest are:

$$K_{oc} = 0.53 K_{ow} \quad (20)$$

and

$$\log K_{oc} - 1.00 \log K_{ow} - 0.21 \quad (21)$$

These results were substantiated by Means *et al.* (1979) for several PAH/sediment combinations. Their average K_{oc} value for pyrene was 64,590 (+30 percent). Karickhoff (1979) reported that the rate of sorption was fast (minutes) up to 50 percents equilibrium, but slowed to (~50 hours) for 90 percent (pyrene) sorption on various classes of sediments. Desorption was slower yet. In our first-order model we will assume that sorption is "instantaneous" and remains at equilibrium (steady state) within the lake.

Our studies were initiated to quantitatively assess the effect of solids concentration on the partitioning of organic compounds, using particles indigenous to the Great Lakes. Four solutes of concern in this system and three sediments from Lake Michigan were selected for study. Table 9 lists these materials along with the octanol/water partition coefficients of the solutes and the organic carbon contents of the sorbents. This range of solute and sorbent properties was selected to allow the development of a model that includes an organic carbon dependence (Karickhoff *et al.*, 1979) and also incorporates a solids effect. This study attempts to conduct the necessary experimental tests at solute and sorbent levels as close as possible to those found in the Great Lakes to avoid errors resulting from extrapolation of results outside the development data set.

Sorption isotherms were conducted on various combinations of solids and solutes. All solutes were purchased as carbon-14-labeled compounds, allowing quantification well below 1 ng L^{-1} . Octanol/water partition coefficients were determined by a modification of the technique described by Karickhoff and Brown (1979). The solids were collected from the near-surface sediments of eastern Lake Michigan with a Shipek sampler, washed, dried, and sieved to remove particles larger than $60 \text{ }\mu\text{m}$. The organic carbon contents were measured by the persulfate oxidation technique. For each data point, a complete mass balance of each compound was possible. Recoveries, based on a direct spike of stock solution into scintillation cocktail, were found to range from 80

TABLE 9.--*Experimental materials*

| Solutes | log Kow | Solids | % organic carbon |
|---|---------|--------------------------------|------------------|
| chlorobenzene (MCB) | 2.8 | Offshore Grand Haven (OGH) | 2.9 |
| naphthalene (NAP) | 3.4 | Nearshore Grand Haven (NGH) | 3.4 |
| 2,5,2' trichlorobiphenyl (TCB) | 5.4 | Benton Harbor (BH) | 3.8 |
| 2,4,5,2',4',5' hexachlorobiphenyl (HCB) | 6.7* | | |

*As reported in Chiou *et al.* (1977).

percent to 100 percent. Single isotherm experiments were conducted at constant solids concentration. Reasonable linearity over the range of concentration was observed, and the data support the validity of a linear partitioning model. The partition coefficients were determined from the slope of the linear fit. Partition coefficients found at various solids concentrations using the same solute and sediment combination were replotted using log coordinates, and a high degree of linearity was found (figure 9). In all cases the partition coefficient increases significantly as the concentration of solids in the system decreases. A reasonable degree of linearity can be observed between the log-transformed variables. Similar slopes were found for all combinations. The expected dependence of partitioning on octanol/water partition coefficients and organic carbon contents were observed. An equation was derived by fitting numerical constants to the data. The equation appeared to accurately quantify the dependence of partitioning on solids concentration; however, it offered little insight into the reasons for this behavior.

Any investigation into possible theoretical explanations immediately confronts the unlikely possibility that the observed effect appears to violate the laws of thermodynamic equilibria. The diversity of solute-sorbent combinations that exhibit this behavior (O'Connor and Connolly, 1980) suggest a nonspecific, perhaps physical, explanation. It is believed that the change in partitioning behavior observed in this study can be attributed to a transfer of sorbing, or solute-binding, material from the solid phase to the liquid phase during the course of the partitioning experiment. This material, whether dissolved, macro-molecular, or micro-particulate in nature, is not removed from the liquid phase during the separation procedure and is capable of stabilizing the compound of interest in solution. The amount of material contributed to the liquid phase is most likely proportional to the amount of

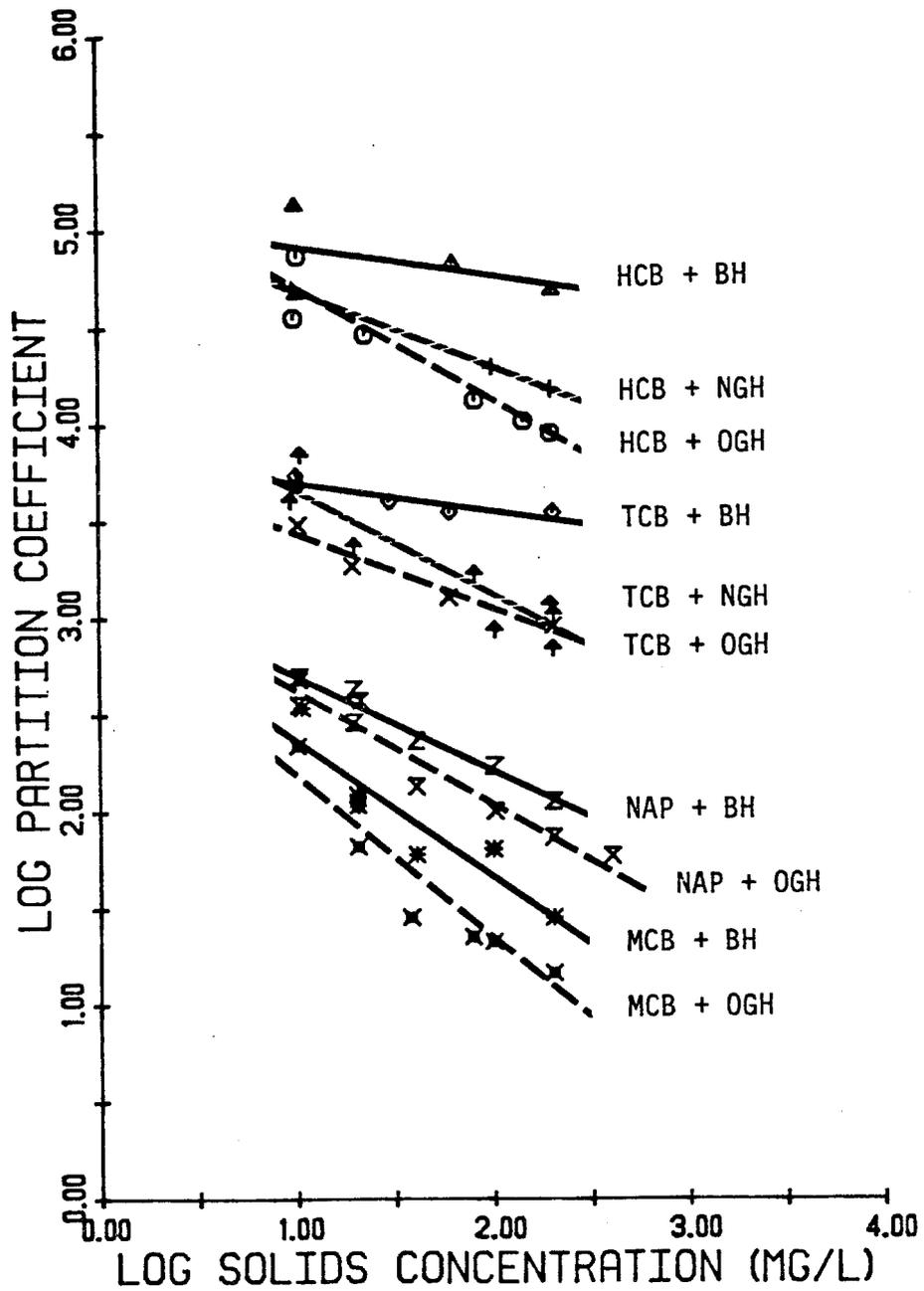


FIGURE 9.--Dependence of partition coefficients on solids concentration for four solutes and three Lake Michigan sediments.

solid phase present, and thus the capacity of the liquid phase to accommodate solute depends upon the concentration of solids in the system. The overall effect can be viewed as either a two-phase system, where the properties of one phase (liquid) vary with the mass of the other (solids), thus resolving the perceived thermodynamic inconsistency, or a three-phase system consisting of water, solids, and a third phase that is not separated from the water but possesses a higher capacity for the solute than the water itself. Given the demonstrated dependence of partitioning on the organic content of the sorbent, it is likely that the material transferred between phases is at least partially organic in nature.

To investigate this explanation, several experiments were performed to elucidate the nature of this third phase. In each experiment, a different mass of solids, but no solute, was added to each of several centrifuge tubes and was treated exactly as in the isotherm procedure. The liquid phase was analyzed after separation for total organic carbon (TOC), turbidity, UV absorbance at 254 nm, and fluorescence (excitation at 365 nm, emission at 415 nm). The results suggested the possibility of a third phase; however, data scatter at the low levels being worked with made absolute verification difficult. From the results generated to this point in the study, we concluded two things:

1. The effect appears to result from the presence of micro-particles contributed to the solution phase by the solids, but not removed in the separation procedure.

2. There are no simple means by which the presence of these micro-particles can be quantified, and thus extrapolation of the results to other systems can only be inferred.

It appears that the traditional single-solute, two-phase (solid/liquid) approach to sorption equilibria is not applicable to partitioning in aquatic systems. The existence of a third phase that is not separated from solution appears to be responsible for the observed solids effect. It is possible, however, that other assumptions of the simple equilibrium model are violated. Phenomena such as nonhomogeneity of the solid phase or solute reactions in either the solution or solid phases may occur and produce the observed results. To investigate these possibilities, a number of models involving deviations from simple phase equilibria were explored. Among these were a phase transfer model, a coupled reaction/sorption model (DiToro and Horzempa, 1982), a heterogeneous solute model, and a heterogeneous sorbent model. None of these models simulated a solids effect that was similar in all respects to combination of processes, or perhaps more accurately, a process that incorporates assumptions from more than one of the models. The model that was finally constructed to explain the data was a synthesis of conceptual elements from the heterogeneous solute and phase transfer models.

The derived model is shown schematically in figure 10. It is based on the following three assumptions:

1. A portion of the organic material in the solid phase becomes part of the liquid phase and is not removed during phase separation;

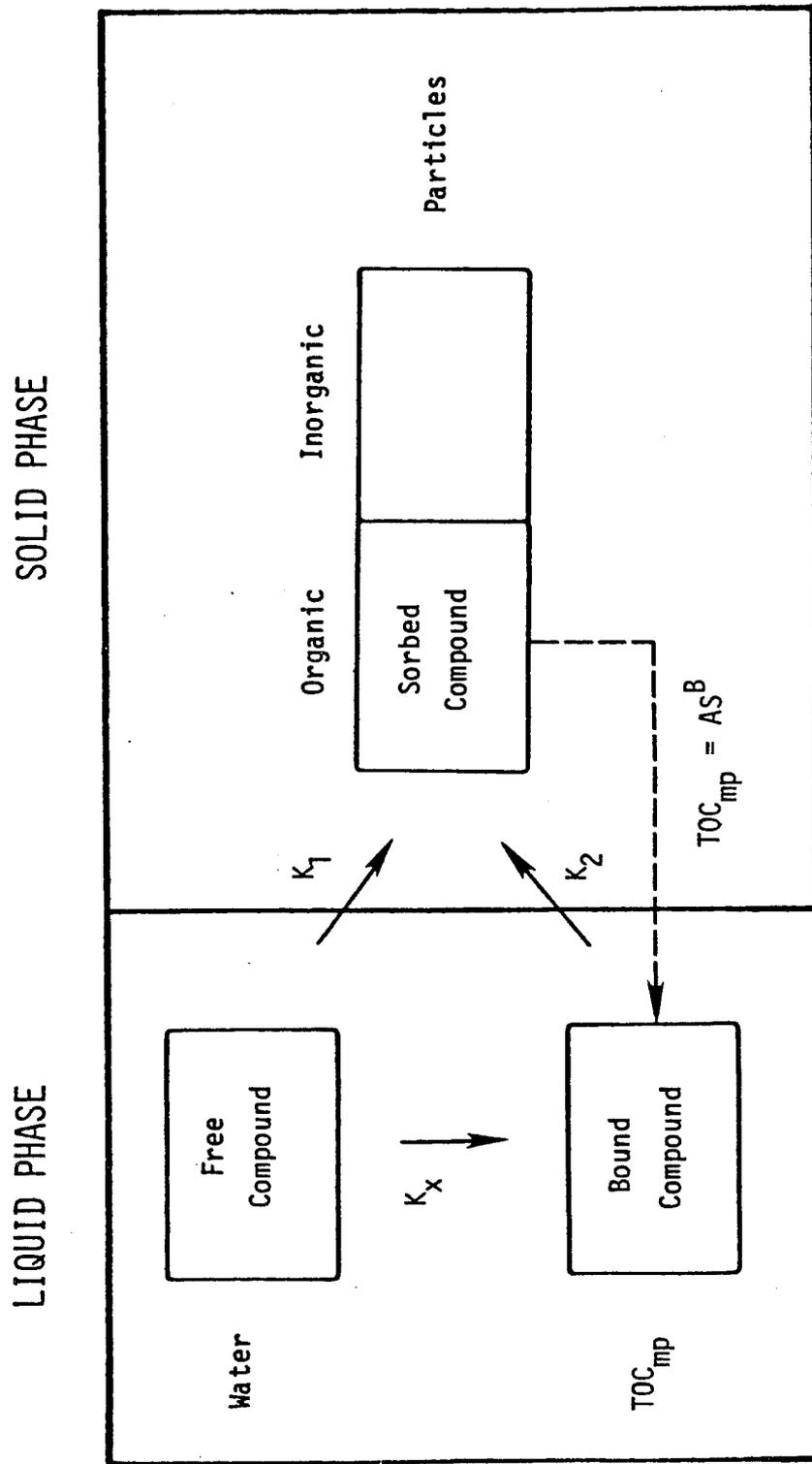


FIGURE 10.--Schematic representation of the solute complexation model.

2. This material is capable of complexing or binding solute molecules;
3. The resultant complex retains some of the solute character, and is thus capable of being sorbed by the solid phase.

Mathematically, this solute-complexation model was formulated as a combination of the phase-transfer and heterogeneous solute models. The derivations will not be repeated here.

The predicted results according to the model were found to fit the data closely in all cases (figure 11). Model verification and sensitivity tests carried out helped to define the limits for the observed K values. An interesting observation from these parameter checks was that the extent to which a solute is complexed is inversely related to the octanol/water partition coefficient of the solute. This can be interpreted by considering that the octanol/water partition coefficient is a measure of hydrophobicity, while the organic material in solution necessarily has a certain hydrophilic character in order to be stable in solution. It is not surprising, therefore, that the less hydrophobic, or more hydrophilic, solutes associate with this material preferentially.

The implications of the major findings of this research--the effect of solids concentration and the proposed explanation--are broad and far-reaching. The initial casualty of this work is the assumption of constant partitioning. It has been shown definitively that partitioning is not constant, but varies with the concentration of solids in the system. This suggests that the distribution of a contaminant in the water column is in all likelihood very different from that in the sediments. Assessments of contaminant burial by sedimentation, desorption, and resuspension all need to address this result.

This laboratory study was complemented by a field program to examine the particle concentration effect at high concentrations in the sediment/pore water environment.

Fourteen pairs of sediment/pore water data were divided into two groups. The first, containing nine sets, represents sediments from regions of recent sediment accumulation or depositional basins. These sediments are fine grained and have an average organic carbon content of 3.2 (\pm 1.0) percent. The second group of five sets represents nearshore or nondepositional regions of the lake. This group is composed of sands to silty sands and has an average of 0.8 (\pm 0.5) percent organic carbon. The mean PAH concentrations from these two regions along with the five particulate/dissolved pairs are listed in table 10. Due to the unequal variances, a parametric comparison of the means of the sediment groups or their pore waters is not valid except for phenanthrene (Ph) and BaP in pore waters. These means are significantly different by Student's t test at the 0.1 level. Other pore water PAH from the two sediment groups are not different at the 0.05 level of the Mann Whitney ranking test for means (Zar, 1974), although the means for all nondepositional pore water PAH are larger than their depositional analogs. PAH concentrations in the pore waters are significantly greater than the dissolved PAH by this test. Figures 12-16 illustrate the measured partition coefficients, along with the effects of substrate and dissolved organic carbon.

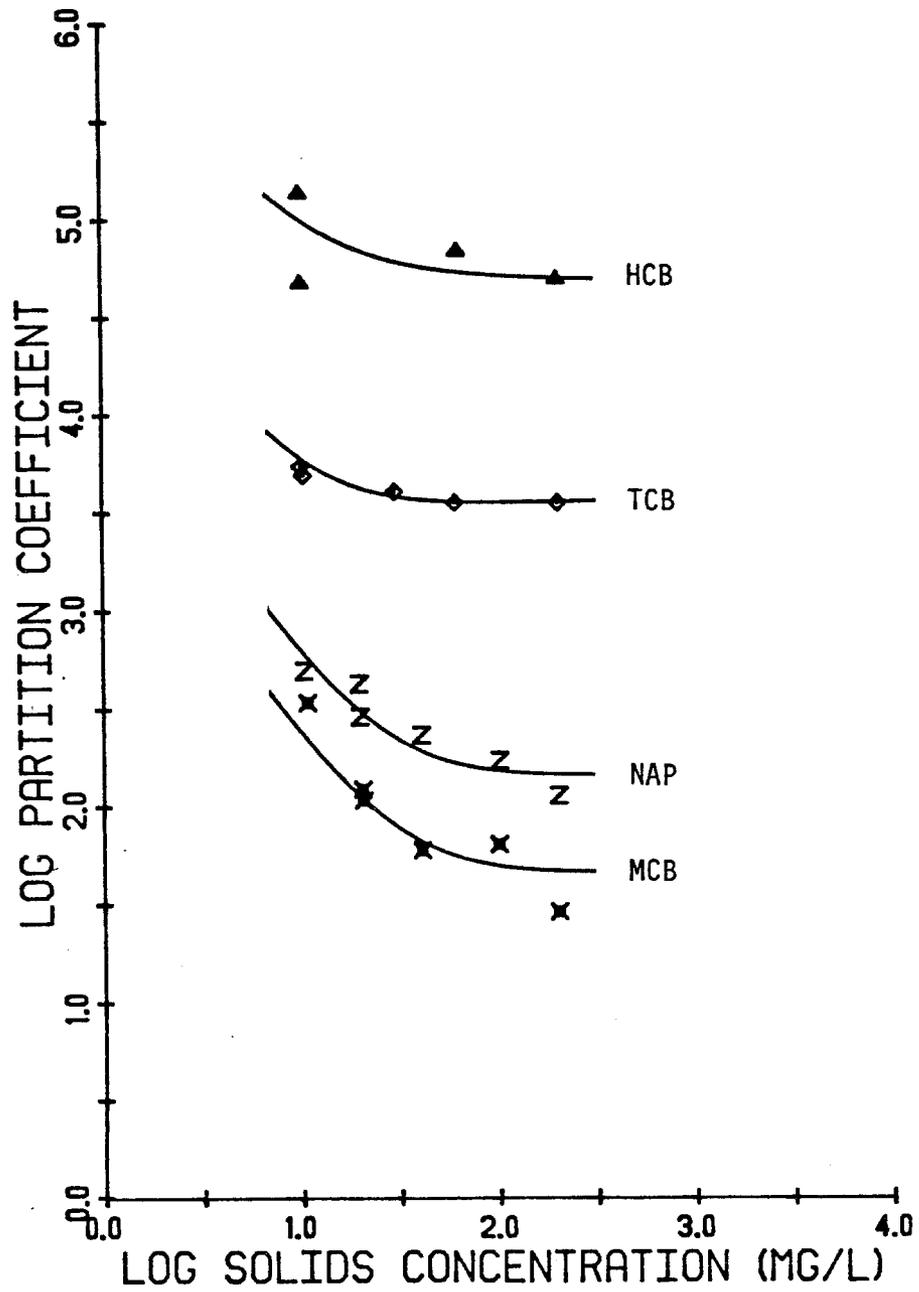


FIGURE 11.--Experimental data and solute complexation model predictions for sorption of four solutes by Lake Michigan sediment (OGH).

TABLE 10.--Mean PAH concentrations (ng g^{-1} or ng mL^{-1}) measured in Lake Michigan sediment, pore water, dissolved, and particulate samples

| Ph | An | FL | Py | Ch | Bap | BgP |
|--|-------|--------|--------|--------|--------|--------|
| Nondepositional Sediments (n = 5) | | | | | | |
| 90.0 | 18.4 | 185. | 148. | 76.1 | 62.1 | 65.7 |
| 82.9 | 2.7 | 132. | 104. | 49.8 | 49.9 | 61.1 |
| Pore Waters From Nondepositional Sediments (n = 5) | | | | | | |
| 0.73 | 0.12 | 2.02 | 1.68 | 2.95 | 2.32 | 1.75 |
| 0.46 | 0.036 | 2.42 | 1.81 | 3.52 | 1.26 | - |
| Depositional Sediments (n = 9) | | | | | | |
| 836. | 195. | 1162. | 999. | 720. | 462. | 369. |
| 252. | 89.0 | 357. | 319. | 338. | 266. | 362. |
| Pore Waters From Depositional Sediments (n = 9) | | | | | | |
| 0.43 | 0.21 | 0.83 | 0.82 | 0.39 | 0.85 | 2.67 |
| 0.53 | 0.30 | 1.29 | 1.09 | 0.23 | 1.26 | - |
| Lake Michigan Suspended Particulate Matter (n = 5) | | | | | | |
| 2,405. | 56.7 | 4,378. | 3,890. | 3,678. | 2,253. | 1,081. |
| 2,411. | - | 1,768. | 1,576. | 2,156. | 1,954. | - |
| Lake Michigan Filtered Water (n = 5) | | | | | | |
| 0.024 | 0.006 | 0.015 | 0.014 | 0.015 | 0.014 | - |
| 0.025 | - | 0.009 | 0.006 | 0.010 | 0.008 | - |

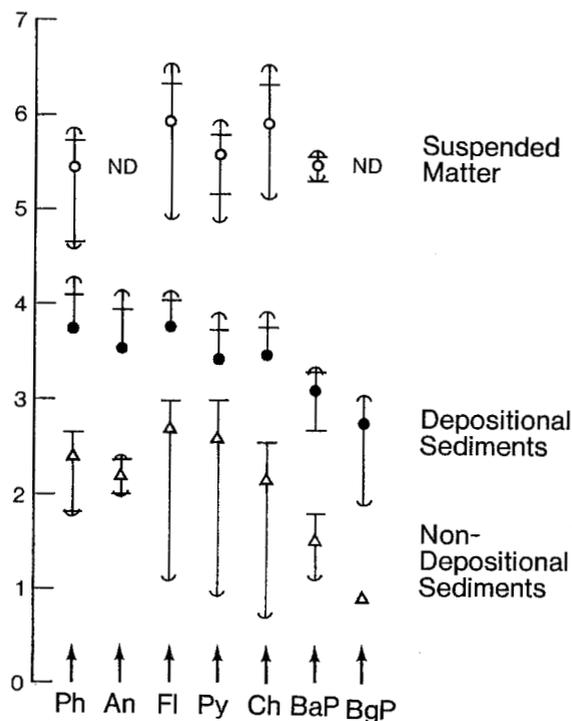


FIGURE 12.--Measured partition coefficients. Open circles represent the log of the mean K_p measured for particulate:dissolved data, solid circles are depositional sediments: pore water, and open triangles for nondepositional sediments:pore water. The straight horizontal lines represent 1 standard deviation and the curved symbols are the values of the maximum and minimum K_p s measured for each compound. Overlapping information between the depositional and nondepositional data were eliminated for clarity.

6. PARTICLE CHARACTERISTICS AND BEHAVIOR

Many of the toxic pollutants in the Great Lakes show a marked tendency to sorb onto particles suspended in the water column and hence be transported with them. Understanding the behavior of these particles is essential if one hopes to predict the fate of these pollutants. Observational, experimental, physical properties of these particles, their distribution as a function of space and time, their dynamic behavior, and transport mechanisms are reviewed in this section.

The types of particles found in the lakes vary with time, depth, and geographic location, but all individual particles are ultimately either biologically or nonbiologically derived. Those of biologic origin include plant and animal remains and other materials produced by organisms (fecal pellets, for example), while those of nonbiologic origin are either precipitated directly from the water or are of terrigenous origin. One complicating factor when considering particle types is the presence of large numbers of

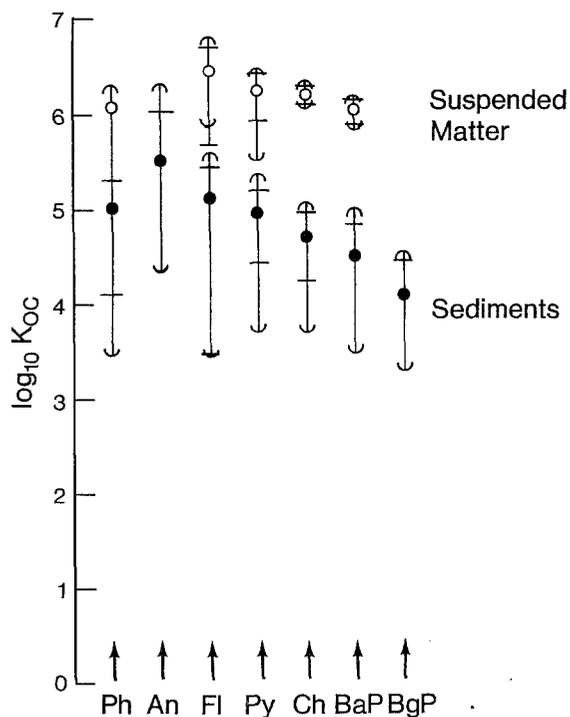


FIGURE 13.--Measured K_{oc} . Open circles represent means of particulate:dissolved data, solid circles represent means of sediment:pore water data. Horizontal bars illustrate 1 standard deviation; curved caps represent the maximum and minimum values used in the calculations. Broad horizontal bars represent the compounds' K_{oc} as calculated from water solubility. (See text.) Solubilities (ppm) used were: Ph (1.002), An (0.0446), Fl (0.206), Py (0.132), Ch (0.002), and BaP (0.0002). Solubility data taken from Neff (1979) and May et al. (1978).

aggregates. These may be of either biologic or nonbiologic origin and consist of both biologic and nonbiologic particles generally held together with some sort of organic matrix. Since the properties of these aggregates differ considerably from those of their constituent parts, they must be considered as a separate particle type.

Most biologic particles are plant material. Diatoms appear to be the most abundant. These siliceous particles have relatively slow settling rates, so they remain in the water column for long periods of time even after death. Relatively little of this material is found in the bottom sediments, most being redissolved at the sediment water interface.

In spite of their relative scarcity, fecal pellets, which are composed of both biologic and nonbiologic particles, have been long recognized as significant agents of vertical transport in the oceans (Honjo, 1980). There seems little reason to doubt their importance in the lakes as well. However, because of the smaller size of pellets in the lakes, they probably settle less quickly than their marine counterparts. Fecal pellets are abundant in

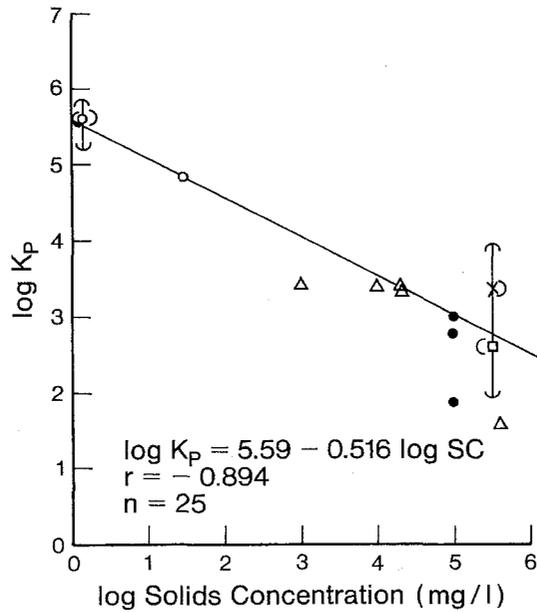


FIGURE 14.--The effect of solids concentration (SC) on the equilibrium partition coefficient (K_p). Open triangles are data from Karickhoff et al. (1979) and solid circles are from Means et al. (1979). Our lake water values are shown as open circles; the curved bars represent the range of measured values. The mean value for depositional sediments is represented by the X and the mean for nondepositional sediments by the open box.

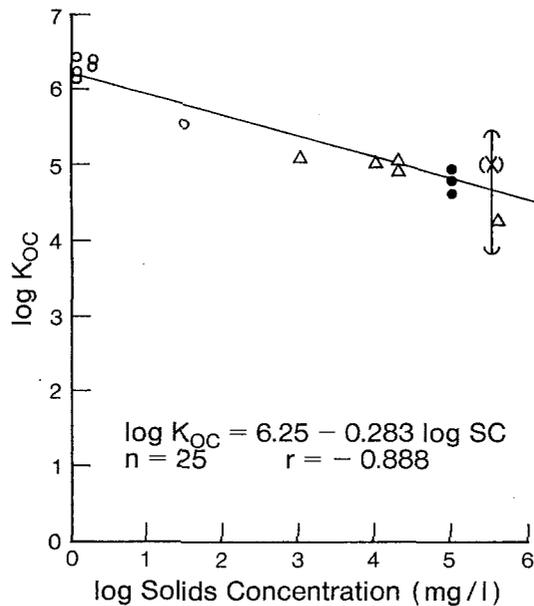


FIGURE 15.--The effect of solids concentration on the substrate organic corrected partition coefficient (K_{oc}). Symbols are described in the figure 4 legend. In this case, the means for depositional and nondepositional sediments are equal. The dashed line is the K_{oc} value calculated from the relationship derived by Kenaga and Goring (1979).

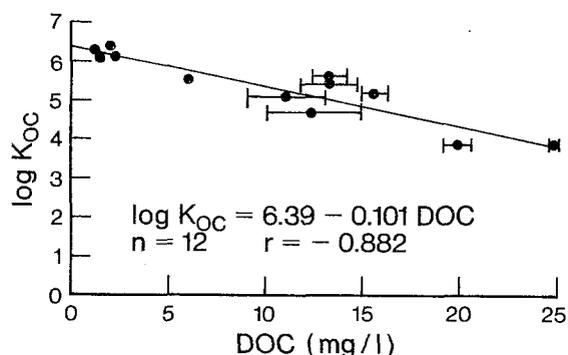


FIGURE 16.--The effect of dissolved organic carbon (DOC) on K_{OC} . The error bars represent 1 standard deviation.

sediment trap samples, where they are identified by their characteristic shape (cylindrical or spheroidal) and high density. Other types of biologic material (spores, zooplankton) are of minor importance.

Terrigenous particles enter the lakes in one of four ways: shore erosion, river discharge, atmospheric deposition, or bottom erosion. Of the four processes, shore erosion is the most important in all but Lake Ontario (table 11). Since much of the shore-derived material is coarse grained, it moves predominantly as bedload across the shelf. Thus, this material plays a minor role in pollutant transport.

River and atmospheric sediments are much finer grained and so remain suspended for lengthy periods of time in the water column. They are considered to be the sources of most of the terrigenous suspended material. River sediments depend on the types of bedrock in the drainage area, which in much of the Great Lakes Basin is glacial till. The composition of the suspended material reflects this origin. It is rich in clay, minerals, quartz, and feldspars, with minor amounts of carbonate minerals.

Atmospheric sediments must be very fine grained. The types of minerals comprising them are probably similar to those of the riverine sediments since the local sources are identical. Although atmospheric loading is only a minor sediment source, it is important since many pollutants are deposited in this way.

Erosion of the lake bed must be distinguished from resuspension of the nonconsolidated sediments resting on the bottom. The distinction is somewhat arbitrary and artificial, but is useful in distinguishing sediments that have been deposited for lengthy periods of time (and have presumably undergone post-depositional alteration) from those that are merely temporarily deposited.

In addition to these sources, nonbiologic materials may precipitate from the lake water itself. The carbonate "whiting" event, which occurs in several of the Great Lakes during late summer, is the most noticeable example (Strong and Eadie, 1978). During this event numerous small (less than 10 μm diameter)

TABLE 11.--Sediment budgets for the Great Lakes (from Rea et al., 1981)

| Lake | Input, 10^6 Mt yr ⁻¹ | | | | | Output, 10^6 Mt yr ⁻¹ | |
|----------------------|-----------------------------------|------------------|-------------------|------------------|-------|------------------------------------|-------------------|
| | Shore | River | Atmosphere | Other | Total | Outflow | Sediment |
| Ontario ^a | 2.8 | 5.6 | 0.1 | 0.6 | 9.1 | 3.4 | 4.8 |
| Erie ^b | 7.9 | 4.1 | 0.5 | 2.4 | 14.9 | 4.5 | 14.3 |
| Huron | 1.8 ^c | 1.1 ^c | 0.4 ^d | ? | 3.3 | 1.4 ^b | 1.9 ^e |
| Michigan | 14.7 ^f | 0.7 ^c | 0.8 ^g | ? | 16.2 | none | 16.2 ^e |
| Superior | 7.2 ^h | 2.4 ⁱ | 0.04 ⁱ | 1.0 ⁱ | 10.6 | 0.10 | 10.5 ^e |
| Total | 34.4 | 13.9 | 1.8 | 4.0 | 54.1 | | |
| Percentage | 64% | 26% | 3% | 7% | | | |

^aKemp and Harper (1976).

^bKemp et al. (1977).

^cPLUARG (1978).

^dEstimate of the authors from Lakes Michigan and Erie data.

^eDetermined by difference.

^fFrom volume inputs of Monteith and Sonzogni (1976) and estimated bulk density of 1.75 g cm^{-3} .

^gEisenreich et al. (1977).

^hAs in footnote f, with no sediment from Lake Ontario shore; estimate by Kemp et al. (1978).

ⁱKemp et al. (1978).

calcite particles are precipitated. Most are redissolved since relatively little calcite is found in the bottom sediments (Harrsch and Rea, 1982).

The aggregates found in the lakes are usually loose collections of both biologic and nonbiologic particles. Some, which have an abundance of diatom parts, are probably degraded fecal pellets, while others are probably formed by the collision of their constituents. Since aggregate formation and breakup occurs constantly, the particle-size distribution also changes with time. This makes predicting the behavior of these particles considerably more difficult.

6.1 Particle Properties

Although particles may be characterized in many ways, when considering the behavior of the particles in the water column, two properties are most important: the electrical forces, which determine whether a particle is cohesive or not, and the settling velocity. These properties are in turn governed by other properties, such as particle composition, size, and shape.

The settling velocity of a particle may be used as a measure of its dynamic behavior in the water column. The settling velocity, in conjunction with current velocity and water depth, determines the residence time of the particle. In addition, it is also used as a measure of the susceptibility of noncohesive particles to resuspension.

For a sphere of radius r and density ρ_p , Stoke's Law gives the settling velocity, w

$$w = \frac{2}{9} r^2 \frac{(\rho_p - \rho_f)g}{\mu} \quad (22)$$

where g is the acceleration due to gravity, μ the kinematic viscosity, and ρ_f the fluid density. Stoke's Law works well for solid particles of known density that are at least fairly spherical, such as sand grains. For many of the particles found suspended in the Great Lakes, however, Stoke's Law cannot be used, although it is applicable to the numerous small mineral grains suspended in the water column.

Equations for the settling velocity of aggregates have been derived by Hawley (1982a) based on the experimental work of Chase (1979). The average fall velocity is shown as a function of size in figure 17.

No direct determinations of freshwater fecal pellet settling velocities have been made. Because of the larger size of marine pellets, measurements of their sinking rates (Small *et al.*, 1979) are probably larger than those obtained in the lakes. The estimates made by Ferrante and Parker (1977) were based on sediment trap data and are probably incorrect. As yet, no measurements have been made of diatom sinking rates, but Glover's work (1982) suggests a velocity of about 1.5 m day^{-1} .

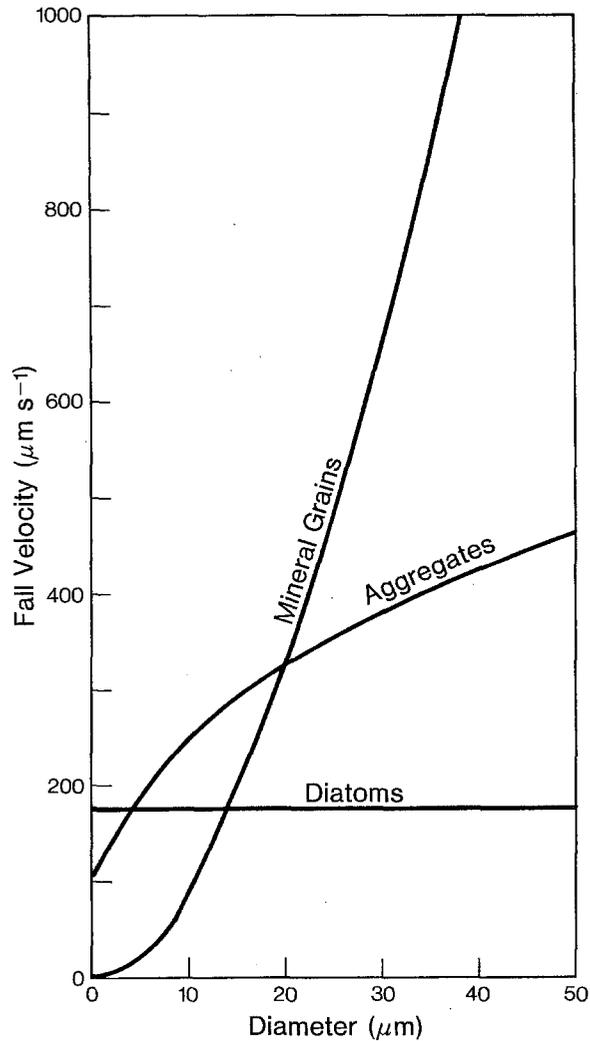


FIGURE 17.--Fall velocity as a function of particle size (from Hawley, 1982b).

The electrical properties of the particles govern their ability to aggregate, the strength of the aggregates, and their susceptibility to resuspension. Unfortunately, due to the complex composition of the aggregates and the minimal knowledge of the forces involved, little can be said on this subject. It is known that the clay minerals will form relatively strong bonds due to double-layer contraction (Krone, 1963). This does not however seem to play a major role in aggregate formation, since most of the material is not clay. There is also some reason to believe that the aggregates found in the lakes have bond strengths far weaker than those formed by clay minerals (Hawley, unpublished data). The presence of cohesive sediments (those that aggregate) also influences the degree of resuspension; as these sediments consolidate, more bonds are formed, making the sediment more difficult to erode.

6.2 Distribution of Particulate Material

Both transparency measurements and determinations of total suspended material have been made over the last 15 years. Typically, total suspended material in Lake Michigan concentrations range from 1 to 3 mg L⁻¹. Both these and the transparency measurements show that during the stratified period (roughly June-October) there are pronounced increases of particulate material at the thermocline and in near-bottom water (Chambers and Eadie, 1981) (figure 18). This bottom nepheloid layer is found in all of the Great Lakes (Bell *et al.*, 1980) and has been investigated in detail in southern Lake Michigan where it is thought to be due to resuspension of nonconsolidated bottom sediments by internal waves impinging on the lake slope (Chambers and Eadie, 1981). The origin of the nepheloid layer at the thermocline is unknown, but it may be the result of decreased settling velocities as particles migrate from the warmer water above to the cooler water below. Upwelling events associated with storms serve to greatly increase the suspended particle concentrations in nearshore waters as bottom material is resuspended offshore and injected into the nearshore areas (Bell and Eadie, 1982).

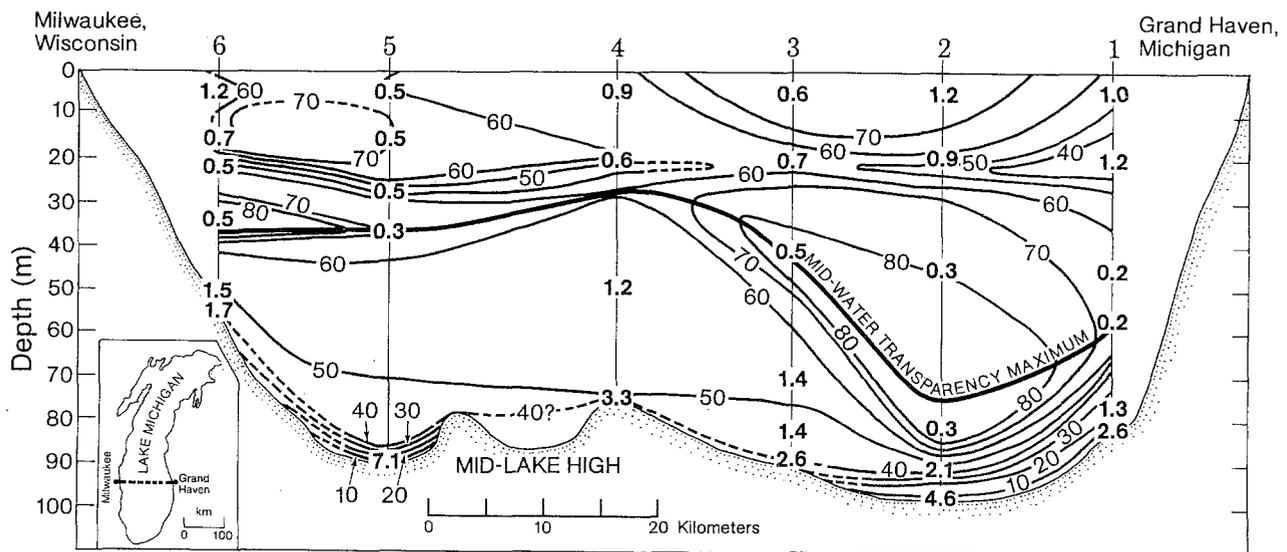


FIGURE 18.--East-west section from Grand Haven, Mich., to Milwaukee, Wis., (see insert) contouring the vertical distribution of water transparency during August 21-22, 1979. Total suspended-matter values are superimposed along the station profiles. The metalimnion transparency minimum is clearly depicted at approximately 20 m by a wedge of turbid water extending lakeward from both shores. Using the marine definition, the nepheloid layer is the region below the mid-water transparency maximum. The largest portion of this water mass has transparency values between 40 and 60 percent with the lowest transparency and maximum TSM confined to the deepest portions of the lake extending 10 to 20 m above the bottom. We define the southern Lake Michigan benthic nepheloid layer as the region in which the transparency and TSM gradients are steeper than in other regions below the hypolimnion transparency maximum (from Chambers and Eadie, 1981).

The types of suspended particles vary as a function of both season and location. Harrsch and Rea (1982) have described the composition of sediment found suspended in Lake Michigan during the summer of 1979. They found that biogenic material was most abundant, with quartz and carbonates also important. Clay minerals were only marginally in evidence. No information is available from this study on the presence of aggregates or fecal pellets.

Hawley (1982b,c) has analyzed suspended particles as a function of size. His results (table 12) show that most of the particles less than 10 μm in diameter are single mineral grains, with aggregates and diatoms predominating in the larger size ranges. These results, though preliminary in nature, also show significant differences between populations collected on different days and different depths.

Size measurements of particles have been conducted in Lake Michigan over the past several years. These results were summarized by Hawley (1982d), who showed that the size distribution of lake particles is weighted more toward the larger particles than similar measurements of oceanic material. Particle concentrations are usually of the order of 1,000 to 2,000 mL^{-1} with the distribution fitting a power law

$$n = 6,804d^{-2.06} \quad (23)$$

where n is the number of particles larger than d , the particle diameter (measured in microns).

TABLE 12.--Percent distribution of particle types as a function of size (from Hawley, 1982a)

| Size | Aggregates | Minerals | Fragments | Diatoms |
|-------|------------|----------|-----------|---------|
| 2-4 | 8.7 | 89.7 | 1.4 | 0 |
| 4-8 | 18.6 | 71.1 | 7.3 | 3.0 |
| 8-16 | 23.7 | 57.1 | 14.9 | 4.3 |
| 16-32 | 57.7 | 17.8 | 16.5 | 8.0 |
| 32-60 | 59.3 | 3.0 | 29.6 | 8.1 |

6.3 Particle Behavior

Obviously it is necessary to predict particulate behavior in changing flow conditions if one is to accurately model sediment transport. Unfortunately, this is one of the areas where very little is known, particularly with regard to cohesive sediments.

The tendency of many particles to form aggregates has already been noted. Since this process and the process of aggregate rupture are continually occurring, the size distribution of the particles, and hence their fall velocity, changes with time, making it exceedingly difficult to predict particle behavior, even in steady flow. Hawley (1980) showed that the size distribution of particles near the bottom was not accurately predicted using a simple diffusion-settling model (Rouse's Law) and concluded that aggregate formation and rupture significantly affected the size distribution. Lo (1981) conducted experiments that showed that particle sizes are significantly altered when placed in a shear flow; unfortunately it is not possible to apply his results to natural settings. Hawley (1982e) has constructed a mathematical model of aggregate formation and rupture, which at the present time is still being refined and calibrated, but preliminary results show that an increase in current velocity homogenizes the vertical distribution of particles and at the same time decreases the average particle size because of rupture of the aggregates. Because most nonbiological aggregation occurs as the result of differential settling, an increase in current velocity does not noticeably increase the rate of formation of new particles.

In contrast to noncohesive sediments, whose deposition and erosion can be predicted fairly well, little quantitative information is available for cohesive sediments. Long-term depositional rates for the lakes, based on lead and pollen geochronology, vary between less than 1 to over 5 mm per year (Robbins *et al.*, 1978). However, the actual processes that result in deposition are not known. If the long-term average rate is used, the rates become microns per day. Experiments on the deposition and resuspension of cohesive sediments with far higher deposition rates (Hawley, 1981a,b) suggest that sediments deposited at such slow rates would be easily resuspended. The resistance of a sediment to resuspension depends on its water content as well as the current velocity (Postma, 1967; Fukuda, 1978). Figure 19 shows the entrainment rate for several sediments collected from Lake Erie as a function of shear stress. All of these sediments have water contents far lower than those found in recently deposited layers (>90 percent water), so one would expect material that had just been deposited to be more easily resuspended. Pore water content is usually reduced by gravitational compaction due to the accumulation of overlying sediment. If one compares the deposition rate to the frequency of current velocity changes, it is hard to imagine how the deposited material could resist resuspension. Biological activity may provide part of the answer since bottom feeders may increase the cohesion of sediments with mucus secretions, but even this process may proceed too slowly to prevent the resuspension of most material. Marked increases in both particle fluxes (Chambers and Eadie, 1981) and total suspended material (Bell and Eadie, 1982) during storm periods indicate that large amounts of sediment are resuspended during these events.

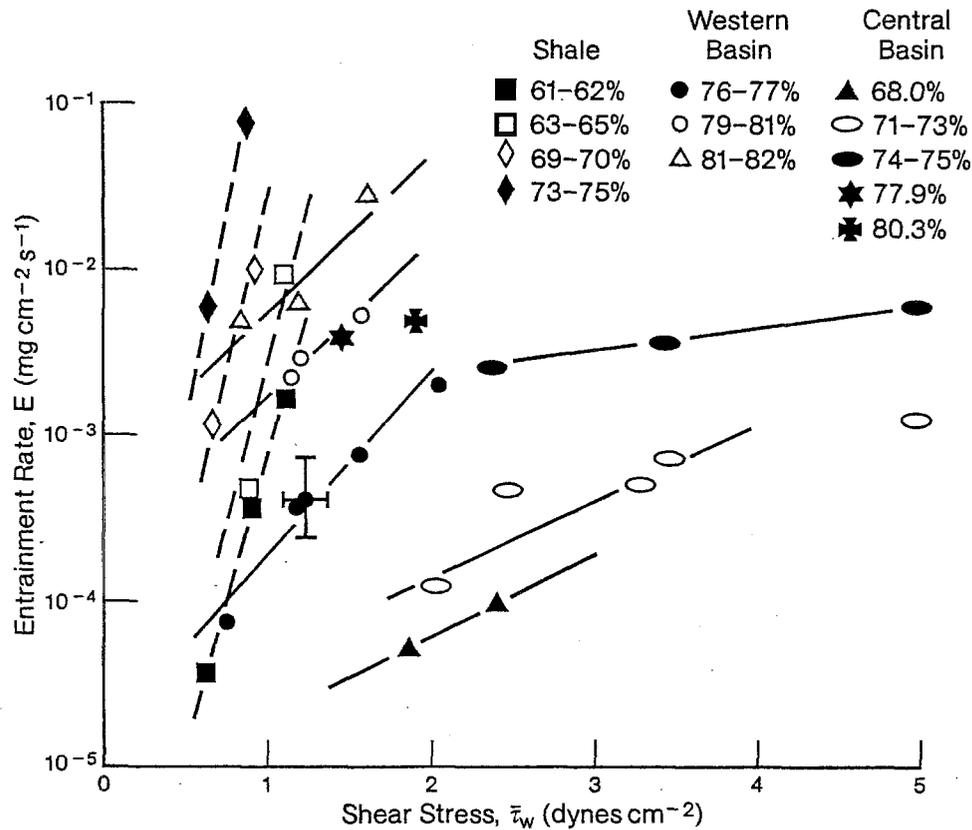


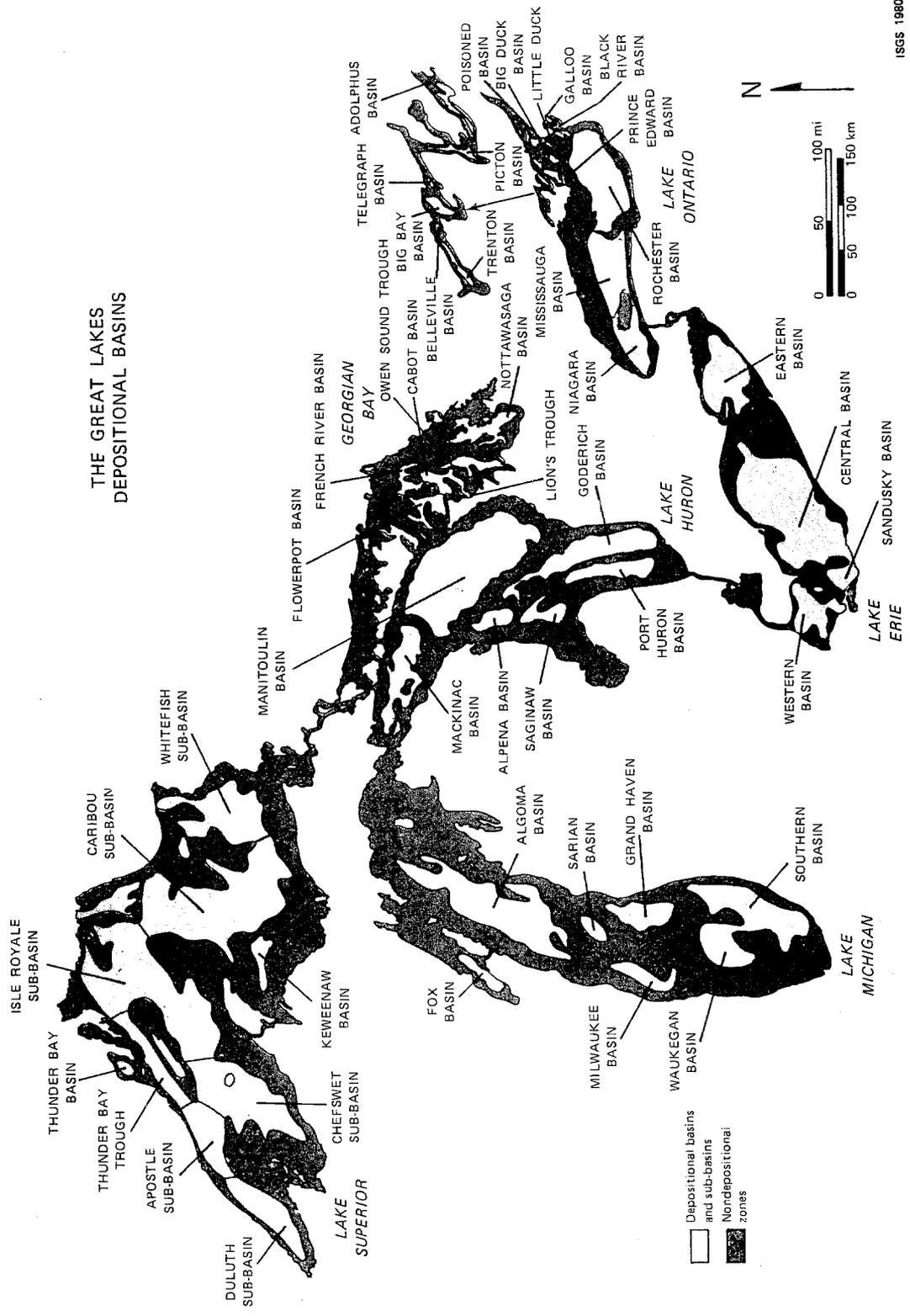
FIGURE 19.--Entrainment rates for three sediment types at various water contents as a function of applied shear stress (from Fukuda, 1978).

6.4 Transport Mechanisms

The general pattern of sediment transport in the lakes is downslope from the coastal areas, where most of the sediment is added to, to the depositional basins, which are mostly associated with the deep basins (figure 20). The actual pathway followed is probably considerably more complex, involving successive cycles of deposition, resuspension, and lateral movement.

The situation is probably simplest for the sand and silt-sized sediments. These are moved mostly as bedload across the shelf by the ambient currents. Occasionally storms may resuspend this material, however, (Lesht, 1981) and transport it large distances. Relatively little of this material escapes from the shelf and upper slope.

Transport of the finer-grained material occurs almost totally in suspension, where it is advected through the lake as it sinks to the bottom. As noted earlier, this process is complicated by the formation of aggregates. If the material reaches the bottom, it may then either be consolidated enough to withstand erosion or, more probably, be resuspended by a subsequent increase in current velocity and mixed into the water column. The process is then repeated until it is finally incorporated into the bottom sediment.



ISSS 1980

FIGURE 20.--Great Lakes depositional basins (from Cahill, 1981).

What role the nepheloid layer plays in the transport is not known. It may be either an active transporting agent or just the result of localized resuspension. If it is, in fact, an agent of sediment transport, its magnitude in relation to storm action needs to be assessed. Storm-generated waves are very efficient agents of sediment resuspension, although as Lick (1980) noted, no quantitative work has been done on the resuspension of cohesive sediments by wave action. The high frequency of storms (approximately one per week), coupled with their ability to suspend and transport large amounts of material, may make them the dominant agent of transport in the lakes.

6.5 Conclusion

Ideally one would like to be able to predict both particle transport paths and depositional sites. At the present time, however, this is impossible since the processes of deposition and resuspension are, at best, only poorly understood. The formation and rupture of aggregates in the water column is a complicating factor of considerable importance since the dynamic behavior of the particles changes with time. It seems likely that, rather than having a simple, one-step transport path, particles move in a series of hops, temporarily being deposited and then resuspended as they move to their ultimate depositional site.

7. SEDIMENT TRAP PROGRAM: FLUX AND RESUSPENSION MEASUREMENTS

The role played by particulate matter in the transport and cycling of nutrients, organics, and trace metals has been investigated by the Great Lakes Environmental Laboratory since 1976. These studies have been primarily in the southern basin of Lake Michigan.

During these studies, Chambers and Eadie (1981) observed a persistent benthic nepheloid layer of suspended materials. The layer is characterized by high total suspended materials (TSM), high total particulate surface area, and low water transparency. They observed that from early March to mid-May the particle concentrations were nearly uniform from the surface to bottom. The nepheloid layer apparently is initiated during the time that the thermal bar is formed and moves progressively offshore. These weak but persistent currents apparently resuspend and transport offshore the low-density materials that collect on the shelf and slope during the winter months. The layer is maintained by lakeward transport of fine particles resuspended during high energy events (storms), and apparently also by the impingement of the thermocline on the bottom near the shelf-slope boundary. A recent study by GLERL shows that pronounced upwelling events can disrupt the nepheloid layer and reintroduce suspended materials into the nearshore area and subsequently into the epilimnion (Bell and Eadie, 1982). A companion study of light transmission and suspended material data shows the presence of a nepheloid layer in all of the Great Lakes with similar profile characteristics and variations as those observed during the detailed studies near Grand Haven, Mich. (Bell *et al.*, 1980).

The importance of the role played by suspended matter in the chemical dynamics of the lake system is well recognized. The published information about the concentration and temporal and spatial distributions of TSM throughout the Great Lakes is limited. Data within the nepheloid layer are notably deficient. The composition, concentration, and distribution of TSM is controlled by many interacting processes, which include chemical and biological production, resuspension of bottom sediments, aggregation, coastal erosion, and river and atmospheric loading (Chambers and Eadie, 1981).

7.1 Sampling Procedures

The Great Lakes have several features characteristic of oceans, such as distinct shelf, slope and basin regions, with basin depths of 80 m or more. Our study area was confined to the eastern half of Lake Michigan's southern basin during 1977 and 1978 (figure 21), and included both the southern and northern basins during the 1980-81 study (figure 22). During 1979, several cruises extended over a wider portion of the southern basin. The bottom is relatively smooth, with a narrow shelf (2 to 5 km wide) and water depths of approximately 25 m over the outer shelf. This region has gentle slopes (6 to 7 km wide) extending to 100 m depth in the northern part of the study area

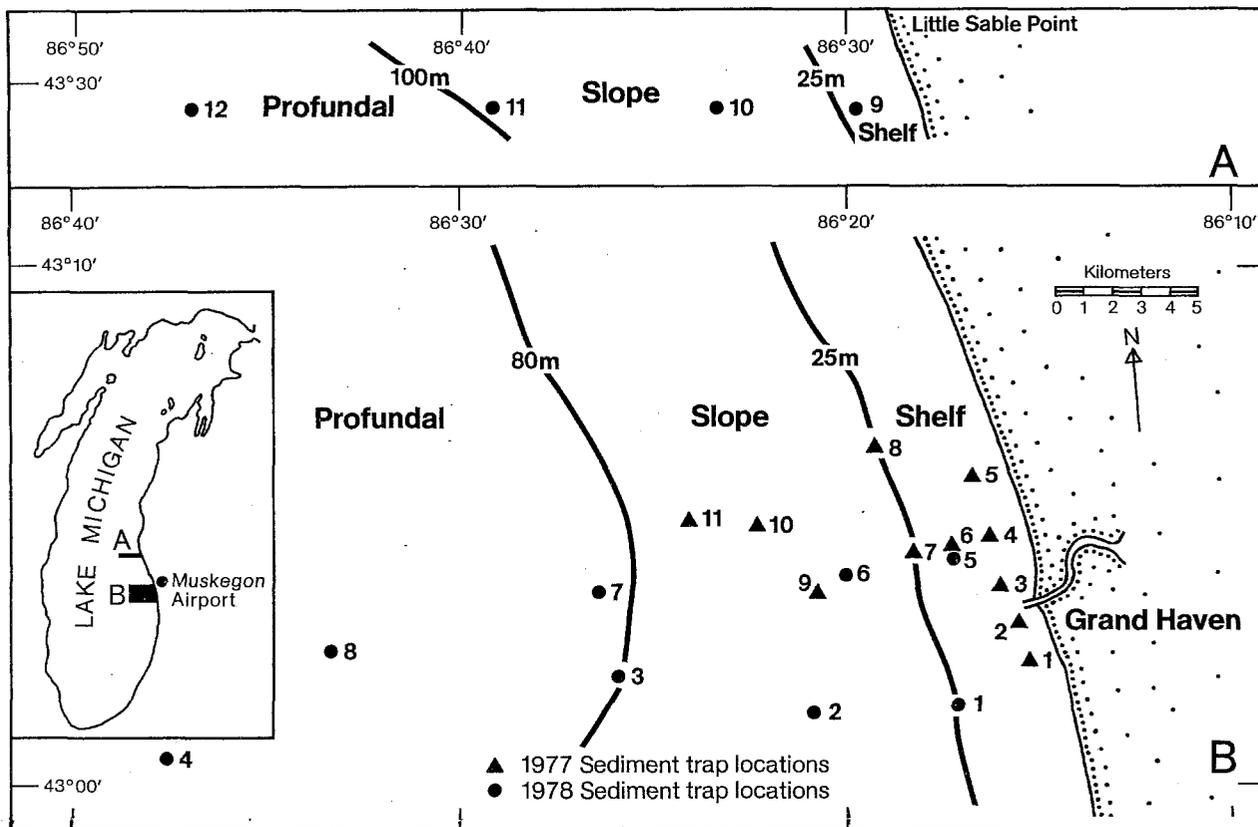


FIGURE 21.--Chart of the study area near Grand Haven, Mich. Sediment trap locations are indicated by a triangle for 1977 and a dot for 1978 (from Chambers and Eadie, 1981.)

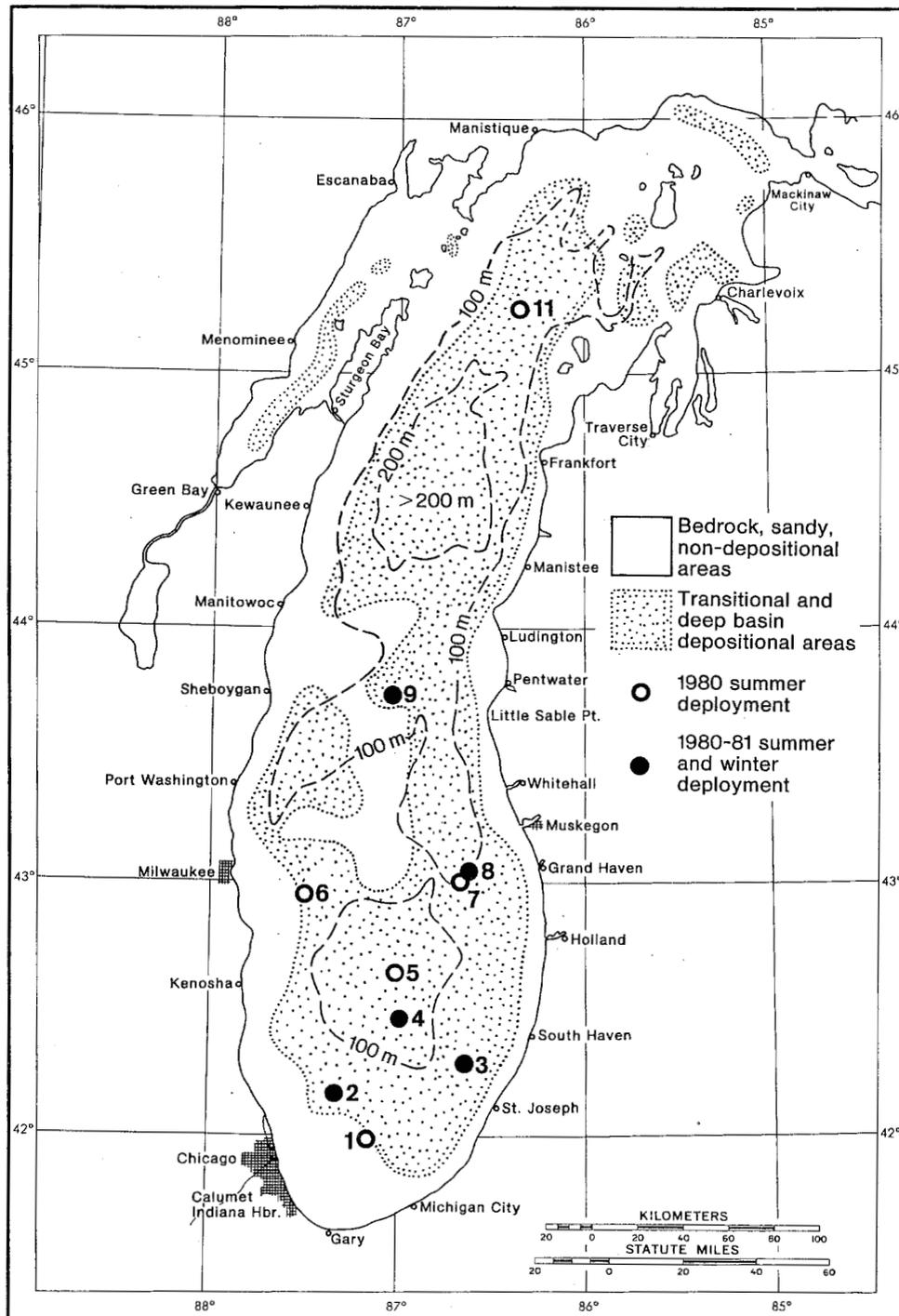


FIGURE 22.--Station locations during the suspended particulate flux study in 1980-81, and their relation to depositional areas (after Cahill, 1981.)

near Little Sable Point, Mich., and to approximately 80 m off the Grand River. A detailed discussion of the bottom sediments is presented by Chambers and Eadie (1980).

Approximately 30 cruises were made from late April 1977 to October 1979 for instantaneous determinations of water transparency, total suspended matter (TSM), and particle size analysis. Sampling depths were determined after inspection of the transparency profiles and water was collected in 5-L Niskin bottles. From late April to mid-November 1977 and 1978, sediment traps were used in southeastern Lake Michigan to study the seasonal gross downward mass flux of TSM. The traps consist of a plexiglass cylinder with a 5:1 height-to-diameter collecting ratio (50 x 10 cm) optimized for Lake Michigan (Wahlgren and Nelson, 1976), a powder funnel, and a 500-mL LPE wide-mouth bottle. Thirty-six sediment traps were deployed at 11 stations in 1977 to study suspended material as it moved offshore from the Grand River (figure 21). Major emphasis was on the shelf and upper slope, with two stations on the mid-slope and one station at its base. Sampling during 1978 provided a more complete investigation of the nepheloid layer, using 71 sediment traps at 12 locations (figure 21). The traps located off Little Sable Point are not influenced by any major point source of particle input, and provide a baseline to compare with those located off the Grand River. Trap depths for 1977 were 1 m above the bottom and 5 m below the surface. However, from August to November the near-surface traps at stations 77-9, 77-10, and 77-11 (year-station) were lowered to the thermocline region (~30 m) to estimate the flux of material through the epilimnion. Fixed trap depths at 1, 3, 5, and 10 m above the bottom and 35 m below the surface were used during 1978. At most stations, duplicate traps were placed at each depth. Total mass was determined by weighing the dried samples to the nearest 0.01 g. Although the traps were changed every month during 1977 and every 20 to 150 days during 1978, the preserved samples did not become anaerobic. Sediment traps placed in triplicate at four stations in 1978 indicated coefficients of variation from 1 to 10 percent, with an average of 5.5 percent.

Sixty-five sediment traps used in the 1977 and 1978 study plus 26 larger diameter (20.6 cm) traps of similar design were deployed at 10 locations during June and July of 1980 (figure 22). Two to three traps were placed at each level and preserved with either chloroform or mercuric chloride. Samples at station 8 were collected and the traps redeployed in July. Samples from all stations were collected in late October and early November. Stations 2, 3, 4, 8, and 9 were reset with an acoustical release at the bottom of the mooring line and a subsurface float at 15 m. These stations collected suspended sediment during the winter and were recovered in late spring 1981. The ten stations were selected to sample areas in which the sedimentation rate varied from high (station 3) to low (station 1). The shipboard-collected water samples gave a temporal view of water column characteristics, and sediment trap results yielded profiles of integrated accumulation rates.

7.2 Temporal Characteristics of the Nepheloid Layer

Total suspended matter measurements made during this study and an earlier study (Eadie *et al.*, 1980) show that concentrations were nearly uniform from surface to bottom (~1.5 mg L⁻¹ from early March to mid-May). By late May

1976, TSM 5 m above the bottom had increased to 7.6 mg L^{-1} (3.6 mg L^{-1} in late May 1979), while the remainder of the water column showed a nearly uniform concentration of 1.3 mg L^{-1} (1.7 mg L^{-1} for 1979) at an 80-m station.

Observations made by Chambers while using SCUBA suggest that the nepheloid layer started to form by late April and was a distinct benthic zone by late May 1977 and 1978. A very sharp visibility discontinuity was observed at about 30 m. The bottom water had a layer several meters thick, inky-black in color, and with zero visibility. These visual observations confirm 0-percent transparency values measured by the *in situ* transmissometer.

Figure 23 shows vertical cross sections of transparency and particle count data beginning at the mouth of the Grand River at Grand Haven, Mich. The transect bisected the river plume, which extended lakeward normal to shore. Analysis of temperature profiles for this cruise (June 15, 1977) show the beginning of stratification with a weak thermocline at 7 m. The river water was 14°C warmer than the lake, which produced a river-derived layer of lower transparency above the colder lake water (figure 23a). Accumulation of material along the thermocline was common and more fully developed after thermocline formation during the summer (see figure 18). The particles contributed by the river (figure 23b) are confined to the first kilometer off the river mouth, with concentrations reaching lake background rather quickly. Eadie *et al.* (1980) also observed this phenomenon.

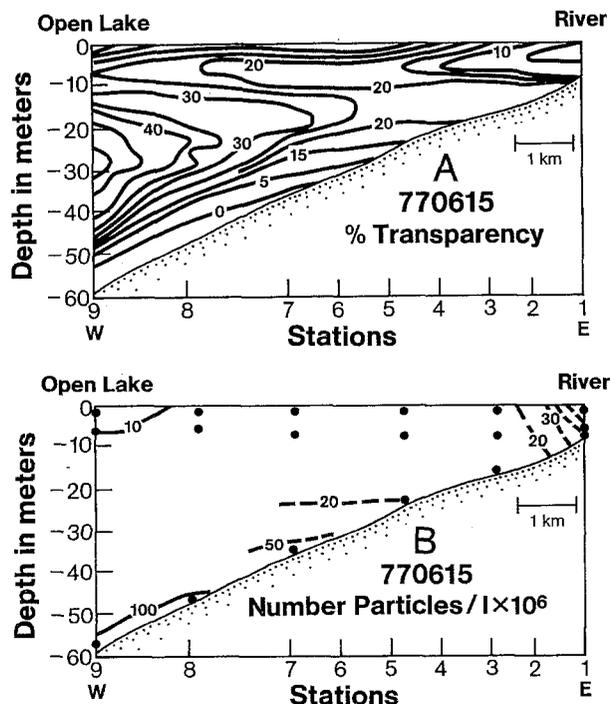


FIGURE 23.--Transparency (A) and particle concentration profiles (B) from a transect directly off the Grand River during June 1977. In these figures a nepheloid layer is seen beginning at about 30 to 40 m. Transect described by the line extending due west from the mouth of the Grand River in figure 21 (from Chambers and Eadie, 1981).

A region of high turbidity, defined in terms of low transparency (0 to 5 percent) appeared below about 30 to 40 m. Within this benthic layer, TSM increased from 1.2 mg L^{-1} and $2 \times 10^6 \text{ counts L}^{-1}$ at station 5 to 4.8 mg L^{-1} and $10^5 \times 10^6 \text{ counts L}^{-1}$ at station 9. The data collected during this cruise illustrate that the particulate matter in the open lake was beginning to partition itself into two regions separated by a zone of clearer, more particle-free water. A river-derived component of the nepheloid particulate material appeared to be negligible.

Seasonal variations in particle concentration near the slope-basin boundary show up to a five-fold increase in the amount of material present within the nepheloid layer when compared to the overlying clearer water. There was a general trend toward decreasing particle concentrations and total surface area values in the nepheloid region from May to October, with a major exception in July. The July sample probably reflected the settling of large amounts of biogenic material from the spring bloom. A similar seasonal trend was also observed during 1979 at station 78-7. Microscopic analysis of TSM aliquots revealed the presence of many aggregates of several morphologies and the dominance of calcium carbonate (calcite) crystals and calcium carbonate aggregates (4 to 20 μm in size) during September and October. The *in situ* production of calcium carbonate peaks in early September (Strong and Eadie, 1978) and continues well into October. The residual carbonate settling probably produced the 10-m particle surface-area maximum observed at station 77-7 on October 19.

7.3 Spatial Characteristics of the Nepheloid Layer

The results from several cross-lake cruises suggest that the benthic nepheloid layer always occurs in water deeper than about 40 m during the stratified period. The metalimnion minimum, mid-water maximum, and nepheloid layer are clearly depicted by open lake transparency profiles for stations 78-7 and 78-8 (figure 24a). During this cruise (September 16, 1978) an unusually thick region of 0-percent transparency was present, and it thickened from about 3 m at 78-6 (mid-slope) to 10 m at 78-7 (basin boundary), but thinned to about 5 m at 78-8. TSM values at 78-7 increased exponentially with depth in this highly turbid zone (figure 24b). The number of particles per litre at the offshore station differed only by a few percent at 1, 3, 5, and 10 m above the bottom. However, particle surface area increased by almost a factor of two at 78-7. The significant increase in surface area reflected a two- to fourfold increase in the number of particles in the >16 to $60 \mu\text{m}$ size range. Particle concentration in the 2 to $16 \mu\text{m}$ range was nearly constant with depth.

Regionally, the most turbid regions of the nepheloid layer were confined to the lower slope and deep troughs of the lake (figure 18). TSM concentrations were 10 to 20 times higher in the bottom 1 m compared to values in the mid-water transparency maximum. The high turbidity may reflect local resuspension by bottom currents. Trends similar to these were also observed on a transect south of this one between South Haven, Mich., and Waukegan, Ill., during mid-September 1979.

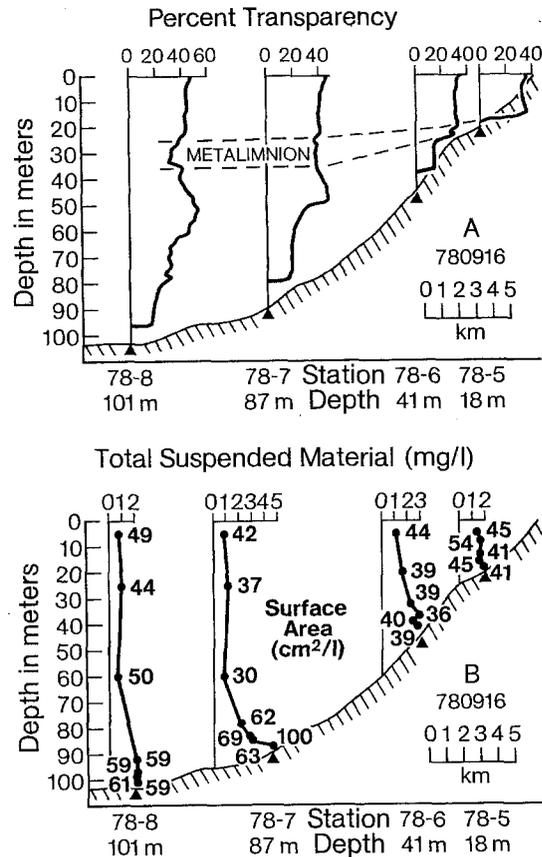


FIGURE 24.--(A) 1978 transparency profiles off Grand Haven, Mich., illustrating the thickness of the nepheloid layer (region of 0-percent transparency). (B) illustration of the increase in TSM (dots) in mg L^{-1} and surface area in $\text{cm}^2 \text{L}^{-1}$ (numerals) associated with the nepheloid layer (from Chambers and Eadie, 1981).

7.4 The Vertical Flux of Particulate Matter

During the spring to fall of 1977 and 1978, 107 sediment traps located in southeastern Lake Michigan were sampled 4 to 6 times. Patterns and rates of accumulation in traps were quite similar in both years, with large differences apparent only during the storm period. Sediment flux at the base of the slope during nonresuspension events was at times an order of magnitude greater than the flux of material at the outer shelf.

The upper traps located at stations over the mid-slope and basin region should reflect more closely the actual sedimentation rate and flux across the thermocline. Sedimentation rates during thermal stratification for nonstorm conditions ranged from 0.21 to $1.7 \text{ g m}^{-2} \text{ day}^{-1}$ with \bar{x} (arithmetic mean) = $0.70 \text{ g m}^{-2} \text{ day}^{-1}$ ($N = 20$), s (standard deviation) = 0.40 . Rates for storm and pre- and post-stratified conditions ranged from 1.2 to $9.1 \text{ g m}^{-2} \text{ day}^{-1}$ with $\bar{x} = 4.8 \text{ g m}^{-2} \text{ day}^{-1}$ ($N = 9$), $s = 2.5$. These fluxes are similar to rates calculated from radioisotope measurements in cores ($\bar{x} = 0.64 \text{ g m}^{-2} \text{ day}^{-1}$, $s = 0.30$; Robbins and Edgington, 1975; Edgington and Robbins, 1976) and from the

Ambrosia (ragweed) pollen ($0.74 \text{ g m}^{-2} \text{ day}^{-1}$; Davis *et al.*, 1971) in the vicinity of our study area.

Particle flux increases exponentially from about 10 m above the bottom to 1 m above the bottom (figure 25), suggesting that a large component of material was resuspended. Assuming steady-state conditions (i.e., resuspension equals the flux determined by near-bottom traps minus the upper trap rates), an average of 84 percent of the material collected in our near-bottom traps could be resuspended sediment. The 1978 flux profiles indicate that most particle mass is confined to the bottom 3 m. Most material was collected by traps located near the base and mid-slope, with lesser amounts collected in the basin. Flux patterns for traps located off Little Sable Point (traps 9 to 12, figure 21), far removed from any river influence, are similar to those off the Grand River, supporting earlier observations that the Grand River input into the nepheloid is not identifiable.

Particle flux profiles (figure 25) can be expressed nearly perfectly by the exponential term

$$J = J_0 \exp^{-\beta z} \quad (24)$$

where J ($\text{g m}^{-2} \text{ day}^{-1}$) is the flux of resuspended material, J_0 ($\text{g m}^{-2} \text{ day}^{-1}$) is the downward particle flux at the sediment-water interface, z (m) is the height above bottom, and β (m^{-1}) may represent the ratio of Stoke's settling velocity to vertical eddy diffusivity, thus β^{-1} will be the resuspension scale length in meters (Wahlgren *et al.*, 1980). β s calculated from the particle flux data ranged in value from 0.08 to 0.55 m^{-1} , with a geometric mean and standard deviation equal to 0.30; 0.17; and 0.12 (+s; \bar{x} ; -s) producing resuspension scales (β^{-1}) of 3.3; 6.0; and 8.7 m.

7.5 Particle Transport Across the Shelf

Data collected during the 1977 sediment trap program provide insight into material transport across the shelf. During the first four collection periods, the outer shelf and upper slope regions had lower trap accumulation rates 1 m off the bottom than did the inner shelf and lower slope (figure 26). The regions of lower flux could reflect sedimentary bypassing where the fine material does not accumulate. Coarsest bottom sediment for this area is at the outer shelf, which contains less than 0.5-percent fines (<64 μm size fraction) on a dry-weight basis (Chambers and Eadie, 1980) and resuspension of the coarser sediment would only occur under severe storm conditions as seen in the last two periods of 1977.

During September and October 1977, several 2- to 3-day storms took place, with waves up to 5 m high and winds in excess of 10 m s^{-1} . Large quantities of material were collected in the inner shelf traps, representing fluxes of up to $560 \text{ g m}^{-2} \text{ day}^{-1}$ at 1 m above the bottom. Particulate material collected in the bottom traps on the mid-slope and lower slope increased by a factor of three to five during September and October. The flux 20 to 30 m above the bottom at these stations also increased, but rarely exceeded 20 percent of the

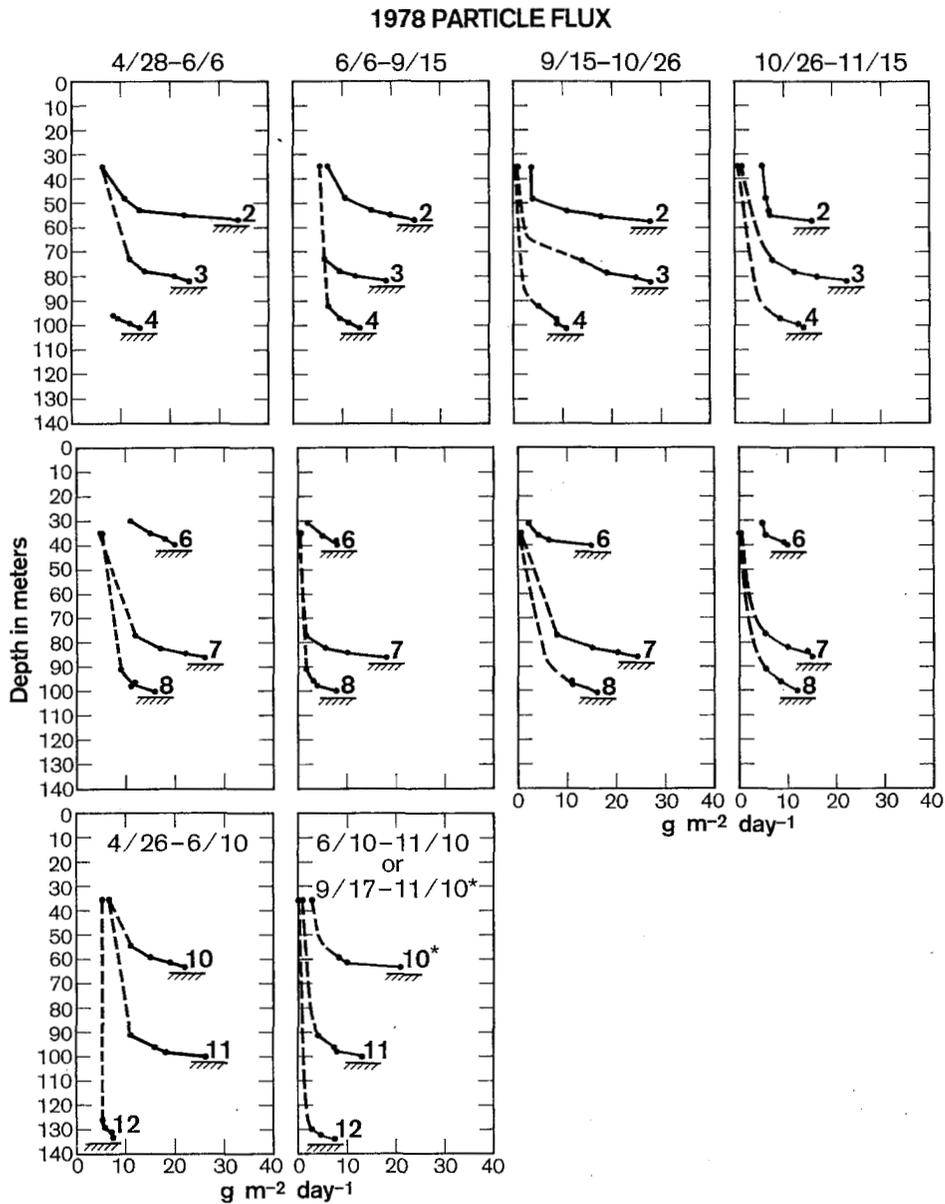


FIGURE 25.--Particle flux profiles of the 1978 sediment trap data. Units are $g\ m^{-2}\ day^{-1}$. The numbers correspond to 1978 station locations. (See figure 22.) The profiles are nearly exponential, with a resuspension scale length of approximately 6 m (from Chambers and Fadie, 1981).

1977 Sediment Trap Accumulation at 1 m above the bottom ($\text{g m}^{-2} \text{ day}^{-1}$)

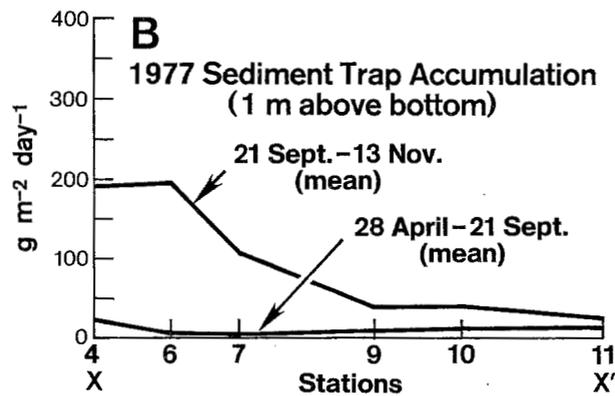
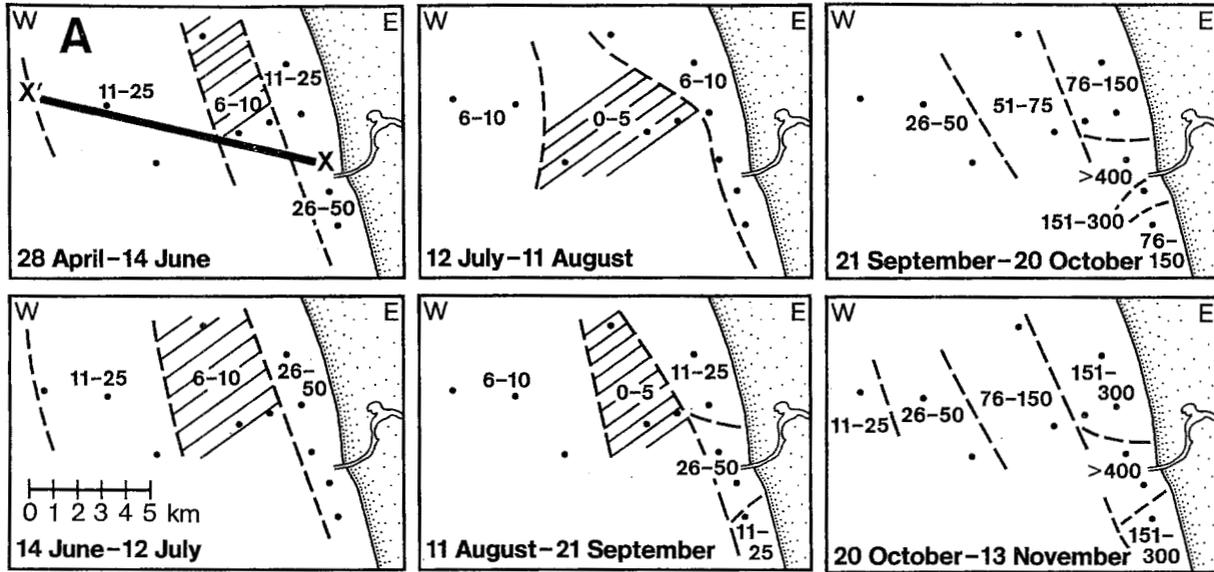


FIGURE 26.--Seasonal sediment trap accumulation rates at 1 m off the bottom for 1977 (A). Transect of mean nonstorm (April-September) and storm (September-November) particle fluxes (B). Transect X to X' shown in upper left of figure 26(A). Units are $\text{g m}^{-2} \text{ day}^{-1}$ (from Chambers and Eadie, 1981).

flux measured near the bottom. In contrast to the slope fluxes, the rates measured 5 m below the surface (7 to 20 m above the bottom) at the shelf locations accounted for more than 50 percent of the flux measured at the bottom. However, flux gradients were steep because at 3 m above the bottom the flux still only accounted for 60 percent of the flux at 1 m above the bottom. Although large amounts of material were resuspended on the shelf and upper slope, most of the sediment transported offshore was probably confined to the near bottom and supplemented the mass of material in the nepheloid layer.

The trap program during 1980-81 provided data that allow the mass flux rates during the thermally stratified period to be compared to the rates during the winter and spring months. Figure 27 shows that the flux rates in three different areas during the unstratified period are higher at all three

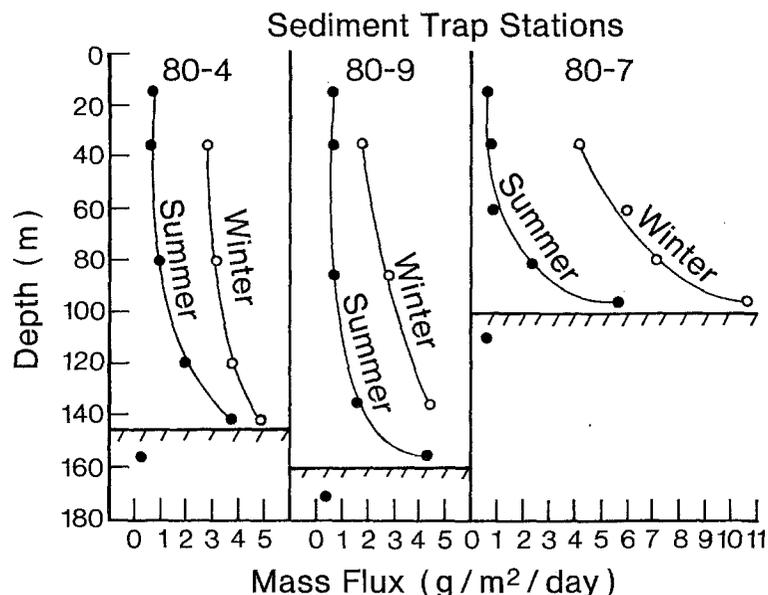


FIGURE 27.--Particle mass flux profiles from three trap profiles in Lake Michigan. (See figure 22.) Summer profiles represent the period mid-June through mid-November; winter profiles represent the period mid-November through mid-June. Sediment accumulation rates are from local cores measured by Edgington and Robbins (1976) (from Eadie et al., 1982c).

stations (figure 22) than the rates during the stratified period. Both rates are much higher than the sediment accumulation rates shown by the data point below the profiles for each station. The size and number of particles at various depths are shown in figure 28. These data are from sampling near the base of the slope and inshore from stations 7 and 8.

Particle-size distributions during the unstratified period generally show a relatively high concentration of fine (2 to 8 μm) particles. These fine-grained particles are high in organic carbon and are the materials that eventually collect in the lakes' depositional basins. They are also, presumably, the vehicle upon which hydrophobic contaminants are transported.

7.6 Contaminants and Resuspension Effects

The Great Lakes are particularly susceptible to contamination by synthetic materials, primarily because of the heavy industrialization of the region (leading to high loads) and the slow flushing times of the lakes. Slow flushing causes compound residence times to be scaled to internal removal process rates. The disposition of synthetic organics in aquatic environments depends strongly on their solubility. Chlorobiphenyls range in solubility from ~ 1 ppm to ~ 1 ppb and, in general, the group of compounds can be classified as hydrophobic, characterized by a strong tendency to sorb onto particles and settle. For compounds characterized by slow decomposition rates, such as highly chlorinated PCB isomers, settling into the benthic boundary layer (BBL)

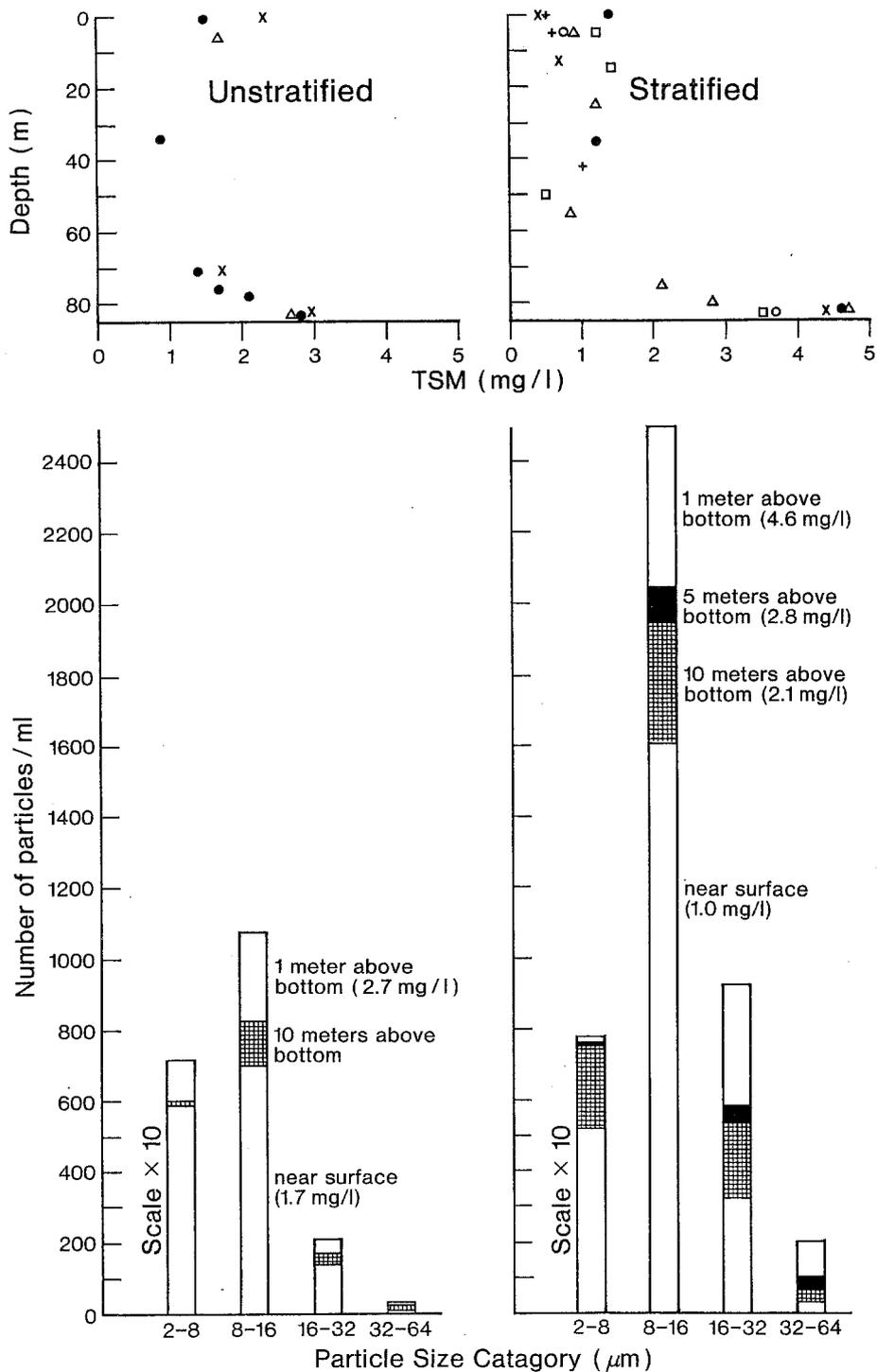


FIGURE 28.--Composite profiles of total suspended matter for the unstratified (A) and stratified (B) periods at station 7/8. (For location, see figure 22.) The unstratified composite represents three sets and the stratified composite represents five sets of samples. Characteristic particle-size distribution profiles for the unstratified (C) and stratified (D) periods at the same location. Size data were determined on a HIAC® instrument. The number of particles at each depth (within each size category) are cumulative. In all cases, the samples collected near the surface had the smallest number of particles per milliliter, while the sample from 1 m above the bottom had the greatest number (from Eadie et al., 1982c).

and burial are a prime removal mechanism. Calculations based on analyses of materials collected in sediment traps in southern Lake Michigan indicate a significant reentrainment of sediment-bound PCB. Approximately 14 percent of the current water column inventory of particle-associated PCB can be accounted for by winter resuspension. Reentrainment of pore-water-associated PCB is small, but may be significant if associated with soluble natural organics of colloidal material. The net effect of resuspension is to increase the residence time for contaminants in the active ecosystem (Eadie *et al.*, 1982c).

From the data in figure 27 and other data, it appears that the winter mass flux (at 35 m) is conservatively estimated at $1 \text{ g m}^{-2} \text{ d}^{-1}$ greater than the flux during the stratified period. From a 200-day period, this represents 200 g m^{-2} of resuspended sediment reaching near-surface waters. Assuming the PCB concentration in surficial sediments subject to resuspension to be 100 ng g^{-1} , then approximately $20 \text{ g m}^{-2} \text{ year}^{-1}$ of particle-associated PCB would be reintroduced into the water column. In Lake Michigan, the inventory of PCB in 1 m^2 of water column is approximately $425 \text{ } \mu\text{g PCB m}^{-2}$ ($5 \text{ } \mu\text{g PCB m}^{-3} \times 85 \text{ m}$).

From the data for the dissolved fraction in table 13, an estimate of the importance of entrainment of dissolved material can be made. Assuming the water reentrained is four times the particulate resuspension (vol vol^{-1}) or

TABLE 13.--Sediment/pore water PCB data and apparent partition coefficients

| | % O.C. | 1242 | 1254 | Total |
|-----------------------------------|--------|-------|---------|-------|
| Nearshore* (Sandy) | | | | |
| Pore Water (ng L^{-1}) | | 0.153 | 0.006 | 0.159 |
| Sediment (ng g^{-1}) | 0.7 | 31.9 | 31.6 | 63.5 |
| K | | 208. | 5,267. | 399. |
| Station 7 (Clay:Silt) | | | | |
| Pore Water (ng L^{-1}) | | 0.201 | 0.013 | 0.214 |
| Sediment (ng g^{-1}) | 1.7 | 69.0 | 91.0 | 160.0 |
| K | | 343. | 7,000.0 | 747. |
| Station 3** (Clay) | | | | |
| Pore Water (ng L^{-1}) | | 0.308 | 0.034 | 0.342 |
| Sediment (ng g^{-1}) | 3.8 | 64.4 | 86.1 | 150.5 |
| K | | 209. | 2,532. | 440.0 |

*Inshore of Station 7/8 (see figure 22); 45-m depth.

**Off Benton Harbor, Mich.; highest recorded accumulation rate in Lake Michigan; $3 \text{ g m}^{-2} \text{ day}^{-1}$.

approximately 400 mL m^{-2} and has a PCB concentration of 200 ng L^{-1} , one can calculate a dissolved PCB flux of $80 \text{ ng m}^{-2} \text{ year}^{-1}$. This is about 0.4 percent as large as the particulate reentrainment and less than 0.1 percent of the water column inventory. The importance of this small load may be increased if the dissolved reentrained PCB is complexed with soluble natural organic matter. Such an association would affect the cycling of this fraction and tend to increase its residence time in the active ecosystem. These indicate that reentrainment from sediments can be very important, but more data are needed to get reliable estimates.

Atmospheric and total load numbers obtained from the literature (table 14) are seriously out of balance with the estimated sediment accumulations. This indicates either that the lake is far from steady state and PCBs are building up in the water column, in contradiction to the apparent decline of PCBs in fish, or that reported load estimates are not representative of current loads. Other reports indicate that our estimate of the sediment inventory of PCB might be a little high (D. Armstrong, University of Wisconsin, pers. com.) and that atmospheric loads are probably high by an order of magnitude (A. W. Andren, University of Wisconsin, pers. comm.). These adjustments would bring the system near to balancing.

A study of the suspended fine-grained materials reintroduced into the euphotic zone from the nepheloid layer during an upwelling event in

TABLE 14.--PCB loads (Mt yr^{-1}) for Lake Michigan

| | |
|------------------------------------|-------|
| Atmospheric Input ¹ | 6.9 |
| Total Load ² | 8.95 |
| Sediment Accumulation ³ | 0.6 |
| Particulate Resuspension | 1.0 |
| Dissolved Resuspension | 0.005 |
| Upwelling ⁴ | 0.4 |

¹Eisenreich *et al.*, 1981a.

²Murphy and Rzeszutko, 1978.

³Average sediment accumulation = $10 \text{ mg cm}^{-2} \text{ yr}^{-1}$; PCB concentration = 100 ng g^{-1} .

⁴Bell and Eadie, 1982.

southeastern Lake Michigan allows an estimate of the sediment-associated contaminant, such as PCB, that can be reintroduced into the surface waters (Bell and Eadie, 1982). Assuming 10 upwelling events affecting an area of 125 km², and an increase of 0.2 mg L⁻¹ (figure 29), there are approximately 7.5 x 10⁶ kg of suspended materials reintroduced from the nepheloid layer. Using PCB concentrations of 100 ppb (Rice *et al.*, 1982b; Eadie *et al.*, 1982c) and atmospheric PCB inputs of 6,900 kg yr⁻¹ (Eisenreich *et al.*, 1981a), the calculated upwelled load is 6 g km⁻² yr⁻¹ or approximately 5 percent of the estimated atmospheric PCB load of 119 g km⁻² yr⁻¹. This estimate may be too conservative since the increase in TSM produced by a strong upwelling event may well exceed 0.2 mg L⁻¹ and does not take into consideration the effects of lesser events or the seasonal differences.

As the loading of PCB and other contaminants to the lake decreases, the fine-grain-associated contaminants injected into the euphotic zone through upwelling events will play a larger role in the long-term behavior and fate of such compounds. The reentrainment of sediment-associated contaminants will undoubtedly increase the residence time of these materials within the active ecosystem.

8. PRESENT AND HISTORICAL FLUXES OF CONTAMINANTS TO GREAT LAKES SEDIMENTS

Most of the load of organic, as well as inorganic, contaminants entering the Great Lakes ends up on the bottom. The predominance of sedimentation and

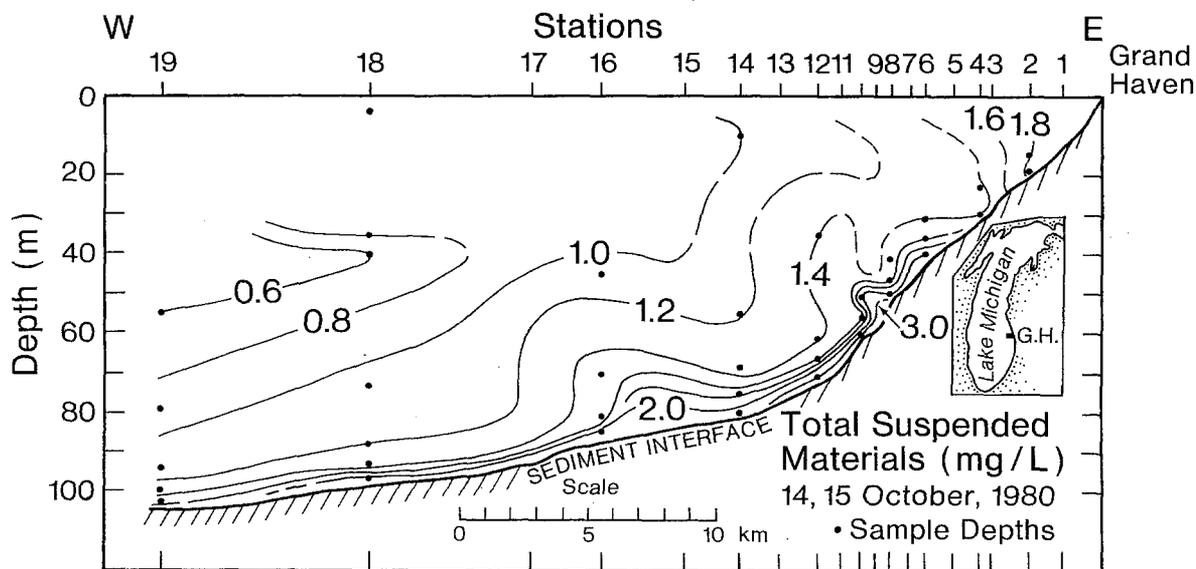


FIGURE 29.--Total suspended matter contours (mg L⁻¹) during an upwelling event. A comparison with transparency and temperature profiles shows suspended materials being transported up the slope into the nearshore area then lakeward in the epilimnion. Water samples were collected at each dot (from Bell and Eadie, 1982).

burial as a removal pathway is in part due to the strong affinity of many contaminants for particulate matter and to the long hydraulic residence times of most of the lakes. Although some organic compounds are subject to evaporative or degradative losses in the water column, sedimentation and burial generally remain the major removal route.

Transport of contaminants between their source and final burial is complex, involving a cycle of resuspension and redeposition the net effect of which is the preferential deposition of recent materials in selected areas of the lake bottom. The so-called focusing of sediments and associated contaminants occurs to such a great extent that only about 30 percent of the bottom of the Great Lakes may be considered to have active long-term deposition. (See figure 20.) In other areas (usually in shallower water), contaminants may be initially stored, but seasonal or longer-term resuspension events reentrain materials, which then generally move off to quieter portions of the lake bottom. Resuspension is a widely occurring process, which serves to couple recent sedimentary deposits to the water column.

The coupling brought about by resuspension affects the response of the lakes to contaminant loading in two contrasting ways: upon introduction of a new contaminant, resuspension provides a source of scavenging particles that facilitate its removal from the system; on cessation of the contaminant loading, resuspension serves to maintain levels in the water as the resuspended particles are then contaminated. The extent to which levels of contamination are maintained by resuspension depends not only on the degree of coupling but on the rapidity with which contaminated sediments are buried.

In the Great Lakes the burial process is altered by the presence of a variety of organisms (macrobenthos such as *Pontoporeia* and tubificid worms) that mix sediments as a result of their life activities. In the lakes their range of interaction in sediments is the order of 2 to 10 cm and for sedimentation rates encountered in the lakes this range corresponds to 5 to 100 years of sediment. To the extent that sediment particles are resuspended out of the zone mixed by macrobenthos, the effect of these organisms is twofold: at the onset of lake contamination they retard the buildup of levels in the lake, but on abatement they prolong the contact.

Whole lake modeling of the behavior of contaminants must thus not only take account of seasonally varying water column processes, such as particle-solution exchange, particle settling, resuspension, (and for organics photolysis, biodegradation, evaporation, etc.), but also sedimentation processes, such as bioturbation (biological mixing), sedimentation, diffusion, and degradation.

The purpose of the present study is (1) to build an optimally self-consistent description of sedimentation, bioturbation, diffusion, and reaction for 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. In the case of complex organic contaminants, often very little if anything is known about the loading history, so predictive models have relatively little historical basis for success. But since any satisfactory predictive model for

the water column also produces a prediction for the flux to the sediments, sediment contaminant profiles can provide a calibration if the sedimentary processes themselves can be properly understood and modeled.

To this end, cores have been or will be collected from areas of the open lake with maximum sedimentation. High sedimentation rates improve the time resolution in reconstruction of time-dependent fluxes. As such areas occur generally in the open lake, profiles are more likely to reflect the average history of contamination in the water rather than the influence of local sources. Box cores (and a set of subcores) are being taken at at least two locations within each area of high deposition. Locations are chosen to provide a set of cores with significantly contrasting sedimentation rates (roughly a factor of two difference). Comparison of contaminant profiles in cores with differing sedimentation rates is expected to help in sorting out the effects of post-depositional movement or degradation of contaminants from real changes in the time dependence of the inputs. Areas cored to date are illustrated in figure 30. Sediment cores are being collected by state-of-the-art oceanographic box coring methods and by open-tube triple gravity coring techniques. Because adequate characterization of sedimentary materials requires interdisciplinary efforts, the skills and interests of a number of individuals and institutions are being applied in the study. Listed in table 15 are individuals presently involved. As the nature and scope of the study are being more widely recognized, additional people are coming forward. The project commenced in June 1981 with the coring of Lake Ontario sediments by R. Bourbonniere under the auspices of the Canada Centre for Inland Waters. In October 1981, cores were collected from the other lakes indicated (figure 30)

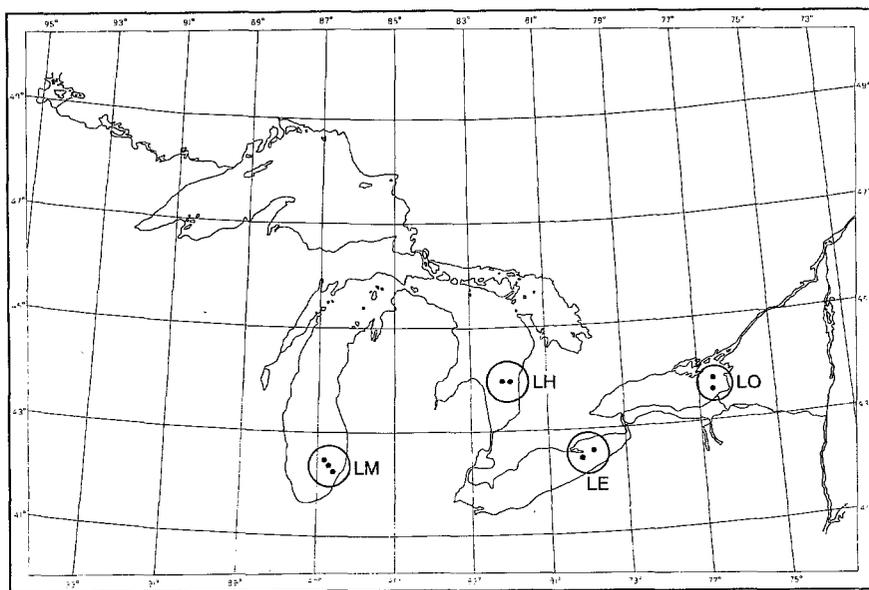


FIGURE 30.--Locations of cores collected in 1981 (Lake Ontario, CSS Limnos; other lakes, R/V Roger R. Simons).

with the use of the EPA research vessel *Roger R. Simons*. In June 1982, additional cores were taken in Lake Erie aboard the Canada Centre for Inland Waters research vessel *Limnos*.

Multiple subcores from each box core (up to 20) were sectioned aboard ship and subsamples distributed to various participants. Subcores are first analyzed at the GLERL-U.M. Nuclear Measurements Laboratory to determine their suitability for detailed analysis. Qualifying cores are then analyzed by other researchers for constituents indicated in table 15.

Although this project has been funded for less than a year, the Lake Ontario cores were soon available for analysis. Most of the work to date concerns the Lake Ontario cores, although some radiometric measurements (especially the short-lived gamma emitters) have been completed in cores from the other lakes.

8.1 Radiometric Measurements

Determination of the distribution of lead-210 and cesium-137 provides the basis for determining sedimentation rates and the extent of biological mixing in this study. (Details of the methods are given by Robbins (1978), Robbins *et al.* (1978), and Robbins and Edgington (1975).) Distributions of these two radionuclides are shown in figures 31 and 32 for Lake Ontario stations G32 and E30. The excess lead-210 profiles show the features commonly encountered in recent sediments of the Great Lakes: a zone of essentially constant activity at the sediment-water interface and an exponential decrease below that zone. Such profiles are considered to arise as a result of a process of sedimentation, mixing, and radioactive decay. The half-life of lead-210 is 22.3 years. The solid lines for lead-210 are the predicted distributions based on the assumption of a constant sedimentation rate, constant flux of lead-210, and rapid steady-state mixing of well-defined range. As new sediment is added, the zone of mixing is envisioned to retain the same thickness and thus move upward at a rate equal to the sedimentation rate. In these figures sediment depths are expressed in units of grams of dry material per square centimeter and sedimentation rates in units of $\text{g cm}^{-2} \text{ yr}^{-1}$ to correct automatically for effects of compaction. The regularity in the excess lead-210 data provides a very precise determination of the sedimentation rate in each core. Values for the rates and depths of sediment mixing are provided in table 16. The two sites differ roughly by a factor of two in sedimentation rate.

Distributions of cesium-137 in these cores are shown in the right-hand panels of figures 31 and 32. This radionuclide, which has a 30-year half life, results primarily from atmospheric nuclear testing. Levels of cesium-137 were highest during the period from 1963 to 1964 and since that time have been markedly lower as a result of the test ban treaty between the U.S. and the U.S.S.R. As the residence time of the radionuclide in the lakes is very short (about 1 to 2 years), sedimentary profiles of cesium-137 might be expected to mimic the history of atmospheric deposition unless there are near-bottom integrative processes such as biological mixing. The distribution of radiocesium expected in the absence of mixing is shown as the shaded area in each of the two figures. Actual cesium activity extends downward farther than

TABLE 15.--*Current participants in the High Sedimentation study*

| Name | Affiliation | Contribution or Interest |
|----------------------------|--|--|
| Dr. Richard Bourbonniere | Canada Centre for Inland Waters (CCIW) | Photographic documentation, organic, inorganic carbon, fatty acids humic materials |
| Mr. Murray Charleton | CCIW | Sediment oxygen demand |
| Dr. Brian Eadie | NOAA/GLERL | Polyaromatic hydrocarbons |
| Dr. Steven Eisenreich | University of Minnesota | PCB isomers, other chlorinated organics (mirex, toxaphene, etc.) |
| Dr. Wayne Gardner | NOAA/GLERL | Forms of phosphorus |
| Dr. Efriam Halfon | CCIW | Sedimentary process modeling |
| Dr. Kjell Johansen | University of Michigan | Cesium-137, lead-210 |
| Dr. Jim Kitchell | University of Wisconsin | Copepod fragments |
| Dr. Peter Martin | University of Guelph | Descriptive sedimentology, sedimentary structures |
| Dr. Gerald Matisoff | Case Western Reserve Univ. | Nutrient/stable element chemistry, process modeling |
| Dr. Philip Meyers | Univiversity of Michigan | Lipids, hydrocarbons |
| Mr. Donald Nelson | Argonne National Laboratory (ANR) | Short-lived alpha emitters |
| Dr. Jerome Nriagu | CCIW | Sulfur compounds |
| Dr. John Robbins | NOAA/GLERL | Lead-210, cesium-137, short-lived gamma emitters, bioturbation, sedimentation modeling |
| Dr. Ronald Rossmann | University of Michigan | Major and minor metals (AAS), grain size |
| Dr. Claire Schelske | University of Michigan | Amorphous and diatom silicon |
| Dr. Jacob Sedlet | ANL | Tritium |
| Ms. Karen Thomson | CCIW | Bacterial activity |
| Dr. David White/Tim Keilty | University of Michigan | Macrobenthic organisms |

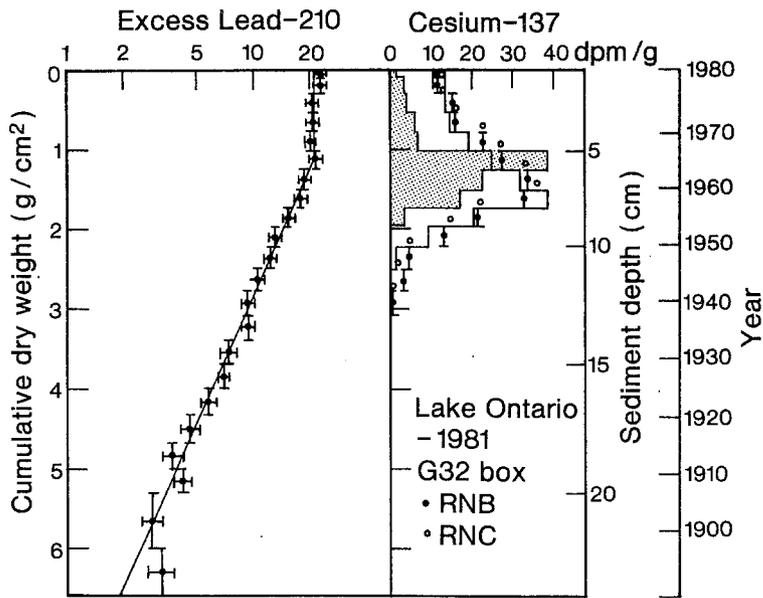


FIGURE 31.--Distribution of excess lead-210 and cesium-137 in Lake Ontario core G32. The solid lines are fits using the steady-state mixing model. The shaded histogram indicates the distribution of cesium-137 expected from direct fallout with no sediment mixing. (Data and model of J. Robbins/K. Johansen.)

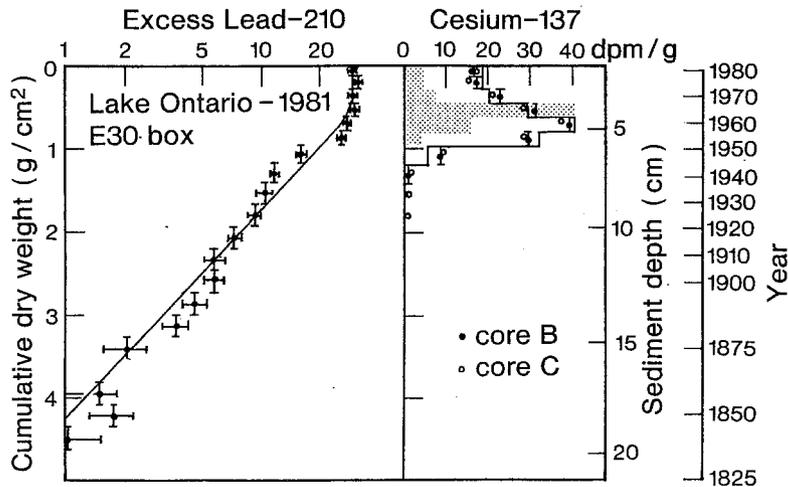


FIGURE 32.--Distribution of excess lead-210 and cesium-137 in Lake Ontario core E30. The sedimentation rate in this core is about half that for core G32. (Data and model of J. Robbins/K. Johansen.)

TABLE 16.--Sedimentation rate and mixed depths for the Lake Ontario (1981) core inferred from distributions of cesium-137 and excess lead-210

| Core | Cesium-137 Distribution | | Excess Lead-210 Distribution | |
|----------------------|--|--|--|--|
| | Sedimentation [†] Rate (g cm ⁻² yr ⁻¹) | Mixed* Depth (g cm ⁻²) | Sedimentation [†] Rate (g cm ⁻² yr ⁻¹) | Mixed* Depth (g cm ⁻²) |
| L0-81- | | | | |
| E30-RNA (Gravity) | 0.0153 | 0.160 | 0.0248 | 0.04 |
| E30 RNB (Box) | 0.0314 | 0.312 | 0.0343 | 0.519 |
| E30 RNC (Box) | 0.0319 | 0.28 | 0.042 | |
| G32 RNA (Gravity) | 0.0494 | 0.436 | 0.062 | |
| G32 RNB (Box) | 0.0692 | 0.588 | 0.0714 | 1.12 |
| G32 RNC (Box) | 0.0693 | 0.589 | | |

[†]Least square increments for the best value of high sedimentation rates:
0.0001 g cm⁻² yr⁻¹.

*Least squares search increments for the best value of the mixed depth:
0.001 g cm⁻².

expected without mixing and post-1963 levels are considerably higher than expected from the fallout record. Application of the steady-state mixing model using the known deposition history yields the theoretical profiles shown as solid lines in each figure. The steady-state, finite-range mixing model provides an excellent description at the observed profiles. Moreover, sedimentation rates based on this analysis of cesium-137 profiles are in excellent agreement with rates from lead-210. However, depths of mixing are twice as great for lead-210. Further analysis is required to understand this difference. While distributions of cesium-137 and lead-210 are generally consistent with the concept of instantaneous homogenization of near-surface sediments, distributions of shorter lived particle-bound radionuclides suggest improvements in modeling. On time scales on the order of decades, particle-bound radionuclides appear uniformly mixed, but on scales on the order of months to years, they are generally not.

Shown in figure 33 are the distributions of three radionuclides in a high sedimentation rate core from Lake Michigan. The distribution of cesium-137 (right panel) is consistent with the rapid steady-state model, indicating a mixed depth of about 5 cm. The histogram shows the distribution expected in the absence of mixing, while the shaded area is the predicted distribution. In contrast, the distribution of beryllium-7 in the core is essentially exponential (decreasing with about a 1 cm half depth). This isotope is produced by cosmic ray interaction with air molecules and is introduced into the lake primarily via precipitation. Because of its short half-life (53.5 days), its penetration into sediments is restricted. In the absence of sediment mixing, the beryllium-7 would be confined to a submillimeter veneer of material. If the mixing process were solely advective (only conveyor-belt feeding worms were present), then for an essentially constant input of beryllium-7, the expected profile is given by

$$A(g) = A_0(g) e^{-\lambda g / (r_r + r_s)} \quad (25)$$

where g is the cumulative dry weight of sediment, r_s is the sedimentation rate, r_r is the advective reworking rate ($\text{g cm}^{-2} \text{yr}^{-1}$), and $\lambda = 0.693/53.5$ (d^{-1}). A fit of this equation to the data yields a rate of $0.55 \text{ g cm}^{-2} \text{yr}^{-1}$ which is about 10 times as high as the sedimentation rate of about $0.06 \text{ g cm}^{-2} \text{yr}^{-1}$. Cerium-144, which has a half-life of 284 days, shows greater penetration into the sediments, as expected. However, assuming the flux of this fallout radionuclide to be constant, the purely advective model yields a reworking rate of only $0.27 \text{ g cm}^{-2} \text{yr}^{-1}$. Smaller advective reworking of this

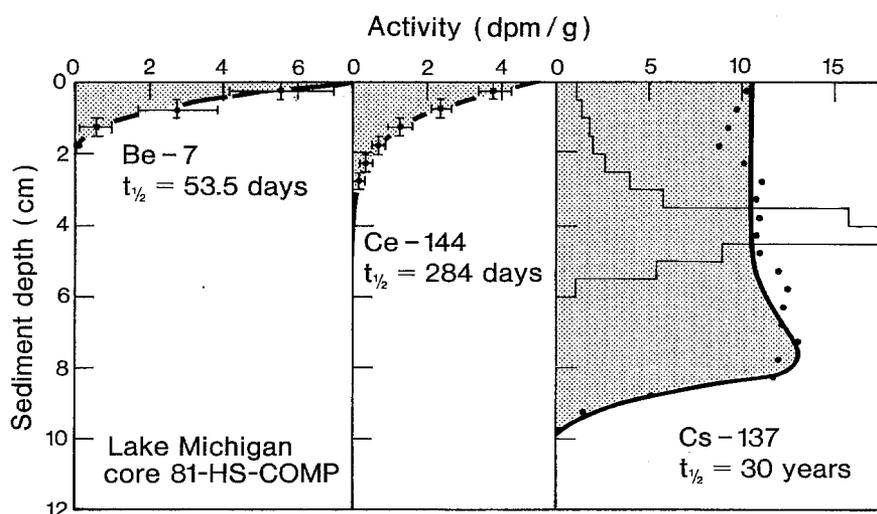


FIGURE 33.--Distribution of beryllium-7, cerium-144, and cesium-137 in a high sedimentation rate core from Lake Michigan. While cesium-137 appears uniformly mixed, the two short-lived isotopes are not. The uniform mixing model can only apply to processes occurring on time scales of decades. (Data and model of J. Robbins.)

nuclide suggests a decrease in the extent of advection with increasing sediment depth. Such a reduction is expected on the basis of several laboratory studies involving the use of radiolabeled sediment microcosms containing conveyor-belt species (Fisher *et al.*, 1980; Krezoski and Robbins, 1980). The conveyor-belt species feed with their heads extending downward into sediments and tails protruding above the sediment surface. Ingested material passed through the gut is redeposited on surface sediments. If a population of worms feeds uniformly over some depth, then the velocity of particles initially at the sediment surface decreases with depth since worms feeding above the level of the particle can contribute longer to its downward motion. In this case it can be shown that the time for a particle to reach a depth of g is

$$t = \int_0^g \frac{dg}{r_r(0)(1 - g/g_m)}$$

where g is the maximum depth of feeding ($g\ m^{-2}$) and $r_r(0)$ is the advective reworking rate at the sediment surface. The expected activity is then

$$A(g) = A(0)e^{-\lambda t}$$

Application of this model yields 0.62 and 0.43 $g\ cm^{-1}\ yr^{-1}$ for beryllium-7 and cerium-144 respectively, which is necessarily more consistent.

In reality both advective and diffusive processes conspire to produce the observed profiles. The nature of sediment reworking depends in detail on the type of organisms present. The distribution of macrobenthos in the Lake Michigan core is shown in figure 34. The center panel shows the vertical distribution of tubificid and lumbriculid worms, which transport sediment in the advective conveyor belt mode. Their range of occurrence is comparable to the range of penetration of cesium-137--a result anticipated from application of the mixing model to the distribution of this radionuclide. Also shown is the distribution of *Pontoporeia hoyi*, an amphipod that churns up surface sediments in an eddy diffusive manner. Their range of penetration (roughly 2 cm) is consistent with the results of laboratory tracer studies with sediment microcosms (Robbins *et al.*, 1977). The results of this and related studies indicate development of a model for mixing of sediment particles that has (1) a diffusive component with a range of 1 to 2 cm and (2) an advective component derived from uniform feeding and redeposition of materials on surface sediments. Further developments in modeling will probably have to take account of the particle selective nature of the process.

8.2 Geochemical Characterization of Sediments

Interpretation of metal and organic contaminant distributions in sediments requires a comprehensive model that takes into account processes such as

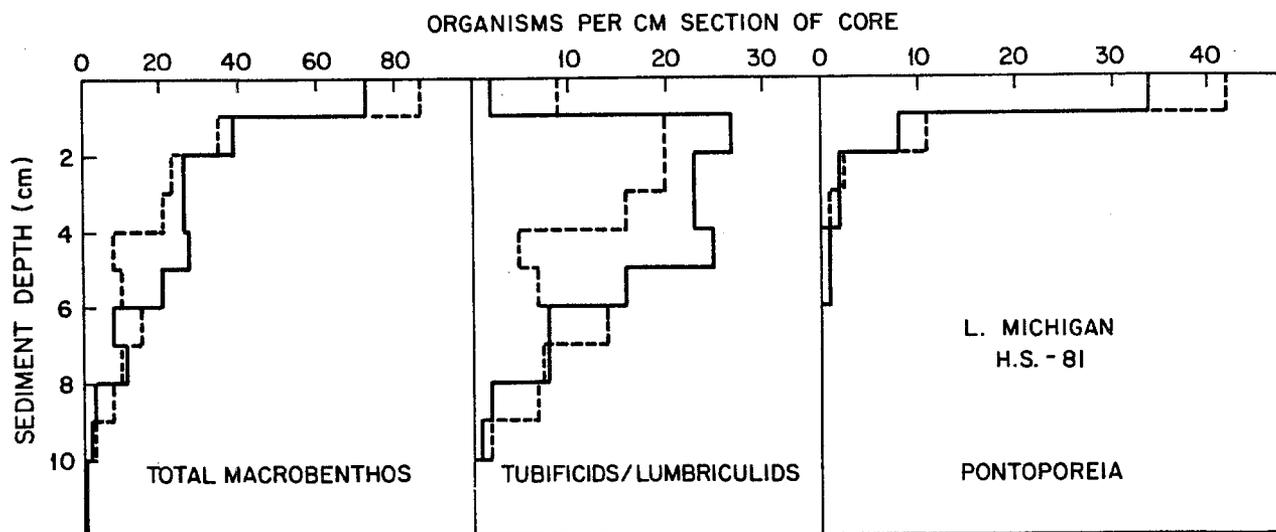


FIGURE 34.--Distribution of macrobenthic organisms in the Lake Michigan high sedimentation core. Tubificid and lumbriculid worms advectively recycle sediment particles over a range consistent with cesium-137 mixed depths. In contrast, Pontoporeia, which mix sediments diffusively, are confined to the upper few centimeters. Their effect must be included in describing short-term sediment redistribution processes. (Data of T. Keilty.)

diffusion, advection, bioturbation, chemical or biochemical reactions, and time-dependent changes in contaminant flux. Chemical processes are primarily a product of the oxidation of organic matter in surficial sediments. This oxidation has three results: 1) the consumption of organic matter; 2) the consumption of oxygen; and 3) a decrease in the EH and pH of the sediment. This diagenesis can serve to mobilize, alter, or preserve deposited contaminants. The net impact of diagenesis depends upon the contaminant's chemical characteristics and the geochemical environment to which the contaminant is subjected.

Sectioned cores from Lakes Ontario and Michigan are being analyzed for vertical variations in their content of calcium, magnesium, iron, manganese, lead, mercury, arsenic, zinc, chromium, antimony, cadmium, bismuth, copper, organic carbon, inorganic carbon, and acid insoluble materials. To date, only the analyses of the Lake Ontario cores are complete enough to allow a preliminary interpretation of the results.

Several major components exist within Great Lakes sediments. These include carbonates (calcite and dolomite), ferromanganese compounds (hydrated manganese oxides and ferric hydroxides), silicates (quartz, feldspars, and clay minerals), and organic matter. Components that may be important in deeper sediments are iron sulfides. A contaminant's concentration will vary with the occurrence and post-depositional alteration of the major component with which it is associated.

Within Lake Ontario surficial sediments, carbonates probably dilute radionuclide, metal, and organic contaminant concentrations. The majority of carbonate in the near-surface sections of each core is calcium carbonate. In core L081-E30-RNB, the inorganic carbon and calcium profiles, both indicative of calcite, reflect major decreases in amounts of the mineral with depth in the top 14 to 18 cm (figure 35). The maximum calcite content is about 21 weight percent. In core L081-G32-RNB, the calcium and inorganic carbon profiles indicate the presence of calcite between 0 and 22 cm. The maximum calcite content in the upper region of this core is nearly 12 weight percent. Whether concentrations of metals, organic contaminants and radionuclides should be corrected for the decrease in carbonate content with increasing depth depends on whether the profile is due to change in the calcite flux over time or to steady-state diagenesis.

A fraction of the carbonate may also be present as dolomite, $\text{CaMg}(\text{CO}_3)_2$, which is thermodynamically more stable than calcite (Rossmann, 1980). Since magnesium concentrations are relatively constant with depth in both cores, a dolomite correction of the radionuclide or contaminants data is not necessary (figure 36). Major variations in calcite (carbonate) content appear restricted to the Lake Ontario cores and probably reflect significant sources of eroded limestone in this lake.

Like the carbonates, organic carbon may dilute radionuclides and contaminants by varying amounts at different depths within a core, although the effects of dilution are smaller. In core L081-E30-RNB, organic carbon decreases between 1 and 14 cm (figure 36). Its maximum concentration is 4.81 weight percent. In core L081-G32-RNB, it decreases in concentration between 0 and 26 cm and reaches a maximum concentration of 4.18 weight percent.

Another possible diluent of lead-210 and cesium-137 activities and contaminant concentrations is silicate. The most often encountered silicate in Great Lakes sediment is quartz. The method used for extraction of the samples for lead-210 and metals analyses does not dissolve silicates. Since these are the only fraction of the sediment not dissolved, the acid insoluble fraction is a direct measure of silicate concentration. Both Lake Ontario cores have a variable silicate content (figure 37). Core L081-E30-RNB has a silicate concentration varying from 55 to 75 weight percent, and core L081-G32-RNB has a silicate concentration varying from 62 to 76 weight percent. For both cores, the weight percent insoluble decreases with decreasing depth in the core in response to increasing carbonate and organic carbon content.

Because manganese oxides are very sensitive to changes in dissolved oxygen, they serve as an excellent marker for depth of sediment oxygenation. To exist, manganese oxides require a highly oxygenated environment (Rossmann, 1973). Sediments are oxygenated by both diffusion, and more importantly, physical processes that mix the surficial sediments. In both cores, the depth of sediment oxygenation defined by manganese profiles is 2 cm (figure 37).

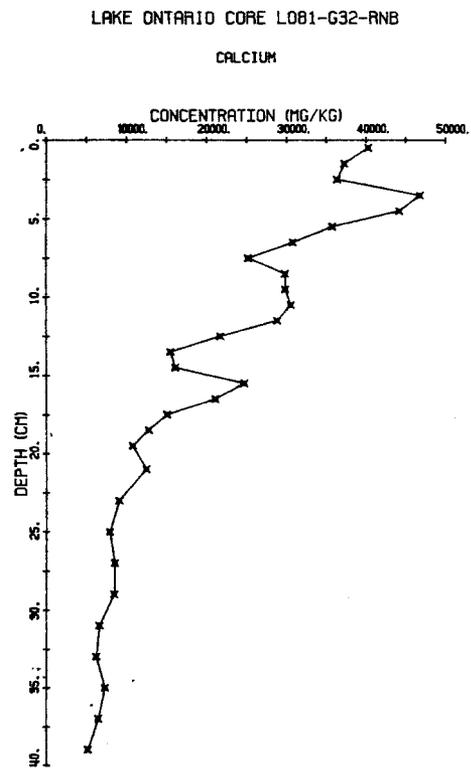
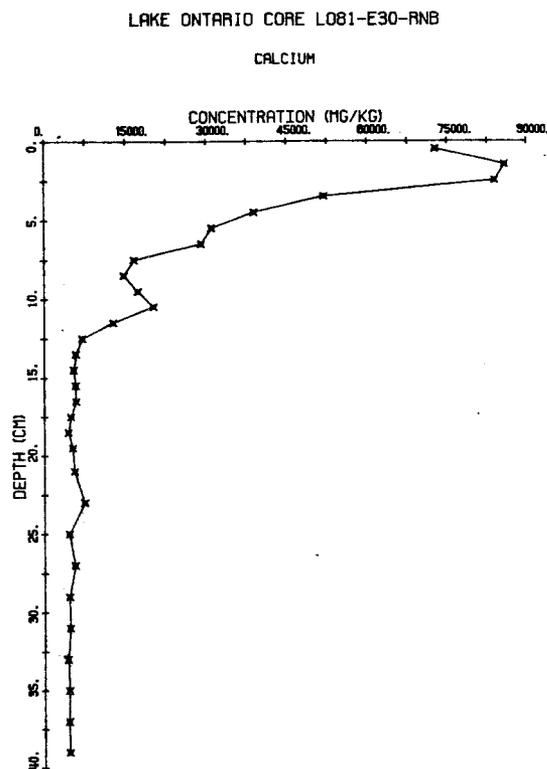
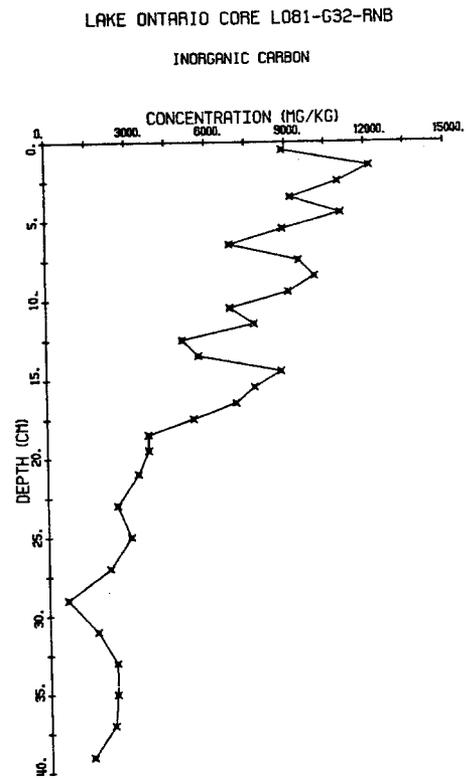
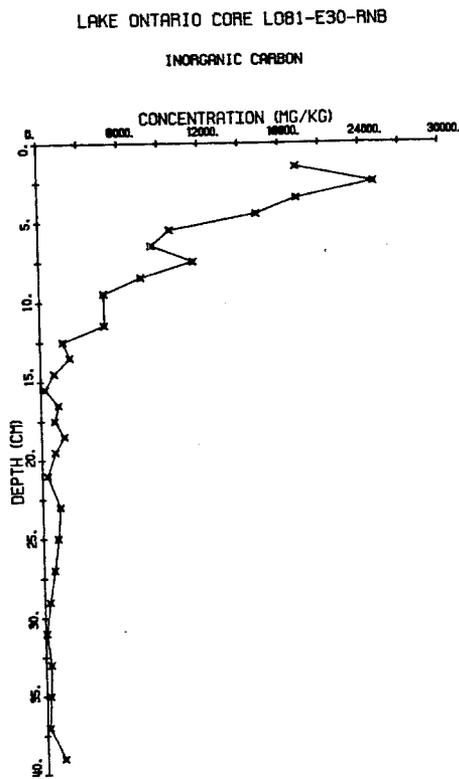


FIGURE 35.--Vertical distribution of inorganic carbon and calcium in the Lake Ontario cores. These strongly varying constituents constitute a significant mass of the sediments. Proper modeling of sedimentation, reworking, and geochronology must include a treatment of such profiles. (Data of R. Bourbonniere/R. Rossmann.)

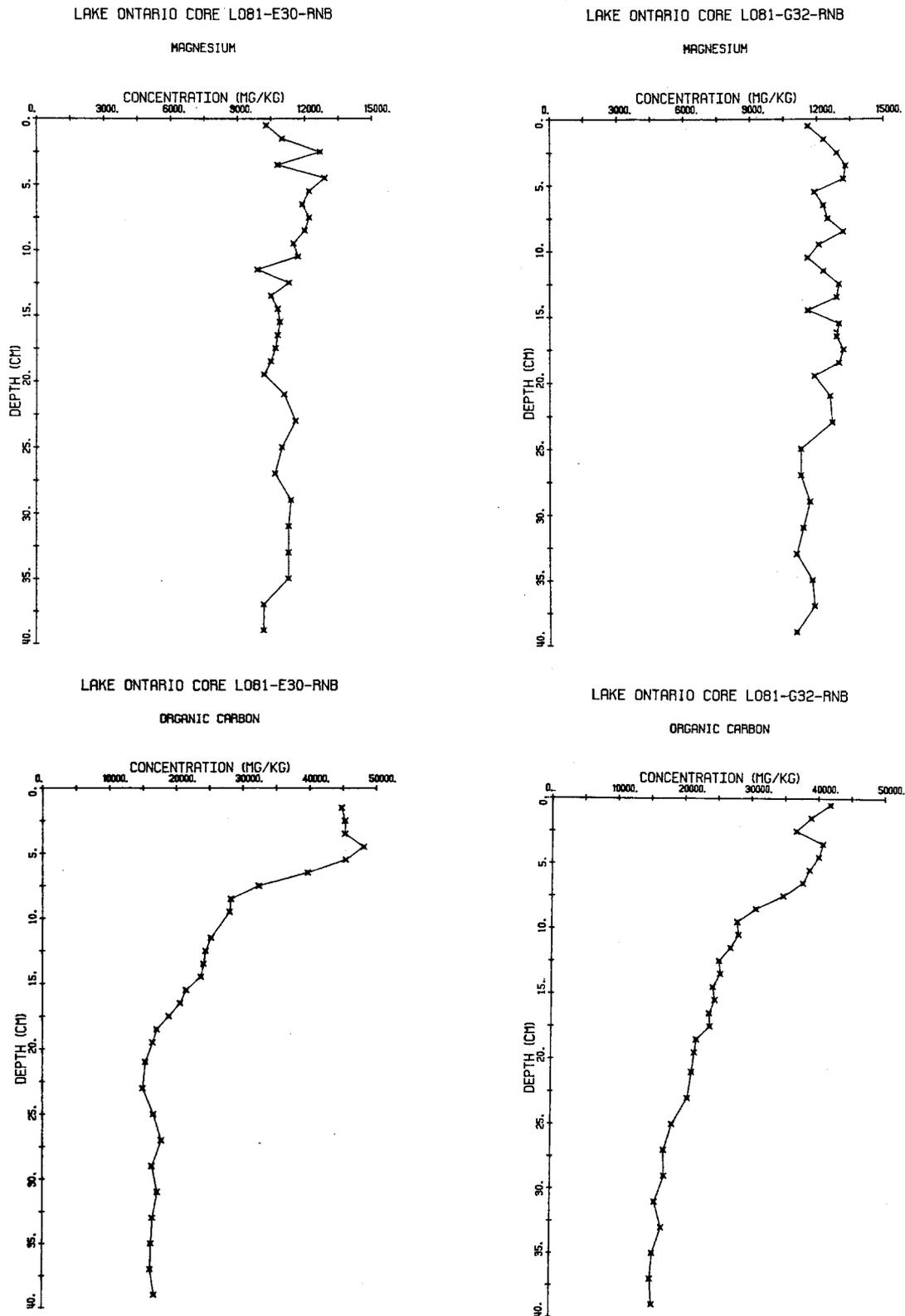


FIGURE 36.--Vertical distribution of magnesium organic carbon in the Lake Ontario cores. The comparatively constant concentration of magnesium indicates that the probable form of inorganic carbon is calcium carbonate, a material probably lost from sediments by dissolution on burial. (Data of R. Bourbonniere and R. Rossmann.)

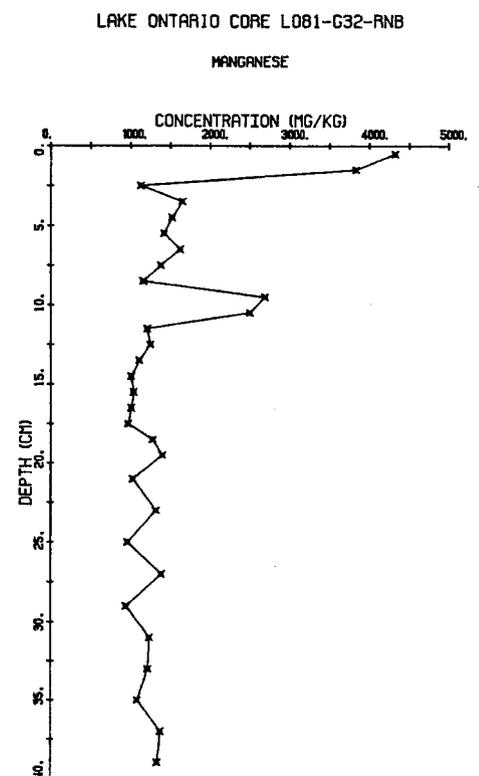
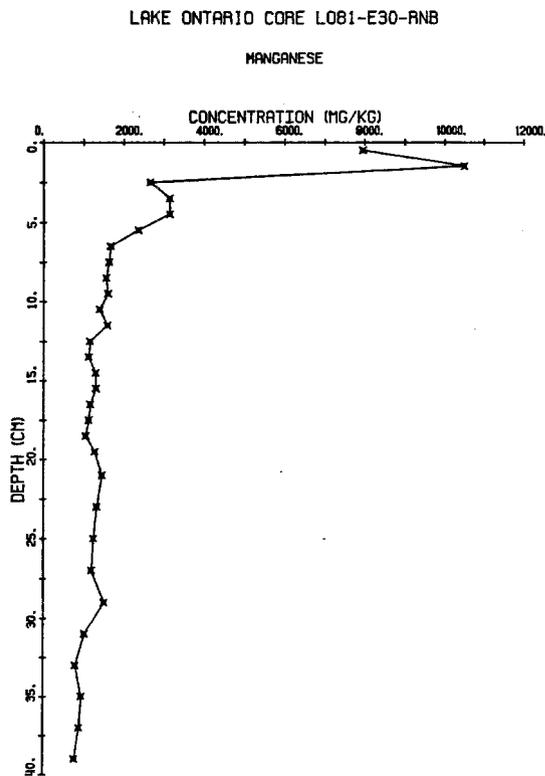
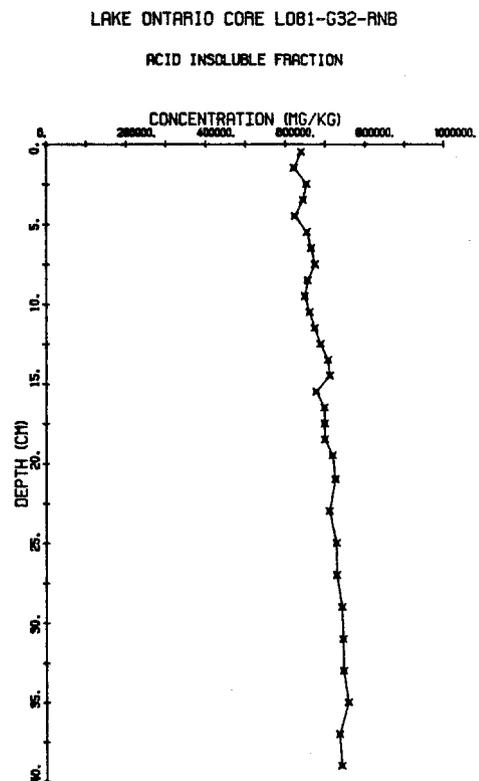
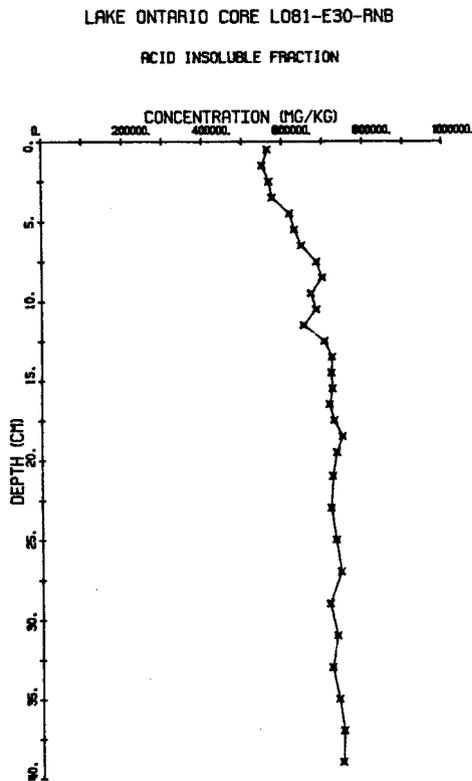


FIGURE 37.--Distribution of acid insoluble fraction and manganese in the Lake Ontario cores. High near-surface manganese concentrations result from a cycle of subsurface dissolution, diffusion, and surface reprecipitation. (Data of K. Johansen and R. Rossmann.)

8.3 Selected Metal Contaminants

The vertical distributions of several trace elements (chromium, copper, mercury, lead, zinc, antimony, and bismuth) measured in the Lake Ontario cores are very similar. Each element reaches a maximum concentration at 3 to 7 cm below the sediment-water interface and then decreases more or less exponentially to a constant concentration at greater depths in the cores. Data from the Great Lakes (Kemp and Thomas, 1976; Kemp *et al.*, 1976; Edgington and Robbins, 1976; Robbins, 1980) and elsewhere (Creclius and Piper, 1973; Hamilton-Taylor, 1979), indicate that elevated concentrations of these elements (except previously unreported bismuth) in surface and near-surface sediments, as compared to deep sections in the cores, are anthropogenically derived.

The vertical distributions of lead (figure 38) illustrate the relationship between anthropogenic sources and deposition in the lake. Because geochemical evidence indicates that lead will be relatively immobile in these sediments, the shape of the observed profiles should be the result of lake processes and the history of lead emission within the Great Lakes region (Robbins, 1980). In contrast to lead profiles in earlier (1971-73) cores from Lake Ontario in which the lead concentration peaked at the sediment-water interface (Farmer, 1978), the lead concentrations in cores E30 and G32 increase with depth to a subsurface maximum before decreasing to pre-cultural concentrations. In both cores, the lower lead concentrations in the upper few cm of sediment may reflect declining lead use in the Great Lakes region.

A correspondence between lead emissions and lead profiles can be illustrated quantitatively by independent determination of the loading of lead to the lake. This approach was first taken by Edgington and Robbins (1976) who constructed the historical loading of anthropogenic lead to Lake Michigan from regional records of coal and gasoline consumption. These two sources constitute the major environmental burden of lead. As the residence time of lead in the waters of the lakes is expected to be short (roughly 1 year), profiles of lead should be congruent with the historical loading (source function). Edgington and Robbins showed that this is true within limits imposed by sediment mixing. The Lake Ontario cores provide a significant continuation of the approach since, in the decade since Edgington and Robbins analyzed the Lake Michigan cores (collected in 1972), there has been a substantial reduction in the amount of atmospheric lead produced. This reduction should be apparent in areas of the Great Lakes where sediments accumulate rapidly and provide good time resolution. To construct the source function, a piece was tacked on to the Edgington-Robbins source function to extend it from 1972 through 1981, using currently available information on lead emissions and their reduction in gasoline combustion (Shelton, 1982; Anonymous, 1982). The results of using this source function in the steady-state mixing model with the sedimentation parameter fixed from lead-210 are shown in figure 38 as the dashed lines. The excellent quality of the fits supports the validity of the approach, suggesting a common time-dependent lead flux to the lake and a very limited mobility of lead in the sediments. The model results (and data) indicate that the average lead flux in Lake Ontario increased 680 percent from the early 1800s to the time of maximum lead usage in the mid-1970s.

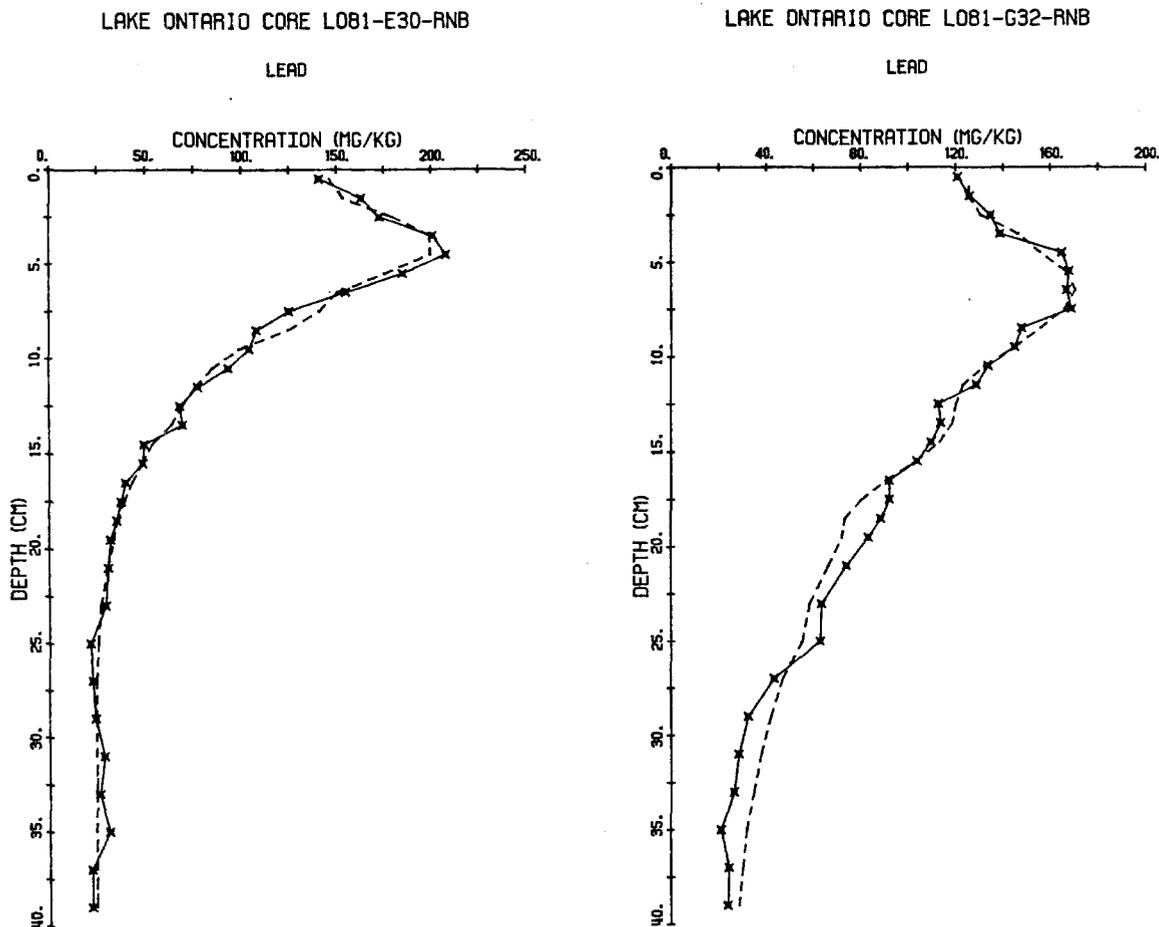


FIGURE 38.--Vertical distribution of stable lead in the Lake Ontario cores. The solid lines connect data points, while the dashed lines are the distributions predicted on the basis of lead atmospheric emissions inventories and the steady-state mixing model. The sedimentation rate is fixed in each case by the lead-210 data. Recent decreases in the use of leaded gasoline are reflected both in the emissions inventory and in sediment lead profiles. The excellent quality of the model fits encourages use of refined models to treat distributions of contaminants with more poorly known loadings and more complex sedimentary behavior. (Data of R. Rossmann/K. Johansen; model of J. Robbins.)

In contrast with lead, the time-dependence of the loading of mercury to the lakes is poorly known, and may involve significant local sources. The self-consistency of the assumption that profiles in the two Lake Ontario cores reflect a common flux time dependence may still be quantitatively illustrated. Because the sedimentation rate is comparatively high in core G32, the mercury profile in this core is taken as the source function (using lead-210 data). Given this source function, the steady-state mixing model predicts the distribution shown in figure 39 as the dashed line for core E30. The agreement is extremely good and suggests 1) a common time-dependent flux, and 2) limited post-depositional mobility of mercury. Note that the double peak observed in

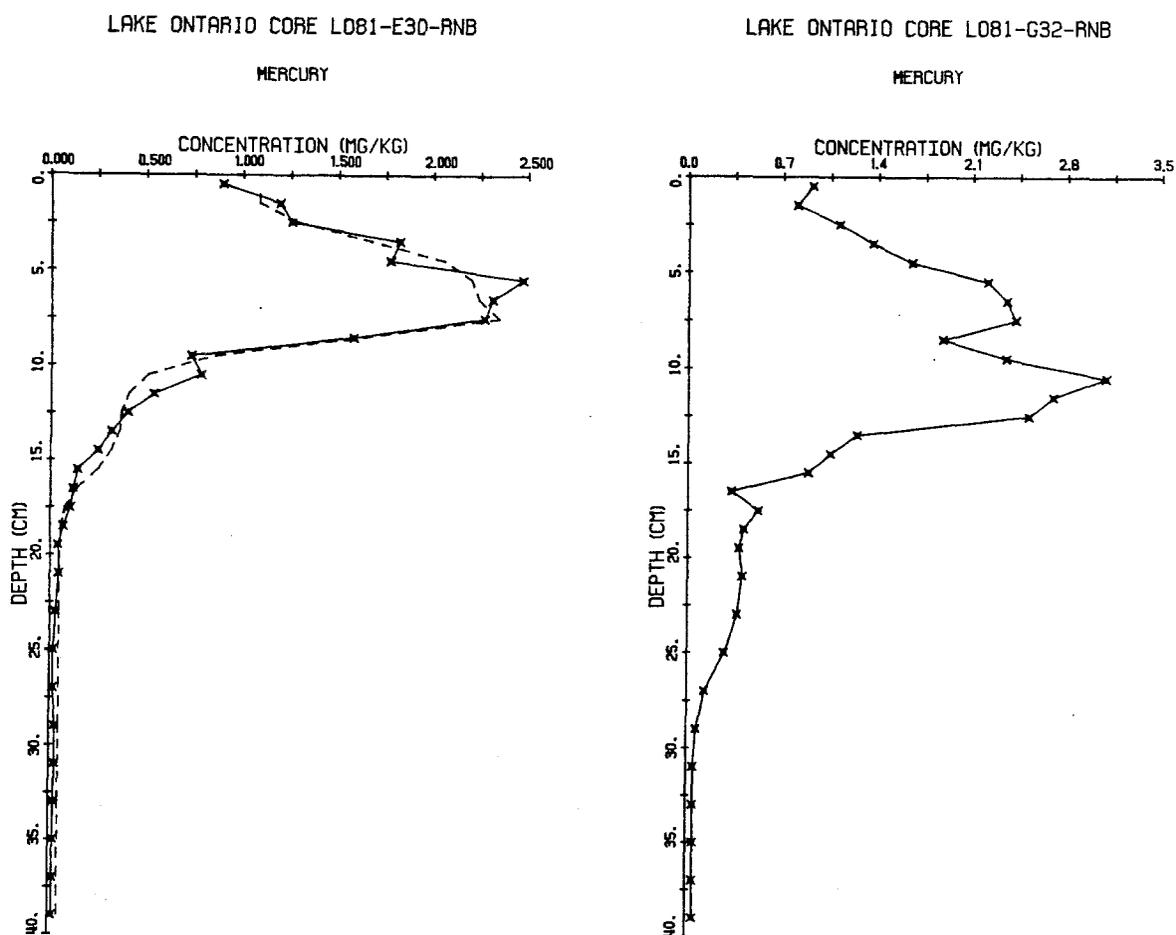


FIGURE 39.--Vertical distribution of mercury in the two Lake Ontario cores. As the flux to this area is not known, it is inferred from the high sedimentation core (G32), assuming no remobilization. The dashed line in the left panel is the flux expected in core E30 using that from G32. The agreement with experimental results implies limited mobility of mercury in these sediments. (Data of R. Rossmann/K. Johansen; model of J. Robbins.)

core G32 is not predicted to occur in core E30. As the sedimentation rate is considerably smaller in core E30, a given sediment section averages concentrations over a greater number of years. This loss of resolution is predicted by the model, which computes profiles by averaging theoretical concentrations over interval thicknesses.

An important early result of this study has been the discovery of a maximum in the distribution of amorphous silicon at depths corresponding to about 1840 A.D. in the Lake Ontario core E-30 (figure 40). Amorphous silicon in sediments is considered to be largely of biogenic origin, resulting from the deposition of diatoms and their remains. The 1840 maximum is interpreted as due to a major increase in the rate of diatom production in Lake Ontario study just after the turn of the century (~1800). The diatom "explosion" is

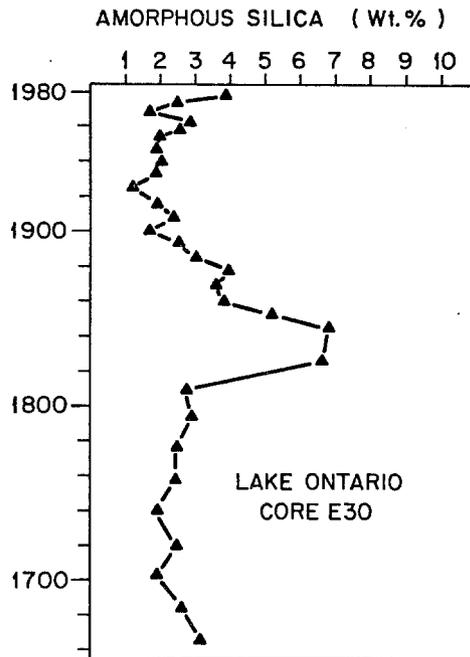


FIGURE 40.--Vertical distribution of amorphous (biogenic) silica in Lake Ontario core E30. The broad subsurface maximum is interpreted as due to early eutrophication of the lake as a result of forest clearance in the mid-1800s. Associated increase in phosphorus loading is thought to have accelerated diatom production, which eventually cleared much available silicon from the lake water. (Data of C. Schelske.)

conjectured by C. Schelske to have been set off by increased loads of phosphorus to the lake as a result of forest clearance activities. Post-1840 decline in silicon deposition should correspond to establishment of silicon depletion of Lake Ontario waters. Further evidence for the early eutrophication of Lake Ontario is being sought by W. S. Gardner in the distribution of phosphorus forms in this core. The idea of early eutrophication of Lakes Erie and Ontario is not entirely new as several others have chronicled the changes in plankton species in these lakes based on dated cores.

The distribution of mirex and total PCBs are shown in figure 41 for core G32. The dashed lines in each case are distributions computed using the steady-state mixing model and annual U.S. production figures for the source function. In the case of mirex there may be a strong regional source. Apparently a major quantity of the compound was introduced into a tributary to western Lake Ontario and this pulse reached the mouth around 1963. Shown in figure 41 as the solid line is the distribution expected to result from a slug of mirex deposited in 1970. There is roughly a 7-year difference between the optional model date and the estimated time of introduction. The difference is worth following as it may be important for understanding in-lake processes. Some explanations worth considering include: predominance of other more

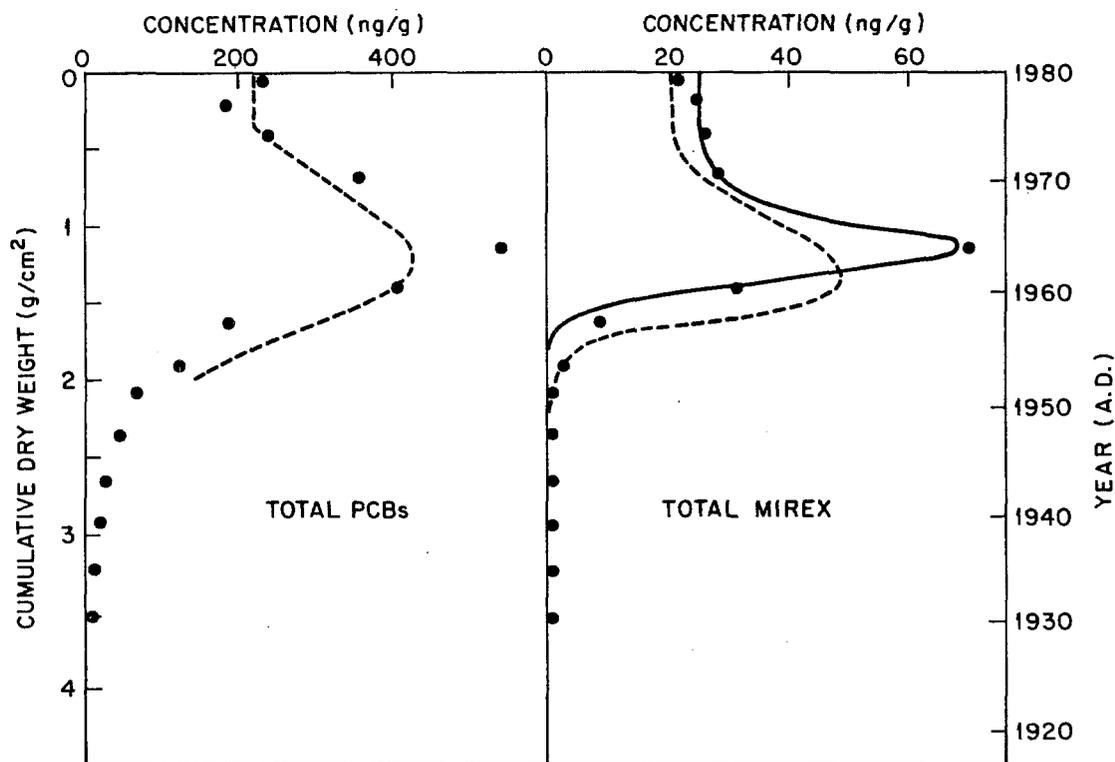


FIGURE 41.--Distribution of mirex and total PCBs in the Lake Ontario cores. The dashed line in each case is the distribution predicted from total sales figures for the compounds. The solid curve for mirex is the distribution expected for a pulse entering the lake around 1970. As the PCBs show sediment degradation rates or mobility that depend on isomeric composition, any relation between sediment profiles and production figures must be considered fortuitous. Distribution of PCBs will ultimately be treated in terms of specific isomers. (Data of S. Eisenreich; model of J. Robbins.)

distributed sources, delay in appearance of signal at the offshore location, and processes of external integration of the signal as a competitor to local integration (mixing).

In the case of the PCBs, little relation is expected between annual production numbers and profiles. Distributions of individual isomers generally have an appearance similar to the total PCB profile, but ratios of specific isomers to total PCBs group systematically. The four chlorinated isomers generally have ratios that decrease less with increasing sediment depth than do the five chlorinated isomers. Similarly, the six chlorinated isomers decrease more rapidly than their five chlorinated counterparts. This behavior is interpreted by S. Eisenreich as due to a higher post-depositional mobility of the lower chlorinated species. Evidently, modeling the behavior of these compounds in sediments will require the use of diffusion/advection models with isomer-dependent parameter values.

8.4 Directions

Next spring, a set of cores will be collected from suitable locations in Lake Superior. This sampling will complete the five-lake survey of high sedimentation areas.

Radiometric, metal, and organic contaminant analysis of cores will continue with widening participation of individuals with skills critical to the study.

Modeling efforts at GLERL will be devoted to the development of sediment bioturbation equations that include the effects of solids dispersion and advection and are appropriately coupled to solution phases. Improvements will be made in the definition of source functions, where possible, and in estimates of the relative importance of nonlocal versus local sources. Sediment profiles will be predicted on the basis of coupled whole lake models that take account of the losses through decay and degradation as well as integrative processes occurring in the water column prior to deposition.

Uncertainty in the estimate of the sedimentation rate is primarily due to the uncertainty in estimating the activity of supported lead-210.

9. ROLE OF BENTHIC INVERTEBRATES IN THE FATE OF POLLUTANTS IN THE GREAT LAKES

PCBs, chlorinated pesticides, and PAHs are examples of pollutants of major concern in the Great Lakes (Delfino, 1979). These compounds are readily sorbed to particles and sediments, due to their limited water solubility. As a result, benthic organisms will be exposed to high sediment concentrations of pollutants in addition to the dissolved component. Under these conditions, benthic organisms can potentially influence three major xenobiotic fate processes in the aquatic ecosystem: xenobiotic distribution within the sediments, remobilization out of the sediments, and biodegradation. The above processes in combination with the previously described physical fate processes serve to determine the bioavailability and ultimately the effect of xenobiotics on the ecosystem.

Redistribution of xenobiotics within the sediment by benthic organisms can be divided into two major classes, physical reworking of the sediments resulting from bulk sediment movement and differential movement through ingestion, and elimination of selected sediment particles resulting in zonal redistribution of some materials (Robbins and Edgington, 1975; Robbins *et al.*, 1977; White and Klahr, 1982). Most of these effects have been attributed to the oligochaetes; however, *Pontoporeia hoyi* and other benthic organisms are thought to contribute to the overall mixing of sediments. The result of this redistribution is predicted to extend the time for complete burial and thus prolong the bioavailability of xenobiotics.

As a result of sorption, the water concentrations are very low; therefore, the appearance of these pollutants in the food chain must result, at least in part, from a remobilization out of the sediments. This

remobilization may result from both physical and biological processes. The biological processes involve absorption of xenobiotics from contaminated sediment and pore water and elimination into the water column or passage of the xenobiotic up the food chain. This remobilization by benthos may be the major source for some components in the higher trophic levels of the food chain (Weiniger, 1978; Jarvineu *et al.*, 1977).

Lastly, biological degradation provides a potential route for the loss of xenobiotics from the system. Benthic organisms such as chironomids and polychaetes have the capability to biotransform xenobiotics (Ernst *et al.*, 1977; Laversee *et al.*, 1982). Other benthos are expected to be able to biotransform as well and would contribute to the loss of xenobiotic from the system.

Little is known about the influence of the above processes either on the fate of xenobiotics or their accumulation in ecosystem components. Laboratory accumulation of pollutants from contaminated sediments has been examined for few marine species (Roesijadi *et al.*, 1978; Elder *et al.*, 1979, McLeese *et al.*, 1980) and for no freshwater species.

The studies reported attempt to examine the role of benthos in the fate of xenobiotics, in particular PAHs, using both laboratory and field experiments. Further, these studies attempt to examine the significance of the above-mentioned processes in xenobiotic fate and provide data for inclusion in a general overall fates model.

9.1 Laboratory Studies

The approach for these studies was to employ pharmacokinetic experiments similar to those of Neely (1979) and Laversee *et al.* (1982) and focus on the use of carbon-14-labeled anthracene as a representative PAH. These studies examined the uptake, depuration, and biotransformation of anthracene in two amphipods, *Pontoporeia hoyi*, the most abundant invertebrate in the Great Lakes, and *Hyaella azteca*, a warmer water form. The effects of environmental factors such as temperature, pollutant concentration, and season on kinetics were examined for *P. hoyi*, while the influence of sediment on kinetics was followed for *H. azteca*.

Pontoporeia hoyi were collected approximately 3 miles south of Grand Haven, Mich., (figure 21) at a depth of 23 to 25 m, using a PONAR grab sampler. The animals were gently removed from the sediment and placed in plastic bags filled with water. They were transported on ice to the laboratory (transport time was 4 to 5 h) and held in incubators in shallow aquaria containing 3 to 4 cm of Lake Michigan sediment (as a food source) and approximately 10 cm of Lake Michigan water at 4°C. The incubators were illuminated with red darkroom lights to help keep the *P. hoyi* in the sediments (Donner and Lindstrom, 1980). Low background concentrations of some PAHs (<0.01 μmole^{-1} maximum concentration) were found in *P. hoyi* collected at the same site as the animals used for study (see Field Studies). Anthracene was not detected and it was assumed that the other PAHs would not interfere with the anthracene kinetics because of their low concentrations.

Hyalella azteca were dip-netted from ponds at the Botanical Gardens of The University of Michigan, Ann Arbor, Michigan, and transported to the laboratory in pond water. Animals were held at 24° to 25°C on a 12:12 h light:dark cycle in shallow aquaria containing algae and macrophytes collected at the same time. Water and sediments for the experiments were collected from Sugarloaf Lake, Washtenaw County, Michigan. Those sediments contained 5 percent organic carbon on a dry weight basis (method of Menzel and Vaccaro, 1964).

Anthracene (9-¹⁴C, specific activity 3.3 mCi mmole⁻¹, lot #770824, California Bionuclear Corporation) was dissolved in acetone and radiopurity determined using thin layer chromatography (TLC) on silica gel plates (E. Merck, 250 μm coating) with hexane:benzene (4:1 v:v) as the solvent system. Anthracene was 99.6 ± 0.6 percent pure and was used as purchased. All preparative and analytical procedures were performed under gold fluorescent light (λ > 500 nm) to minimize the photodegradation of anthracene.

Lake Michigan water for *P. hoyi* or Sugarloaf Lake water for *H. azteca* was filtered through 3-μm membrane filters (Gelman, AN-3000), labeled in bulk (5 L) and dispensed to replicate test chambers after 1- to 2-h equilibration. Acetone carrier (<20 μg mL⁻¹), in addition to the experimental pollutant, was added to the water. Since acetone had only marginal effects on the uptake of nonpolar compounds after 52 days of exposure (Mac and Seelye, 1981), its influence on anthracene kinetics should be negligible under the experimental conditions. All studies were done at or below the reported solubility of the anthracene. Actual anthracene water concentrations were determined from calculations based on measured DPM mL⁻¹ and known specific activity.

Uptake rates were determined in quadruplicate in temperature-controlled flow-through chambers containing 0.2 L of water, 30 to 60 animals, and one of three physical environments: no substratum, sand substratum, or Sugarloaf Lake sediment substratum for *H. azteca* and with no substratum for *P. hoyi*. Labeled water flowing at approximately 100 mL h⁻¹ maintained constant toxicant-water concentration during the study. The temperature for the *H. azteca* studies ranged from 21° to 25°C, with less than 0.5°C variation for each study.

For *P. hoyi*, the experiments were run at 4°C under low level red light to minimize response to light (Donner and Lindstrom, 1980). For studies with *P. hoyi* above 4°C, the animals were acclimated gradually by elevating the aquarium temperature 1°C per day and holding the animals at the study temperature for 5 days prior to experimental use.

Depuration experiments were performed by transferring 10 to 20 labeled animals into flow-through chambers or 6-L glass aquaria containing clean water (no added anthracene). The flow-through depuration experiments lasted 8 h, with two to three animals removed at 0.5, 1, 2, 4, and 8 h, weighed; and frozen for later analysis. The flow rate was approximately 100 mL h⁻¹ of clean water to wash out excreted metabolites. Depuration studies performed in 6-L aquaria under static conditions lasted approximately 1 week. Animals were transferred to aquaria containing both clean water and sediment. Three replicates of two animals each were removed at approximately 1.5-, 3-, and 5-day intervals (exact times were used for calculations).

All animals were analyzed for carbon-14 by the Mahin and Lofberg (1966) procedure in a Beckman Model LS-150 Liquid Scintillation Counter using 3a70b (Research Products International) scintillation cocktail. The external standards ratio method was used and samples were corrected for background and quench.

Biotransformation rates were determined for animals removed after 8-h exposure to anthracene. The animals were kept frozen (-20°C) prior to analysis. Ten to sixty *H. azteca* or *P. hoyi* were extracted with 2 x 20 mL ethylacetate:acetone (4:1 v:v) and 1 x 20 mL cyclohexane. The extracts were combined and filtered through Whatman No. 1 filter paper, reduced in volume by a combination of rotary flash evaporation and evaporation under a stream of nitrogen to approximately 500 µL, and analyzed by TLC using hexane:benzene (9:1 v:v) and cyclohexane as solvents. Developed plates were divided into a total of four sections corresponding to anthracene and three other sections, including the origin. The silica gel from each section was scraped from the TLC plate and carbon-14 activity determined. The extracted animal carcasses were also assayed for carbon-14 activity by the same method as the whole animals. Total metabolite was determined as the sum of all non-anthracene carbon-14 on the TLC plate plus unextractable carbon-14 residue.

Water samples (500 mL) removed at the end of the uptake phase of experiments were extracted with 3 x 100 mL hexane. (The extraction efficiency, based on measurements of carbon-14 activity remaining after extraction, was greater than 99 percent.) The hexane extracts were combined and dried over anhydrous Na₂SO₄, reduced in volume, and analyzed by TLC as previously described; carbon-14 activity was found to be 97.4 percent anthracene, indicating that its degradation was negligible in the water after 8 h.

Depuration rate data were fit to a first-order decay model:

$$C_a(t) = C_a(0)e^{-K_2 t} \quad (26)$$

where $C_a(0)$ = initial concentration in animal (nmole (g wet wt)⁻¹)

K_2 = depuration rate constant (h⁻¹)

t = time (h)

Assuming constant uptake and depuration rate constants and water as the only source of toxicant, the concentration of anthracene in the animal (C_a) during the uptake phase of the experiment should be described by the following two-compartment model:

$$\frac{dC_a}{dt} = K_1 C_w - K_2 C_a(t) \quad (27)$$

where K_1 = uptake rate constant ($\text{mL}(\text{g animal wet weight})^{-1} \text{h}^{-1}$)

K_2 = depuration rate constant (h^{-1})

C_w = water concentration (nmol mL^{-1})

t = time (h)

C_a = concentration in animals [$\text{nmol}(\text{g animal wet weight})^{-1}$]

If C_w is held constant, as in our experiments, the equation has the following solution:

$$C_a(t) = \frac{K_1}{K_2} C_w (1 - e^{-K_2 t}) \quad (28)$$

Time-course measurements of C_a in the absence of sediment or with sand substratum (sand does not absorb significant amounts of anthracene) were analyzed with this model; K_1 and K_2 were estimated by nonlinear, least-squares regression of C_a on time. Alternatively, K_1 can be estimated using $C_a(t)$ and independently determined K_2 by averaging:

$$K_1 = \frac{C_a(t)K_2}{C_w(1 - e^{-K_2 t})} \quad (29)$$

for all corresponding $C_a(t)$ and t during each experiment.

A further simplification can be employed where K_2 is very small.

$$C_a(t) = K_1 C_w t \quad (30)$$

Therefore, K can be estimated from the slope of the line resulting from a plot of C_a versus t .

The two-compartment model is inappropriate for experiments with natural sediment because it does not allow for transfer of toxicants within that compartment. Allowing for the transfer of anthracene from sediment to animal (K_3) and varying the concentration of sediment-associated anthracene, $F(t)$, since the sediment is originally uncontaminated, the following is an appropriate three-compartment model.

$$\frac{dC_a}{dt} = K_1 C_w - K_2 C_a(t) + K_3 F(t) \quad (31)$$

Because this equation has no simple solution and because we have independent estimates of K_2 in the presence of natural sediment, time-course measurements of C_a and estimates of $F(t)$ were fit to the following model:

$$\left(\frac{\Delta C}{\Delta t} + K_2 C_a(t)\right) = K_1 C_w + K_3 F(t) \quad (32)$$

with linear, least-squares regression. Derivatives ($\Delta C_a/\Delta t$) were estimated directly from data collected at times 0, 0.5, 1, 2, 4, and 8 h. $C_a(t)$ corresponding to each derivative was calculated as the average value between measurements, C_w was held constant, and $F(t)$ was assumed to vary according to the sorption kinetics of anthracene on high organic sediment (Giesy *et al.*, 1982) (organic carbon content 20 percent; J. Haddock, Savannah River Ecology Laboratory, pers. comm.).

Analyses of the two-part model for experiments with sand or no substratum and of the three-compartment model for experiments with natural sediment provide independent estimates of uptake constants from water (K_1). These analyses also provide an estimate of uptake kinetics of sediment-associated anthracene (K_3).

The uptake rate constants for anthracene were determined for *P. hoyi* using the one-compartment model. This model assumes that elimination is unimportant over the time period for which the uptake rate constant is calculated and that the water concentration remains constant. The water concentration had a relative standard deviation of 8.4 ± 3 percent ($n = 13$) for anthracene. The curves for determination of the rate constants were all linear ($r^2 > 0.9$). Elimination rates were very slow and less than 10 percent of one elimination half life occurred over the course of the uptake exposure. Therefore, the model assumptions were not violated.

The uptake rate constant at 4°C ranged from 83 ± 15 mL(g animal wet weight)⁻¹ h⁻¹ (hereafter mL g⁻¹ h⁻¹) to 141 ± 10 mL g⁻¹ h⁻¹ ($\bar{X} \pm 1SD$) over a concentration range of 4.6 ± 0.2 ng mL⁻¹ to 16.9 ± 1.4 ng mL⁻¹. The uptake rate constant for *P. hoyi* was independent of anthracene concentration, an assumption often made but rarely tested.

Although *P. hoyi* were held in the laboratory for 1 to 96 days, no correlation between time held and uptake rate constant was found. In contrast, changes in the physiological state of aquatic organisms brought about by removing animals from their natural environment and holding them in the laboratory have resulted in an alteration of toxicokinetics (Landrum and Crosby, 1981a,b).

The effect of temperature on poikilotherm physiology and biochemistry is of major importance. It could be expected that *P. hoyi* would be exposed to a maximum range of 0 to 23°C for the Great Lakes, the extremes occurring at the surface and nearshore areas (Pinsak, 1976). Laboratory studies, however, indicate that the extreme temperature limit for *P. hoyi* for 24 h is 12°C (Smith, 1972) to 14.5°C (Thienemann, 1928). Therefore, the uptake was

followed over the temperature range 4° to 15°C. The anthracene uptake rate constant increased with temperature (figure 42).

Additionally, the uptake rate constant for *P. hoyi* appeared to show some temporal variation. It appeared to increase to a plateau by late summer and early fall (figure 43).

The elimination of anthracene by *P. hoyi* in the presence of sediment substratum was slow and fit a first-order elimination curve of equation (1)

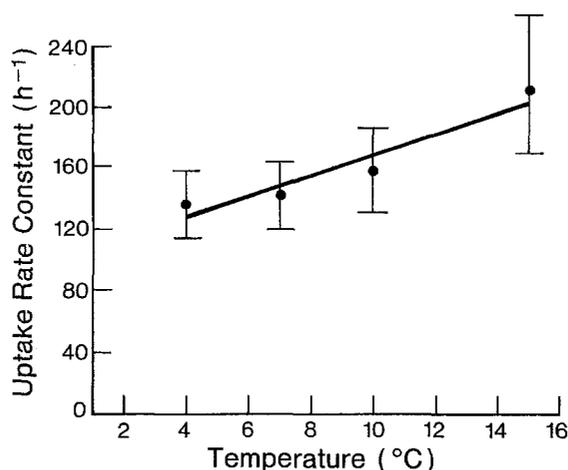


FIGURE 42.--Temperature variation for anthracene uptake rate constants by *Pontoporeia hoyi* ($n = 4$).

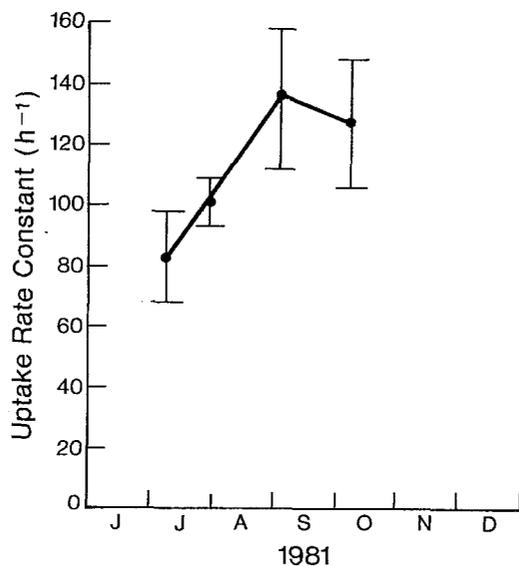


FIGURE 43.--Temporal variation of anthracene uptake rate constants for *Pontoporeia hoyi* ($n = 4$, experimental temperature 4°C).

($r^2 > 0.9$). The depuration rate ranged from 0.004 h^{-1} to 0.00 h^{-1} ($t^{1/2}$ 77–173 h) at 4°C and had an apparent maximum at 7°C (figure 44). This coincides with the maximum temperature reported for successful reproduction in the laboratory (Smith, 1972). Depuration was also examined at 15°C ; however, the data were deemed unsuitable because of high mortality. No depuration occurred with *P. hoyi* in the flow-through system containing no sediment substratum.

9.2 Biotransformation and Bioconcentration

The bioconcentration factor (BCF) for compounds can be predicted from the ratio of the uptake and depuration rate constants, assuming biotransformation is unimportant (Leversee *et al.*, 1982). The biotransformation of anthracene by *P. hoyi* was undetectable even after 48 h exposure. BCF predicted from the 14°C kinetics averaged 16,800 ($n = 2$) for anthracene at 4°C . The BCF reached a minimum at 7°C , reflecting the maximum depuration rate (figure 45).

Rate constants for uptake of anthracene from water as determined with the two-compartment model for *H. azteca* exposed to no substratum or to a sand substratum are statistically indistinguishable, but are higher than those for animals exposed to natural sediment (table 17). However, rate constants for uptake from water for animals exposed in the presence of natural sediment, determined with the three-compartment model, are not statistically different from those determined with other substrates (table 17). The rate constants for anthracene uptake from water are within the range of values previously determined for other benthic and pelagic invertebrates (Gerould *et al.*, 1982; Herbes and Risi, 1978).

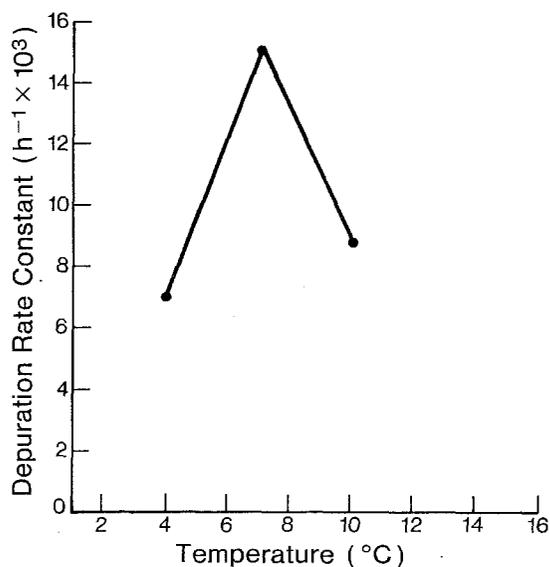


FIGURE 44.--Temperature variation of the depuration rate constants for anthracene by *Pontoporeia hoyi*.

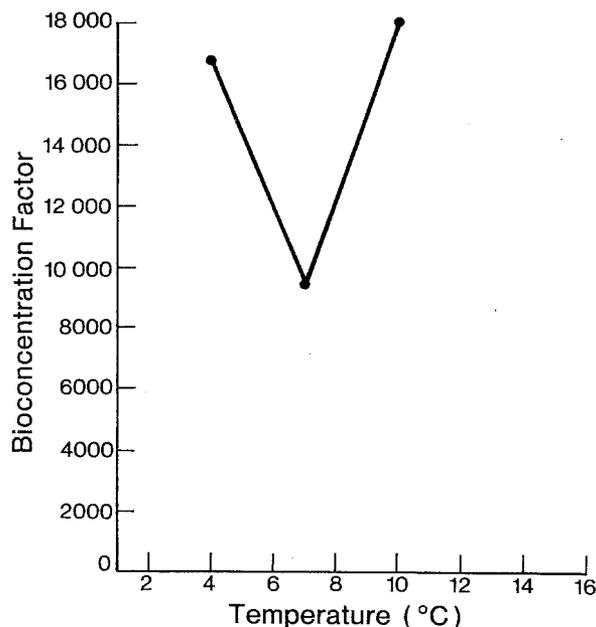


FIGURE 45.--Temperature variation of the predicted bioconcentration factor for anthracene by *Pontoporeia hoyi*.

The rate constant for uptake of sediment-associated anthracene in the presence of natural sediment is 19 ± 5 g dry sediment (g animal wet weight)⁻¹ h⁻¹. The rate constant estimate is dependent on the values used for $F(t)$. These values are based on sorption-desorption kinetics of a sediment of different composition. [Although both were high in organic carbon, the sediment from Sugarloaf Lake was 5 percent organic carbon, while that used by Giesy *et al.* (1982) was 20 percent organic carbon.] Thus the rate constant can be considered to be only of order of magnitude accuracy.

H. azteca in the presence of natural sediment eliminated carbon-14-labeled compounds significantly faster ($P < 0.005$) than those in the presence of no substratum or sand substratum (table 17). Presence of a substratum other than pure sand has previously been shown to increase the elimination rate of PAH (Gérould *et al.*, 1982; Leversee *et al.*, 1982). Depuration rate constants for *H. azteca* estimated from the two-compartment model, however, suggest that depuration is slower in the presence of organic sediments. This disagreement between independently determined depuration constants and those estimated via the two-compartment model has not previously been observed and is attributable to bias introduced by violating the assumptions of the two-compartment model. That is, by ignoring the large contribution of anthracene from sediment, estimated depuration rates have to be artificially lower to compensate for the increased body burden.

H. azteca biotransformed anthracene slowly but measurably (table 18). The rate is much greater than that found for the coldwater amphipod *P. hoyi* and

TABLE 17.--Uptake and depuration rate constants for *Hyalella azteca*
(from Landrum and Scavia, 1982)

| Experiment | Two-Compartment Model | | | Three-Compartment Model | | | Experimental Depuration h ⁻¹ |
|------------------------|---|--|---|---|--|-------------------------------|---|
| | Water Uptake (K ₁) mL(g wet weight) ⁻¹ h ⁻¹ | Depuration (K ₂) h ⁻¹ | (K ₁) mL(g wet weight) ⁻¹ h ⁻¹ | Water Uptake (K ₁) mL(g wet weight) ⁻¹ h ⁻¹ | Sediment Uptake (K ₃) g dry sediment (g wet weight) ⁻¹ h ⁻¹ | Depuration h ⁻¹ | |
| No Substratum* | 303 ± 45 | 0.57 ± 0.7 | 224 ± 71 | --- | --- | --- | 0.22 |
| | 212 ± 6 | 0.15 ± 0.1 | 193 ± 14 | --- | --- | --- | 0.09 |
| | 270 ± 48 | 0.44 ± 0.1 | 227 ± 54 | --- | --- | --- | 0.24 |
| | 227 ± 35 | 0.22 ± 0.07 | 210 ± 63 | --- | --- | --- | 0.06 |
| | 432 ± 85 | 0.52 ± 0.14 | 311 ± 45 | --- | --- | --- | 0.23 |
| 342 ± 85 | 0.43 ± 0.15 | 245 ± 19 | --- | --- | --- | 0.10 | |
| Sand Substratum* | 213 ± 24 | 0.21 ± 0.43 | 191 ± 65 | --- | --- | --- | 0.12 |
| | 250 ± 54 | 0.38 ± 0.12 | 215 ± 39 | --- | --- | --- | 0.25 |
| Sediment Substratum* | 175 ± 20 | 0.16 ± 0.04 | --- | 226 ± 16 | 25 ± 4 | --- | 0.56 |
| | 187 ± 33 | 0.31 ± 0.88 | --- | 250 ± 42 | 10 ± 10 | --- | 0.63 |
| | 119 ± 32 | 0.10 ± 0.09 | --- | 187 ± 37 | 13 ± 9 | --- | 0.48 |
| | 88 ± 26 | -0.03 ± 0.08 | --- | 147 ± 13 | 27 ± 12 | --- | 0.23 |
| No Substratum + Sand** | 218 ± 27 | 0.37 ± 0.06 | 227 ± 14 | --- | --- | --- | 0.16 ± 0.03 |
| Sediment Substratum** | 142 ± 23 | 0.15 ± 0.06 | --- | 202 ± 23 | 19 ± 5 | --- | 0.48 ± 0.09 |

*Mean ± standard deviation of estimate from regression.

**Mean ± standard error of the individual estimates.

TABLE 18.---Biotransformation of anthracene by *Hyalella azteca*
(from Landrum and Scavia, 1982)

| Experiment | Water Concentration ng mL ⁻¹ | Biotransformation Rate at 8 h nmole g ⁻¹ dry wt h ⁻¹ | Biotransformation Rate Constant h ⁻¹ | Ratio Bound to Extractable Metabolite |
|-------------------------|---|--|---|---|
| No Substratum | 7.65-8.7 | 2.2 ± 0.5* (n = 6) | 0.024 ± 0.005* (n = 6) | 0.72 ± 0.08* (n = 6) |
| Sand Substratum | 7.65 | 3.0 ± 0.08 (n = 2) | 0.030 ± 0.007 (n = 2) | 0.75 ± 0.13 (n = 2) |
| Sediment Substratum | 6.1-7.6 | 1.0 ± 0.15 (n = 4) | 0.014 ± 0.005 (n = 4) | 0.42 ± 0.06 (n = 4) |
| No Substratum Plus Sand | 7.65-8.7 | 2.4 ± 0.5 (n = 8) | 0.025 ± 0.005 (n = 8) | 0.72 ± 0.06 (n = 8) |

* $\bar{x} \pm SD$

much lower than that found for the midge larvae *Chironomus riparius* (Gerould *et al.*, 1982). The biotransformation rate constant at 8 h was determined by dividing the biotransformation rate, based on body residue, by the concentration of the parent compound at 8 h. This constant was significantly smaller ($P < 0.005$) for animals in the presence of natural sediment as compared with animals in the presence of sand substratum or no substratum.

The ratio of nonextractable, "bound" metabolites to extractable metabolites is higher (0.72 ± 0.06) for the no-sediment and sand-substratum experiments than for the natural-sediment experiments (0.42 ± 0.05 ; $P < 0.01$). Higher fractions of nonextractable metabolite imply greater binding of metabolites by the organism. The binding of PAH metabolites to macromolecules, in particular DNA and RNA, is the mechanism by which these compounds exert their chronic toxic effects and has been clearly demonstrated for some aquatic species (Varanasi *et al.*, 1981).

The BCF can be estimated from the ratio of the rate constants for uptake from water and for depuration. BCF based on total carbon-14 will be an overestimate if biotransformation is not accounted for (Leversee *et al.*, 1982). For example, the BCF for the no-substratum and sand substratum experiments was estimated to be $2,089 \pm 366$ without biotransformation correction. Correcting the total carbon-14 body burden for the fraction of metabolite at 8 h reduces the BCF to $1,800 \pm 329$. The BCF is higher than that found for anthracene with *Chironomus riparius* (132 ± 39 ; Gerould *et al.*, 1982) and *Daphnia pulex* (760; Herbes and Risi, 1978) determined from similar experiments. However, the BCF is much lower than that estimated for the coldwater amphipod *P. hoyi* (16,800).

BCFs calculated as above are inappropriate for animals in the presence of natural sediment because sediment-associated toxicant contributes to total uptake. For this case, we use the ratio of estimates of steady-state body burden to source concentration. The former was estimated by the steady-state solution of the three-compartment model with parameter estimates from regression (table 17). The steady-state value of $F [1,852 \text{ mg (g dry weight)}^{-1}]$ was calculated from partition characteristics of a high organic sediment (Giesy *et al.*, 1982) and our water concentration. The animal body burden at steady state divided by the water concentration is $10,985 \pm 2,368$. When corrected for biotransformation, the BCF estimate becomes $9,096 \pm 1,960$. This water-concentration based BCF estimate is, however, misleading because, in our experiments, the sediment contributes approximately 77 percent of the body burden at steady state for *H. azteca*. The bioaccumulation factor calculated from the ratio of the steady-state body burden (wet weight basis) to the amount of anthracene in the sediment (dry weight basis) was 41 ± 10 . If one assumes that anthracene is associated only with the organic portion of the sediment (5 percent by weight), then the bioaccumulation factor becomes 2.4 ± 0.4 .

The kinetics of anthracene in *P. hoyi* are different from those of *H. azteca* and other aquatic animals (table 19). The major difference is the very slow depuration rate. This may result from the low temperatures of the experiment; however, the maximum depuration rate constant at 7°C is still approximately an order of magnitude slower than that of chironomids at 16°C (Gerould *et al.*, 1982).

TABLE 19.--Anthracene uptake and depuration rate constants for various aquatic species

| | <u>Uptake Rate</u> | <u>Depuration</u> | Study Temperature |
|---|--|----------------------------------|----------------------|
| | Constants | Rate Constants | |
| | Anthracene (mL × g ⁻¹ h ⁻¹)* | Anthracene (h ⁻¹) | |
| Bluegill sunfish ¹ | 36 ± 3 | 0.04 ± 0.006 | 23° - 25°C |
| <i>Chironomus riparius</i> ² | 77 ± 21 | 0.215 ± 0.006 | 25°C |
| <i>Pontoporeia hoyi</i> | 118 ± 20 | 0.007 ± 0.003 | 4°C |
| <i>Daphnia pulex</i> ³ | 767 | 0.21 | 23°C |
| <i>Hyalella azteca</i> | 130 ± 41 | 0.16 ± 0.08 | 2° - 25°C |

¹Spacie *et al.* (1982).

³Herbes and Risi (1978).

²Gerould *et al.* (1982).

*mL (g wet weight)⁻¹ h⁻¹.

Enhancement of the depuration rate in the presence of a sediment or like substratum for benthic organisms appears to be an important feature. This difference in rates with the presence and absence of a substratum has also been observed in the elimination of PAH for other benthic organisms: *H. azteca* (see section on *H. azteca*) and *Chironomus riparius* (Gerould *et al.*, 1982; Leversee *et al.*, 1982). This likely reflects either enhanced activity because the animals are not stressed from lack of food and/or the partitioning of pollutant into the fecal material as it moves through the gut.

The increase in the uptake rate constant with temperature was similar to that found with the midge, *Chironomus riparius* (Gerould *et al.*, 1982). Unlike the midge, however, *P. hoyi* did not exhibit a change in uptake rate constant with a change in pollutant concentration (Gerould *et al.*, 1982).

P. hoyi did show an apparent change in uptake rate constant with season of the year. Such seasonal variation in kinetics has also been seen with other aquatic animals (Landrum and Crosby, 1981a,b; Dewaide, 1971). These changes may result from various reproductive, nutritional, and disease states that change with the season or from having been acclimated to different temperature, although the experiments were all done at 4°C.

Optimization of the ability of aquatic animals to handle xenobiotics with temperature has been shown with *Chironomus riparius* (Gerould *et al.*, 1982). The temperature optimum for *P. hoyi* appeared to be 7°C and reflected a minimum bioconcentration factor brought about by an enhanced depuration rate relative to the increased uptake rate. The apparent optimum temperature of 7°C also corresponds to the maximum temperature for keeping a reproductive culture in the laboratory (Smith, 1972).

The absence of measurable biotransformation was unexpected, since other crustaceans have been reported to biotransform PAH (Herbes and Risi, 1978; Leversee *et al.*, 1981; Sanborn and Malins, 1980). Failure to detect biotransformation may have been due, in part, to the low experimental temperature.

Uptake of anthracene from water by *H. azteca* was rapid, and steady state was achieved in 4 to 8 h (figure 46). In experiments with a natural sediment substratum, the kinetics were more complex. Initial uptake rates were controlled primarily by uptake from water; however, as the sediment became charged with anthracene, the kinetics were controlled additionally by sediment-associated uptake (figure 46). The sediment contribution at steady state was estimated to be 77 percent of the total body burden. This apparent excessive food-based source is unusual in that it has been observed only for DDT and PCB (Macek *et al.*, 1979; Weininger, 1978; Southworth *et al.*, 1979;

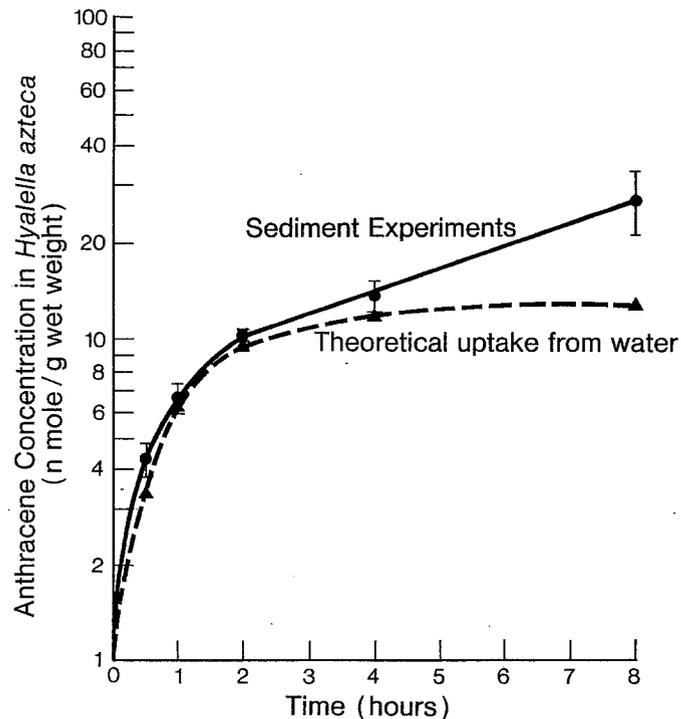


FIGURE 46.--Uptake of anthracene by *Hyalella azteca* in the presence of natural sediment. The theoretical curve for uptake from water employs rate constants from simultaneous experiments adjusted for the difference in the water concentration of anthracene caused by the sediment.

Teal, 1977; Chadwick and Brocksen, 1969; Hansen, 1980). More recently, benzo(a)pyrene and anthracene via food for *Daphnia* feeding on yeast.

The sediment-associated uptake rate constant is high [19 ± 5 g dry sediment (g animal wet weight) $^{-1}$ h $^{-1}$] and even if all the anthracene were in the organic portion of the sediment, the rate constant would imply that the animal processes 0.95 ± 0.4 g organic carbon (g animal wet weight) $^{-1}$ h $^{-1}$. These very high rates suggest that animals are obtaining the toxicant other than via ingested sediment or that the PAH is associated even more preferentially within the organic material and it is only that fraction that is being ingested by *H. azteca*. The latter may be likely since amphipods have food size cutoffs of about 30 μ m (Ankar, 1977) and the fine-grained material should be highly sorptive, with a large surface area to mass ratio and a high organic content. Additionally, uptake from pore water containing relatively high concentrations of compounds may also contribute to the high rate.

The presence of a natural sediment substratum not only increases rates of uptake and elimination (table 17), but also decreases the apparent biotransformation rate and "binding" of metabolite to macromolecules in the animal (table 18). The lower biotransformation rate estimate probably results from bias due to increased metabolite elimination in the presence of sediment. The rate was calculated as the micrograms of metabolite accumulated in the animal, divided by the duration of the experiment. (The rate constant simply normalizes this rate to the body burden of anthracene at the end of the experiment.) The increased carbon-14 elimination rate is probably due to increased elimination of metabolite because the relative pool size of bound metabolite decreased in the presence of natural sediment (table 18). Since elimination increased and apparent biotransformation decreased both by factors of 2.5 to 3.0, it is likely that the biotransformation rate determined in either sand substrate or no substrate is closer to the actual rate. Of course, even these are possibly underestimates due to elimination of metabolite.

Data presented here suggest that BCF, as usually calculated, is an inappropriate comparison for benthic organisms and will result in artificially elevated values because the body burden is achieved by uptake from both water and sediment. Bioaccumulation factors in relation to sediment concentrations may be a better measure of the overall magnification of the compound. In fact, our BCF calculated from dry sediment is similar to bioaccumulation factors for PAH in benthic organisms of Lake Erie. (See Field Studies.)

While natural sediment appears to increase both total uptake and elimination of anthracene for *H. azteca*, the net effect is an increased body burden. After our 8-h experiments, animals in the presence of natural sediment had body burdens more than twice those of animals without that sediment (figure 46). The effect is even more dramatic if the three-compartment model and constants in table 17 are used to extrapolate data from the sediment experiments to steady state. In that case, steady-state body burdens are increased by a factor of five in the presence of sediment. Benthic organisms are, therefore, apparently at greater risk from pollutants that sorb to sediments than are their free-swimming neighbors.

The differences in the kinetics of anthracene in the two amphipods are striking. The major differences are the slow elimination rate and the absence of biotransformation for *P. hoyi*. Since the uptake from water is similar (table 19), it is expected that the contribution from contaminated sediments would be of the same order of magnitude. As a result *P. hoyi* should have high body burdens of PAH due to high BCF and exposure to relatively high sediment concentration.

Therefore, *P. hoyi* may be a major food chain link for biomagnifying important pollutants by remobilizing pollutants from the sediments and concentrating pollutants from water. Studies of direct uptake from sediments remain to be done, however, to confirm the remobilization ability of *P. hoyi*. Additionally, the absence of biotransformation and high BCF may make *P. hoyi* particularly susceptible to even low levels of pollutants and may account for the absence of *P. hoyi* in polluted areas (Nalepa and Thomas, 1976). Lastly, since this organism is an important food chain animal in the Great Lakes (Parker, 1980; Mozley and Howmiller, 1977), the potential loss of animals from pollution and the potential to pass accumulated pollutants up the food chain may have a significant impact on the Great Lakes ecosystem.

9.3 Field Experiments

Since the laboratory experiments pointed toward high concentrations of PAH in *P. hoyi* and the concept that benthic organisms in general would be exposed to high concentrations of pollutants in the sediments, two field collections of benthic organisms and their corresponding sediments were undertaken to examine the relationship between sediment and organism concentrations. Worms, midges from Lake Erie, and *P. hoyi* from Lake Michigan were examined with their respective sediments for PAH.

The study site for the worms and midges (figure 47) was located in the western basin of Lake Erie, offshore from the Detroit Edison Monroe Power Plant in southeastern Michigan. The River Raisin, which loads Lake Erie with approximately 150,000 MT of suspended solids per year (Sullivan *et al.*, 1980), flows past the plant. Prevailing winds are southwesterly, which tends to drive both the river and stack plumes along shore most of the time.

Sediments and benthos were collected with a PONAR sampler at 1, 5, and 10 km from the assumed source. Eleven ponars were taken at the 1-km station and three at each of the other stations in the 5- and 10-km arcs. In order to obtain sufficient biomass for extraction, organisms from the 5-km stations were combined and a similar composite was prepared for the 10-km stations. The density of oligochaetes and chironomids was much higher at the extreme southern stations of both the 5- and 10-km arcs. It is estimated that over 50 percent of the biomass was obtained from these stations. The dominant oligochaete worm in the area is *Limnodrilus hoffmeisteri* and the dominant chironomids are *Chironomus* and *Procladius*.

The three sampling locations for *P. hoyi* were in southeastern Lake Michigan. The first was 3.5-km offshore of Grand Haven, Mich., (43° 03', 86° 17.5') in 23 m of water. The sediment was coarse sand (0.4 percent organic

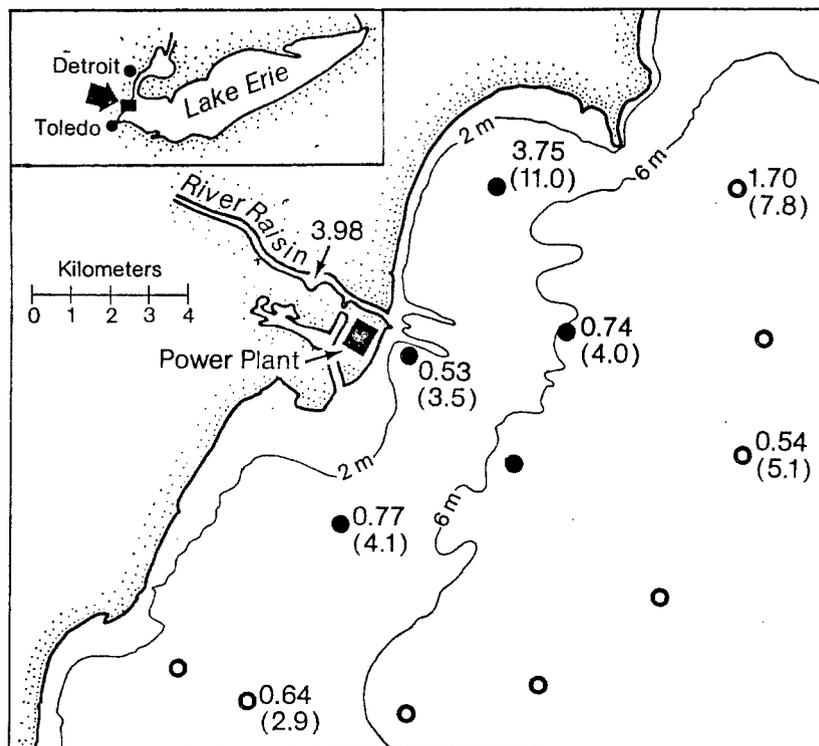


FIGURE 47.--Map of study area. Bold numbers are the concentrations of sedimentary PAH ($\mu\text{g g}^{-1}$); numbers in parentheses are percent organic carbon.

carbon) with approximately 5 percent of the mass less than $64 \mu\text{m}$ in grain size. The second location was 4 km further offshore in 45 m of water. The sediment was a silty sand (1.7 percent organic carbon) with approximately 30 percent of the particles less than $64 \mu\text{m}$ in grain size. The third location, about 90 km south ($42^\circ 18'$, $86^\circ 38'$) in 60 m of water, was in a region of high sediment accumulation. The sediment contained 3.3 percent organic carbon, and approximately 90 percent of its mass had a grain size below $64 \mu\text{m}$.

Sediment samples for comparison with *P. hoyi* were collected with a Shipek grab; the upper 1 cm was removed with a spoon and stored at 4°C in an aluminum foil covered glass jar. Sediments were placed in 250-mL glass centrifuge tubes and spun at room temperature for 20 min at 2,000 rpm. The supernatant was decanted through a precleaned glass fiber filter to remove residual particles. These pore waters (200 to 500 mL) were then extracted with 3 x 30 mL of hexane. The spun sediments were Soxhlet extracted without further drying.

PONAR samples collected at the same location were washed through a $500\text{-}\mu\text{m}$ screen with lake water. Benthic organisms were handpicked from the residue, depurated in filtered lake water overnight, and stored frozen in foil covered glass containers. After thawing, the organisms were blotted dry on paper towels and weighed prior to extraction. Sample extracts were cleaned up by chromatography on Sephadex LH 20 and silica gel (Geiger and Blumer, 1974;

Geiger and Schaffner, 1978). A gas chromatograph (GC; 30 m SE54 WCOT fused silica column; 100 to 260°C at 4° min⁻¹) equipped with a photoionization detector and a high performance liquid chromatograph (HPLC; 25 cm Vydac 201 TC reverse Phase column; 45 to 100 percent MeCN in water; 1 mL min⁻¹ flow) equipped with UV (254 nm) detector were used for quantitative analysis. A fluorescence detector was used on the HPLC for qualitative verification. Extraction yields were calculated by adding a known spike of carbon-14-labeled anthracene or benzo(a)pyrene (BaP) to each matrix prior to extraction and counting a known fraction of the final extract. Yields of the other PAHs were estimated by correcting the yields of standard extractions with the anthracene or BaP extraction efficiency.

Analytical precisions are shown in table 20. The larger variances associated with the midge and multiple sediment analyses are primarily due to small sample size and spatial heterogeneity, respectively. An estimate of accuracy was obtained through the analysis of a sediment sample supplied by NMFS/NOAA, Seattle, which has been used in an interlaboratory calibration (Brown *et al.*, 1980). Our values were the same as those reported in Brown *et al.* (1980) at the 0.05 confidence level of a Mann Whitney test for means.

TABLE 20.--Analytical precision (coefficient of variation)^a

| | Standards ^b n = 5 | Sediments ^b n = 3 | Sediments ^c n = 4 | Midges ^b n = 3 |
|--------------------|---------------------------------|---------------------------------|---------------------------------|------------------------------|
| Phenanthrene | 6.8 | 18.2 | 33.6 | 23.0 |
| Anthracene | 6.0 | - | 66.7 | 41.8 |
| Fluoranthene | 7.4 | 7.8 | 20.8 | 32.6 |
| Pyrene | 7.4 | 17.6 | 19.6 | 26.3 |
| Chrysene | 4.6 | 23.3 | 14.4 | 25.0 |
| Benzo-e-Pyrene | 19.3 | 6.6 | 19.0 | 8.8 |
| Benzo-a-Pyrene | 20.0 | 5.2 | 18.4 | 12.0 |
| Benzo ghi Perylene | 31.6 | 4.1 | 38.4 | - |

$$^a CV = \frac{100 \times \text{Std Dev}}{\text{mean}}$$

^b Replicate analyses from a single sample extraction.

^c Single analyses of replicate extracts of homogenized sample.

Replicate analysis by GC and HPLC yielded coefficients of variation for individual compounds ranging from 5 percent to 25 percent. An apparent systematic difference was observed between the GC and HPLC results. Anthracene, phenanthrene, and most fluoranthene values were not significantly different for the two systems, but pyrene, chrysene, and benzo(a)pyrene values were significantly higher (50 percent to 100 percent) on HPLC than on GC. Reported values are the means of GC and HPLC analyses. Checking our glass capillary GC results with HPLC sometimes prevented a gross overestimate of individual PAH. Samples that disagreed by more than 50 percent were rechromatographed on our silica gel column and rerun on the GC.

PAH in Lake Erie sediment samples were asymmetrically distributed within the study site. Sediments from stations 5 and 10 km to the north contained several times the level of PAH as did those from stations directly offshore or to the south. Surficial (upper 1 cm) sedimentary organic carbon was highest at these northern stations (11 percent and 7.8 percent respectively) due to the presence of abundant leaf litter. The remaining stations (not including the one in the river) contained 3 percent to 5 percent organic carbon and were silty muds. The concentration of the sum of the eight measured PAH correlated significantly ($r = 0.96$, $n = 7$) with percent organic carbon in the sediments.

Concentrations of individual PAH are illustrated in figure 48. The upper panel shows sediment values for the two anomalous northern stations and a station approximately 1 km upriver from the mouth. The concentrations of PAH tend to decrease offshore to the north, indicating a terrigenous source, presumably through the river. As previously mentioned, worms and midges were scarce at these northern stations. This low organism density may be due to the presence of toxic compounds; PAH concentrations are near (phenanthrene) or above (fluoranthene) the 96-h LC50 reported in Neff (1979) for a marine polychaete.

Individual PAH concentrations for the samples of worms, midges, and sediments from 1, 5, and 10 km offshore are shown in figure 48 (B, D). Since the biomass from the anomalous northern stations was insignificant, sediment concentrations from these stations were not included in the averages.

The sediment samples depicted in figure 48B are the averages of the individual samples for which total PAH are shown in figure 47 and a composite sample (1 tablespoon of surficial mud per grab) from each arc. Except for benzo(ghi)perylene (BgP), PAH were homogeneously distributed within the region.

The worms had relatively high concentrations of pyrene (Py), chrysene (Ch), and benzo(e)pyrene (BeP) (figure 48C). For the other PAHs, the concentrations in worms (wet weight) were lower than their associated sediments.

PAH concentrations in midges collected 1 km from shore were high and generally decreased with distance offshore (figure 48D). The data for both organisms were replotted as the ratio of organism concentration (wet weight) to sediment concentration (dry weight) (figure 49). These ratios imply that the midges concentrate several PAH compounds from their surroundings at the nearshore station, but not further offshore. With the exception of phenanthrene (Ph), this trend was not observed for the worms.

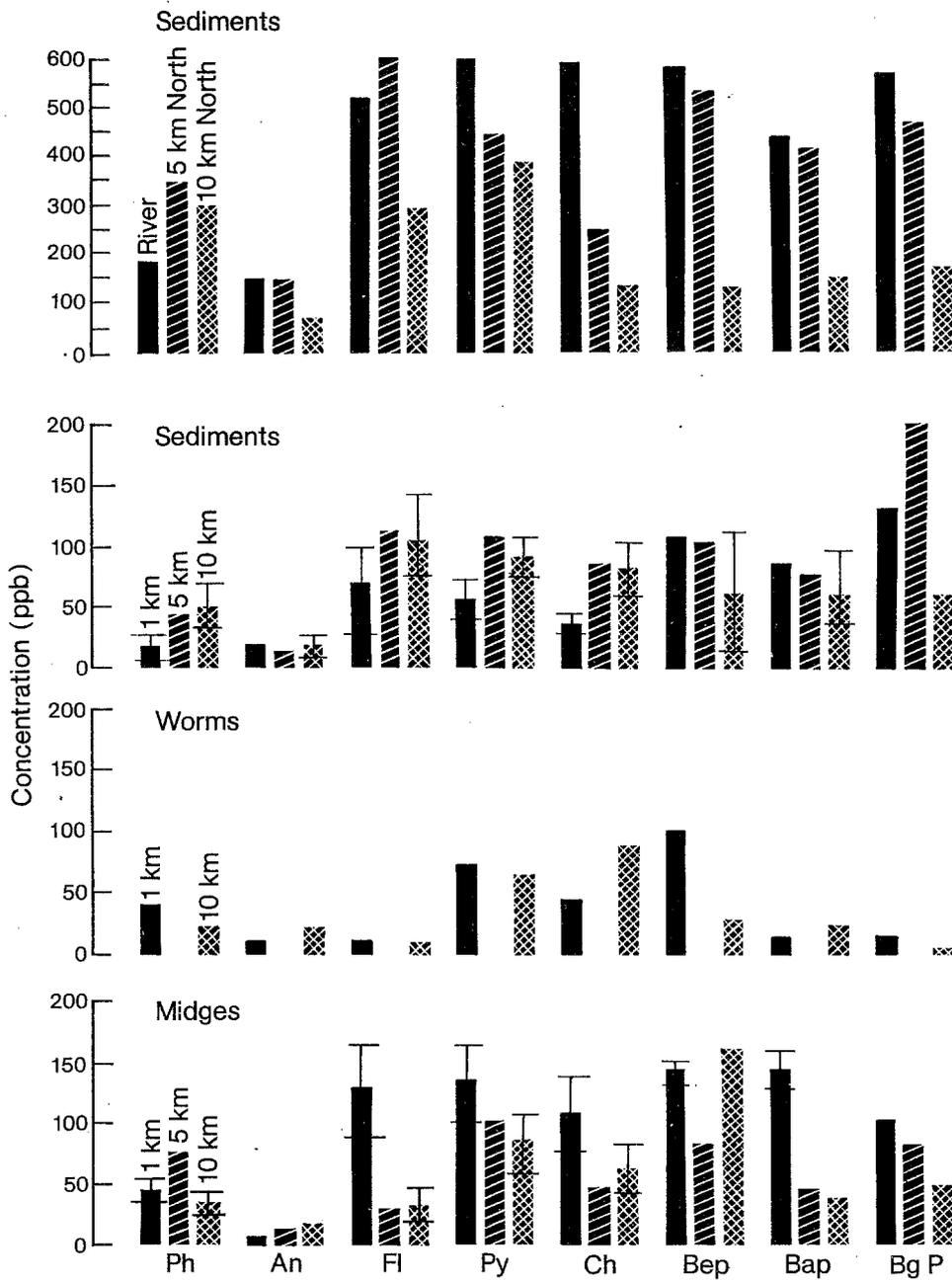


FIGURE 48.--Sediment concentrations of individual PAH. (A) River, 5 km and 10 km north. (B) Surficial sediments from the remainder of the study area. The bar represents 1 standard deviation from one composite sample and the individual samples shown in figure 6. (C) Concentrations in oligochaete worms from 1 and 10 km. (D) Concentration in chironomid midges from 1, 5, and 10 km. Bars represent 1 standard deviation, multiple analyses of a single extract.

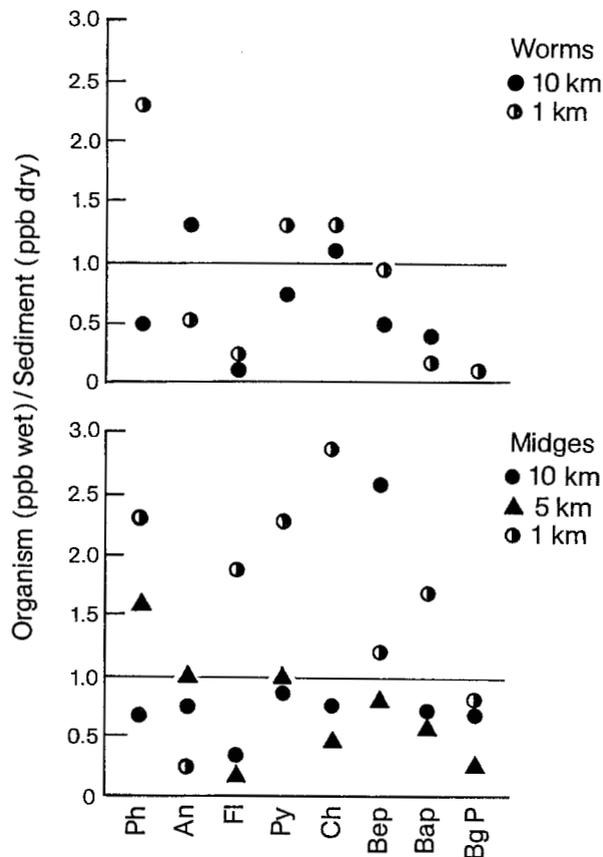


FIGURE 49.--PAH ratios for worms and midges (wet wt.) to local sediments (dry wt.) for 1-, 5-, and 10-km composite samples.

PAH concentrations for pore water, sediments, and *P. hoyi* from Lake Michigan are presented in figure 50. Sediment PAH concentrations for the three environments ranged over more than an order of magnitude. The distribution of individual compounds is very similar to those for western Lake Erie. Concentrations of individual PAH are within the range of those reported from a worldwide distribution of marine sediments (Neff, 1979) with our 60-m (high sedimentation) sample near the highest. The sum of the seven reported sediment PAHs on a dry weight basis were 0.18, 0.77, and 4.6 ppm for the 23-, 45-, and 60-m samples, respectively. In nearshore Lake Erie sediments, these values range from 0.42 to 3.2 $\mu\text{g g}^{-1}$.

Sediments at the 5- and 10-km stations in Lake Erie and from upriver had PAH compositions very similar to those reported by Laflamme and Hites (1978) for sediments near an anthropogenic combustion source. Our 1-km sediments were enriched in BeP and BaP ($\text{C}_{20}\text{H}_{12} \approx 52$ percent) and depleted in Ch ($\text{C}_{18}\text{H}_{12} \approx 10$ percent) relative to their reported global averages. The concentrations of PAH in these nearshore sediments are similar to those reported (Laflamme and Hites, 1978; Hites *et al.*, 1980) for Buzzards Bay, Gulf of Maine, and Hudson Channel sediments, which are similarly near anthropogenic sources.

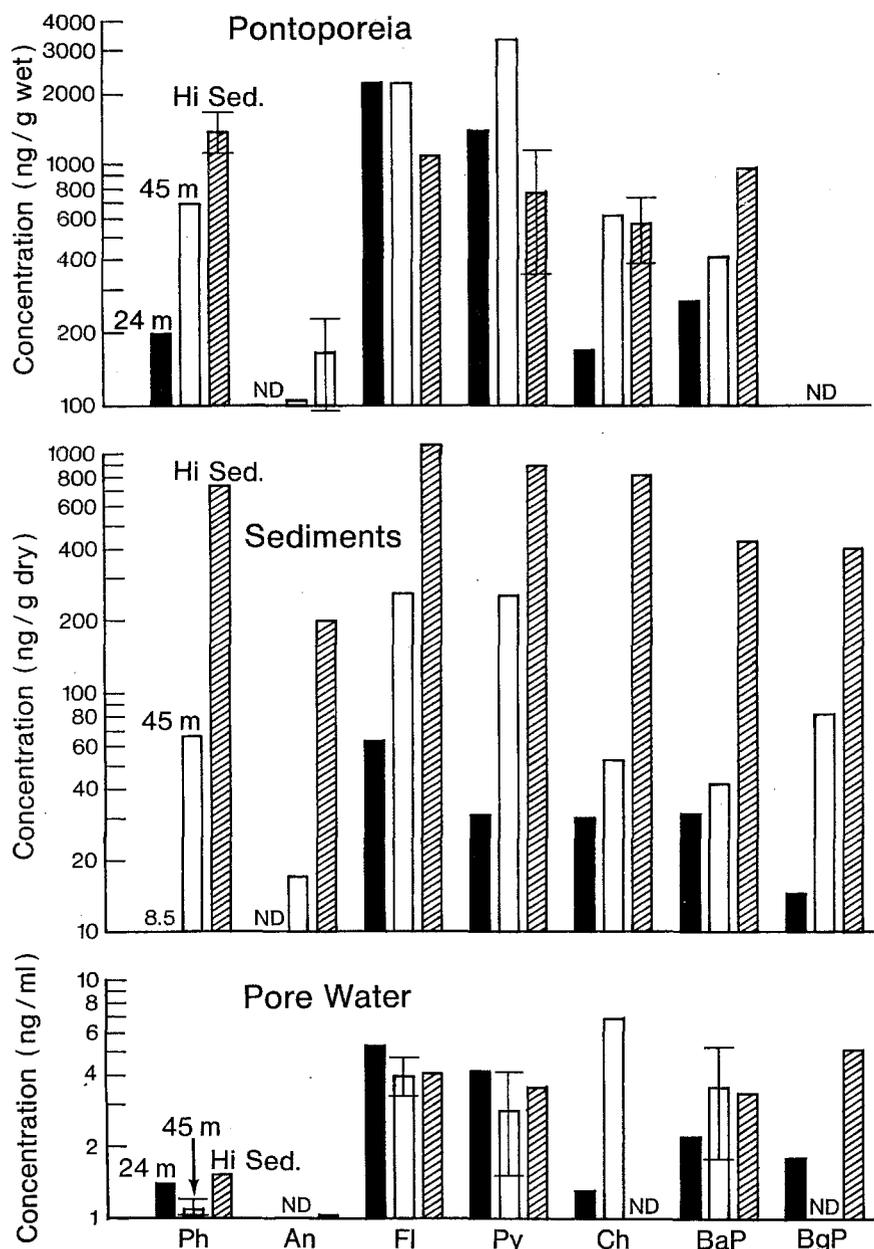


FIGURE 50.--PAH concentrations (log scale) in *Pontoporeia hoyi* (top panel), sediments (middle panel), and pore water (bottom panel) from three stations. Solid bars are data from the 24-m station; open bars are data from the 45-m station, and hatched bars are data from the 60-m high sedimentation station.

The anomalously high sediment concentrations 5 and 10 km to the north are similar in relative composition to the river sediment, their probable source. The PAH levels are high but considerably lower than those of Lake Washington and the three Swiss lakes reported by Wakeham *et al.* (1980) or the highly polluted Charles River (Hites *et al.*, 1980).

A PAH point source load associated with the power plant was not apparent, probably because combustion products are well dispersed and leachate from coal stored on the lakeshore appears to be small in agreement with Carlson *et al.* (1979).

Almost no data are available on PAH levels in aquatic organisms except for fish, mollusks, and crustaceans (Neff, 1979). The oligochaete worms analyzed in this study did not bioconcentrate (on a wet weight basis) any of the PAH. Fluoranthene (FL), BeP, and possibly BaP appear to be depleted in worms with respect to their sediment environment. This depletion may be the result of biotransformation by the worms. Degradation of several PAH including FL and BaP was enhanced by the marine polychaete *Capitella capitata* (Gardner *et al.*, 1979).

The midges display a more complicated accumulation pattern. Those collected at 1-km offshore exhibited bioconcentrations of Ph, FL, Py, Ch, and possibly BaP. Further offshore, these apparent bioconcentrations disappeared, with the midges at near equilibrium with the sediments. In both organisms, FL was the most depleted of the identified compounds relative to local sediments. A similar result was reported for the marine mollusk *Mytilus edulis* (Dunn, 1980).

A possible explanation for this apparent nearshore anomaly lies in the fact that the 1-km station is very near the river mouth and would often (although not during our collection period) be within the plume. The high PAH concentration in the river sediment indicates it is a source, thus the nearshore filter-feeding midges would be exposed to occasional high concentrations of riverine material, and appear to be out of equilibrium with their local environment. The infaunal worms feeding primarily within the sediments would be buffered from this effect.

Although the distribution of PAH in Lake Michigan pore waters resembled those in associated sediments, pore water concentrations did not reflect the order of magnitude differences seen for the sediments. In fact, the concentrations in different pore waters appeared to be about the same except for chrysene and benzo(ghi)perylene. Dissolved organic carbon measured in the pore water was 4.8, 3.7 ± 0.5 , and 19.8 ± 0.7 ppm for the three Lake Michigan environments. PAH in pore water does not appear to be strongly correlated with dissolved organic carbon. Benzo(a)pyrene and chrysene occurred in higher concentration than their reported solubility (<1 ppb, 25°C, distilled water) (Neff, 1979; May *et al.*, 1978), while other PAH compounds, having solubilities ranging from ~1,000 ppb (phenanthrene) down to ~150 ppb (pyrene), were substantially below saturation. Equilibrium partitioning, which is proportional to solubility (Karickhoff, 1981), would predict a dramatically different distribution of PAH; higher concentrations of the more soluble and lower concentrations of the less soluble PAH. The most logical explanation for the observed distribution and invariance of concentration is that fine-grained particles (<1 μm) passed through our filtering process and that the amount of these particles and the PAH associated with them were relatively homogeneously distributed throughout the lake sediments. Thus, our pore water samples were dominated by PAH associated with very fine particles, colloids, and/or humic substances.

The distribution of individual PAH in the *P. hoyi* was similar to those of the sediments and pore water; fluoranthene and pyrene were the most abundant compounds and anthracene the least abundant. The concentrations of the PAH were not nearly as systematic among the animals from the three sites as they

were for sediments, where the 25-m sample had the lowest concentration for all PAH and the 60-m sample had the highest. Nearshore samples of *P. hoyi* had higher concentrations of fluoranthene and pyrene than samples from the 60-m high sedimentation area. In contrast, the sediments from the high sedimentation area had approximately 20 times as much fluoranthene and 30 times as much pyrene as the 23-m sediment.

Ratios of PAH in *P. hoyi* (wet) to PAH in sediments (dry) are shown in figure 51. The 60-m samples had a consistent ratio of 1 (± 50 percent) and was similar to our earlier results on oligochaete worms and chironomids in a fine-grained sediment region of Lake Erie. These benthic organisms appear to be in a secular equilibrium with their sedimentary environment; a substantial fraction of their body burden of PAH, therefore, must come from the sediment or associated pore water. The 45-m samples had a consistent ratio of approximately 10, whereas our shallower samples had a variable ratio, ranging from 5 to 45. We believe that these higher ratios can be explained in terms of the grain-size distribution of the sediments. PAH distribution should be biased toward smaller particles because of their greater surface area per mass and their high organic carbon content, which makes them better sorption substrates. In figure 51B the ratios are again plotted, but this time the PAH concentrations in the sediments were corrected for grain size based on the assumption that particles larger than 64 μm contain an insignificant amount of PAH. These corrected values (PAH(64)) were calculated as follows:

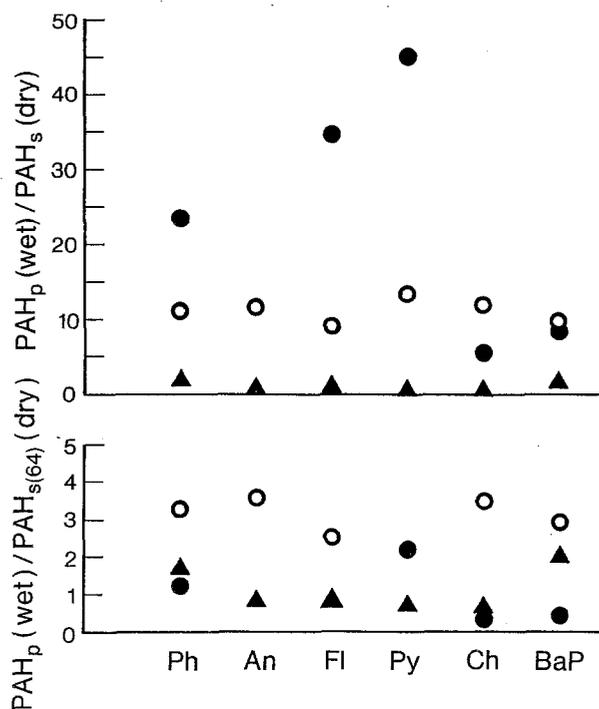


FIGURE 51.--Top: ratio of *Pontoporia hoyi* PAH to sediment PAH (● = 24-m station; ○ = 45-m station; ▲ = 60-m station). Bottom: same ratio; sediment corrected for 64 μm grain size.

$$\text{PAHs}(64) = 100 \times \text{PAHs}/(\% \text{ Mass} < 64 \mu\text{m})$$

Although this calculation brings all of the ratios close to 1, it is not a completely satisfactory correction. Analysis of the gut content of *Pontoporeia femorata* and *P. affinis*, both closely related to our *hoyi*, show a particle-size cutoff at approximately 30 μm , whether the animals were collected from a silty or sandy substrate (Ankar, 1977). We do not have any information on the particle-size distribution (below 64 μm) for our sediments. The concentration of PAH in *P. hoyi* appears to reflect the apparent PAH content of the fine-grained sediment (likely uniform throughout a large region) rather than the bulk sediment that they inhabit.

9.4 Biocentration

The concentrations of PAH in Lake Michigan *P. hoyi* were high, with individual compounds reaching concentrations of greater than 1 ppm (wet weight) or 10 ppm based on organism dry weight. With the exception of those for BaP and chrysene, our measured bioconcentration factors ($\text{BCF} = \text{Pontoporeia PAH} / \text{dissolved PAH}$) presented in table 21 were approximately one order of magnitude higher than those calculated (for fish) from experimental or theoretical relationships (Kenaga and Goring, 1979) based on compound solubility. The fact that our calculated BCFs (based on overlying water) are high may mean that the sediments and/or porewater are important for the more soluble PAH.

9.5 Compartmental Bioconcentration Factors

In order to estimate the contribution of sediment and pore water PAH to the body burden in *P. hoyi*, we assume that the animals are at steady state with respect to their local environment and employ the following relationship:

$$\text{PAH (Pontoporeia)} = \text{BCFw} \times \text{PAHw} + \text{PCFs} \times \text{PAHs} + \text{BCFpw} + \text{PAHpw}$$

The measurement of PAH in *P. hoyi*, water, sediment, and pore water from three locations where concentrations were significantly different yields three equations in three unknowns, BCFw, BCFs, and BCFpw. This allows for a unique solution to the equations. A sample calculation for BaP is:

$$260 = 0.010 \text{ BCFw} + 32 \text{ BCFs} + 2.4 \text{ BCFpw}$$

$$410 = 0.010 \text{ BCFw} + 42 \text{ BCFs} + 3.0 \text{ BCFpw}$$

$$980 = 0.010 \text{ BCFw} + 430 \text{ BCFs} + 3.4 \text{ BCFpw}$$

TABLE 21.--Estimates of bioconcentration factors

| PAH | Solubility (ppm) ² | Calculated BCF ¹ | Ponto(ppb) x s | Water(ppt) ⁴ X | BCF _m ⁵ |
|-----------------|----------------------------------|--------------------------------|-------------------|------------------------------|-------------------------------|
| Ph | 1.002 | 617. | 767 ± 604 | 40 | 19,175 ± 15,100 |
| An | 0.0446 | 3,571. | 200 | 12 | 16,667 |
| F ¹ | 0.206 | 1,507. | 1,833 ± 635 | 23 | 79,696 ± 27,607 |
| Py | 0.132 | 1,939. | 1,767 ± 1,460 | 40 | 44,175 ± 36,500 |
| Ch ³ | 0.0018 | 21,829. | 507 ± 262 | 25 | 20,280 ± 10,480 |
| Bap | 0.0002 | 75,374. | 550 ± 380 | 10 | 55,000 ± 38,000 |

¹log BCF = 2.791-0.564 log S (ppm) (Kenaga and Goring, 1979).

²References (Neff, 1979; Rossi, 1977).

³For triphenylene; s = 0.040; calculated BCF = 3,797.

⁴Mean of two 20-L glass fiber filtered offshore water samples (parts per trillion).

⁵BCF_m = (mean measured PAH in *P. hoyi*)/(mean measured PAH in Lake Michigan water (n = 2)).

Solving this system by substitution yields

$$\text{BCF}_w = -33,014$$

$$\text{BCF}_s = 1.233$$

$$\text{BCF}_{pw} = 229.5$$

Results for the four compounds having a complete data matrix are given in table 22.

Negative BCF values make these results difficult to interpret, and are probably a result of our unsatisfactory analytical precision.

TABLE 22.--BCF calculations from the three-compartment model

| PAH | BCFw | BCFs | BCFpw |
|-----|----------|--------|--------|
| Ph | 66,392. | 2.017 | -1330. |
| FL | 169,583. | -1.310 | -212.8 |
| Py | 324,864. | -1.871 | -1190. |
| BaP | -33,014. | 1.233 | 229.5 |

In an attempt to extract more information from the data, we can remove one of the degrees of freedom from our conceptual model by assuming that the theoretical/experimental BCF calculated from solubility is equivalent to our BCFw. Using the value from table 21, we rewrite our sample calculation (for phenanthrene; calculated BCFw = 617) as follows:

$$200 = 0.040 \times 617 + 8.3 \text{ BCFs} + 1.35 \text{ BCFpw}$$

$$700 = 0.040 \times 617 + 65 \text{ BCFs} + 1.07 \text{ BCFpw}$$

$$1,403 = 0.040 \times 617 + 730 \text{ BCFs} + 1.55 \text{ BCFpw}$$

Reducing and solving the three sets of equations yields

$$\text{BCFs} = 3.83 \pm 4.7 \quad \text{and} \quad \text{BCFpw} = 262 \pm 287$$

The results for the other PAHs are given in table 23.

Sediment and pore water BCF could not be calculated for chrysene and BaP because the theoretical/experimental BCF for water were equal to or larger than our measured total BCF, indicating that (under the assumptions stated) the organisms obtained all of these two compounds from the water. Calculated results for Ph, FL, and Py indicate that BCF calculated independently for pore

TABLE 23.--BCF calculations from the three-compartment model, with BCF for water from table 21

| PAH | BCFw | BCFs | BCFpw |
|-----|-------|-------------|---------------|
| Ph | 17 | 3.83 ± 4.7 | 262 ± 287 |
| FL | 1,507 | 0.17 ± 1.9 | 480 ± 130 |
| Py | 1,936 | 0.25 ± 10.7 | 1,052 ± 1,337 |

water were similar to BCF for overlying water and that the BCF calculated for sediments were small.

The percentage of PAH *P. hoyi* obtained from each of the three sources can now be calculated by going back to our original equations (such as the example set for phenanthrene above) and substituting in the calculated BCFs and BCFpw. The results, presented in table 24, are relatively consistent for the three compounds. They suggest that overlying water plays only a small part in the accumulation of phenanthrene, fluoranthene, and pyrene in *P. hoyi* and that the animals obtain most of their body burden of these PAH from the pore waters.

If we normalize the sediment concentrations to the less than 64 µm grain size (the approximate food size of the *Pontoporeia*), the calculations indicate a slightly higher percentage coming out of the sediments, with an accompanying small reduction in pore water contribution.

Our results imply that *P. hoyi* can remobilize PAH from sediments and move them up the food web, where they have the potential for damaging top predators. These results should be tested in controlled laboratory experiments. The following conclusions can be made from our results to date:

TABLE 24.--Percentage of PAH obtained by *P. hoyi* from water, sediment, and pore water

| PAH | Water | Sediment | Pore Water |
|-----|-----------|-------------|-------------|
| Ph | 4.8 ± 4.3 | 43.3 ± 39.7 | 51.9 ± 38.7 |
| *FL | 1.5 | 7.0 | 91.5 |
| *Py | 2.9 | 25.6 | 71.5 |

1. The distribution of individual PAHs in sediment samples are similar to the distributions reported from other marine sediments collected near urban environments.

2. Concentrations in sediments range up to near the highest reported for marine sediments.

3. Pore water PAH exhibits a distribution similar to that of local sediments, although PAH concentrations are not related to local sediment concentration. This may be an experimental artifact due to PAH association with very fine particles or complexed with naturally occurring organic matter collected and reported as pore water.

4. PAHs measured in *Pontoporeia* do not correlate well with the PAH in their bulk sediment environment, but do appear to correlate with fine-grained sediments that serve as their food source. Grain-size-corrected PAHs in sediments from dramatically different environments appear to have approximately the same concentrations, indicating a large-scale homogeneity (with respect to PAH) in the fine-grained sediments of Lake Michigan and possibly the Great Lakes.

5. Based on a static equilibrium model, *Pontoporeia* may obtain a substantial fraction (>50 percent) of their phenanthrene, fluoranthene and pyrene body burden from local sediment and pore water. They appear to obtain chrysene and benzo(a)pyrene primarily from the water.

6. PAH bioconcentration factors (from water) are calculated to be approximately 10^4 to 10^5 for *Pontoporeia*.

7. Infaunal worms, feeding on the well-mixed upper few centimeters of the sediments and offshore midges, do not appear to bioconcentrate individual PAH relative to the sediment.

8. The high concentrations of PAH (and possibly other hydrophobic organic compounds) in the northern region of the Lake Erie study site may have caused the sediments to be an unsuitable environment for a healthy benthic community.

Both the laboratory and field work indicate that sediment-associated PAH are responsible for a large portion of the body burden of the higher solubility PAH such as anthracene, phenanthrene, pyrene, and fluoranthene for benthic organisms. However, the more insoluble compounds such as BaP appear to be obtained to a much larger degree from the dissolved phase. Further, the sediment-associated material absorbed by the benthic organisms appears to be associated with the fine grain fraction of the sediments.

The bioconcentration factors for *P. hoyi* are high and correlate reasonably well with octanol water partition coefficients and the relationship is approximately parallel to that published by Kenaga and Goring (1979) for fish (figure 52). The bioconcentration factor also shows a good correlation with the second-order molecular connectivity term ($2\chi^b$) (Kier and Hall, 1976) (figure 53). This term is a nonempirical mathematical descriptor for molecules and thus molecular connectivity terms may provide an excellent

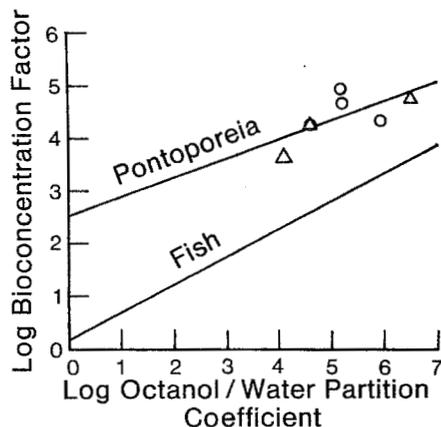


FIGURE 52.--Log of bioconcentration factor for PAH in *Pontoporeia hoyi* versus Log octanol water partition coefficient compared with the similar relationship for fish from (Kenega and Goring, 1979).

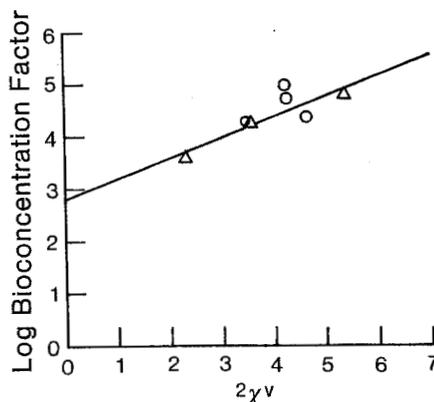


FIGURE 53.--Log bioconcentration factor for PAH in *Pontoporeia hoyi* versus the second order molecular connectivity term ($2\chi^v$).

nonempirical means of describing organic compounds to relate to their physiochemical properties for fate modeling.

The *Pontoporeia hoyi* are very slow to eliminate PAH and have negligible biotransformation; therefore, they will pass materials concentrated from the sediments and water up the food chain. The field studies indicate that worms and midges are at equilibrium with the sediments. While they have lower bioconcentration factors than *P. hoyi*, midges and worms also contribute PAH to higher forms in the food chain. Therefore, preliminary findings indicate that oligochaetes rework the sediments and redistribute compounds to the surface,

slowing burial and making them more available to organisms such as *P. hoyi* (White and Klahr, 1982), while *P. hoyi* bioconcentrate the compounds and pass them up the food chain.

10. VERTICAL DYNAMICS MODELING OF TOXIC CONTAMINANTS IN THE GREAT LAKES

The presence of potentially harmful contaminants (PCB, PAH, toxaphene, etc.) in the Great Lakes has stimulated research on their fate, distribution, and bioconcentrations within the environment. Recent recognition of the problem, coupled with the complex behavior of organic compounds, has left critical gaps toward predicting bioconcentrations with high certainty. This has necessitated that predictions be made from highly idealized models (e.g., Thomann, 1981; Eadie, 1981). Therefore, to provide more reliable estimates of bioaccumulation at different trophic levels requires process-oriented models with physically realistic mechanisms.

Calculations have been made on a fine grid, one-dimensional model as part of an effort to describe the fate and decomposition pathways of toxic organics in the Great Lakes. Herein, we discuss the model conceptualization and then present results of a case study made on the pesticide mirex found in Lake Ontario.

10.1 Model Description

The model is vertically segmented into 16 layers in the water column and 1 layer in the sediments, and represents an offshore region of 1 m² in area. Calculations are performed on a stretched grid where grid size is calculated from the surface down according to

$$\Delta Z_i = 1.28 \Delta Z_{i-1} \quad (34)$$

where ΔZ_i = grid size at level i .

The surface layer is set at 1 m and the sedimentary one at 3 cm.

Model conceptualization is based on carbon flow through three particulate pools and a dissolved pool. Phytoplankton, zooplankton, and detritus represent the particulate material and are described in a mass balance model based on Volterra dynamics, i.e.,

$$dP/dt = GP - gr\Psi P \quad (35)$$

$$d\Psi/dt = -M\Psi + \alpha gr\Psi P \quad (36)$$

$$\frac{dm}{dt} = \gamma M\Psi + (1 - \alpha)g_r\Psi P - w\frac{dm}{dz} + S \quad (37)$$

where P = phytoplankton (mg C L⁻¹)

Ψ = zooplankton (mg C L⁻¹)

m = detritus (mg C L⁻¹)

G = growth rate (day⁻¹)

Gr = grazing rate (L day⁻¹ mg⁻¹)

M = mortality rate (day⁻¹)

α = assimilation efficiency

γ = detrital fraction of dead zooplankton

W = settling velocity (m day⁻¹)

S = detrital load (mg C L⁻¹ day⁻¹)

Rate constants are selected by the set that yields a best fit to available data. The grazing rate is adjusted with depth in order that the plankton dynamics mimic results from more elaborate plankton models (McCormick *et al.*, 1982).

Equilibrium partitioning is assumed between the dissolved and the total particulate material. Equilibrium conditions are approximately maintained by switching on reactions to either sorb or desorb contaminants, as the case may be. Reaction selection is made every time step by comparison of the desired with the calculated partitioning.

Turbulent transport is explicitly considered in the dissolved component only. Turbulent fluxes in the particulate pools are not modeled because their non-neutral buoyancy contributes to particle motion of unknown correlation with the motion of the neighboring fluid. Nonetheless, fluxes due to turbulence indirectly affect concentrations in the particulate pools through the sorption connection. Calculation of the turbulent flux in the dissolved pool is parameterized by an eddy diffusion coefficient calculated according to McCormick and Scavia (1981).

The simulated removal pathways are volatilization, photolysis, sedimentary burial, and outflows. All processes are treated as first order. Volatilization losses are estimated from loss rates set equal to the square root of the ratio of the molecular weights of water/contaminant (Liss and Slater, 1974). Photodecomposition losses are patterned after Zepp and Cline (1977) where loss rates are estimated from compound-specific information on the molar extinction coefficient, absorption spectra, and quantum yield as well as the photon flux. Sedimentary losses are assumed to be proportional to the sedimentary mass loading. Burial rates are calculated by dividing the mass loading to the sediments by the mass of the sediments. This maintains the sediment layer at constant mass and porosity. Finally, losses due to river outflows are estimated by assuming the dilution rate is uniform throughout depth and is equal to the volume outflow rate divided by the lake volume.

The following equations describe how a contaminant is transferred through the system.

$$\frac{d\phi_D}{dt} = \frac{d}{dz} \left(K \frac{d\phi}{dz} \right) + K_e (\eta \phi_\eta + \Psi \phi_\Psi + P \phi_P) / (\eta + \Psi + P) - K_u \phi_D + (1 \cdot \gamma) M \phi_\Psi - (k_p + k_v + K_q) \phi_D \quad (38)$$

$$\frac{d\phi_P}{dt} = -g_r \Psi \phi_P + (K_u \phi_D - K_e \phi_P) P / (\eta + \Psi + P) \quad (39)$$

$$\frac{d\phi_\Psi}{dt} = -M \phi_\Psi + \alpha g_r \Psi \phi_P + (K_u \phi_D - K_e \phi_\Psi) \Psi / (\eta + \Psi + P) \quad (40)$$

$$\frac{d\phi_m}{dt} = -w \frac{d\phi_M}{dz} + (1 - \alpha) g_r \Psi \phi_P + \gamma M \phi_\Psi + (K_u \phi_D - K_e \phi_m) \eta / (\eta + \Psi + P) \quad (41)$$

where ϕ_D = dissolved contaminant concentration ($\mu\text{g L}^{-1}$)

ϕ_P = phytoplankton contaminant concentration ($\mu\text{g L}^{-1}$)

ϕ_Ψ = zooplankton contaminant concentration ($\mu\text{g L}^{-1}$)

ϕ_η = detrital contaminant concentration ($\mu\text{g L}^{-1}$)

K = eddy diffusivity ($\text{m}^2 \text{day}^{-1}$)

K_e = desorption rate (day^{-1})

K_u = adsorption rate (day^{-1})

K_p = photolysis rate (day^{-1})

K_v = volatilization rate (day^{-1})

K_q = dilution rate due to outflows (day^{-1})

ϕ_s = particle associated contaminant loading ($\mu\text{g L}^{-1} \text{day}$)

Material transfer between the sediments, pore waters, and water column is related by

$$\frac{d\zeta_s}{dt} = \frac{K_d}{1 + K_d} \frac{dc}{dt} \quad (42)$$

$$\frac{d\zeta_p}{dt} = \frac{1}{1 + K_d} \frac{dc}{dt} \quad (43)$$

$$\frac{dc}{dt} = w(10^3 \phi_{\Psi} = \frac{\eta\zeta_s}{M_s}) = 10^3 \frac{km}{\Delta Z} \left(\frac{\zeta_p}{V_p} - \phi \right) \quad (44)$$

where ζ_s = sediment contaminant mass ($\mu\text{g m}^{-2}$)

ζ_p = pore water contaminant mass ($\mu\text{g m}^{-2}$)

K_d = mass distribution coefficient

V_p = pore water volume (L)

K_m = molecular diffusion coefficient ($\text{m}^2 \text{day}^{-1}$)

C = total contaminant mass ($\mu\text{g m}^{-2}$)

M_s = sediment mass (gm)

A flow chart of the preceding equations is shown in figure 54.

10.2 Case Study

Thomas *et al.* (1972) estimated that over several hundred kilograms of the pesticide mirex have been introduced into Lake Ontario over the course of its production. Studies have been conducted on its horizontal distribution (Pickett and Dossett, 1979; Pickett and Paduan, 1982) and concern over its future levels has motivated this study, the objective of which is to calculate the background levels of mirex that might be expected in offshore areas. Background levels as used here are defined as those concentrations produced from sedimentary leakage via molecular diffusion from the pore waters into the water column.

The model was integrated over a 10-year period by a paired fifth- to sixth-order Runge-Kutta routine from IMSL. Coefficient values and initial conditions are listed in table 25.

The particle distribution generated by equations (35) to (37) is shown for three of the layers in figure 55. The seasonal plankton dynamics control the large surface fluctuations in the particle concentrations, while lower level dynamics are primarily determined by the magnitude of the settling velocity. Higher sedimentation rates cause larger amplitude signals at depth,

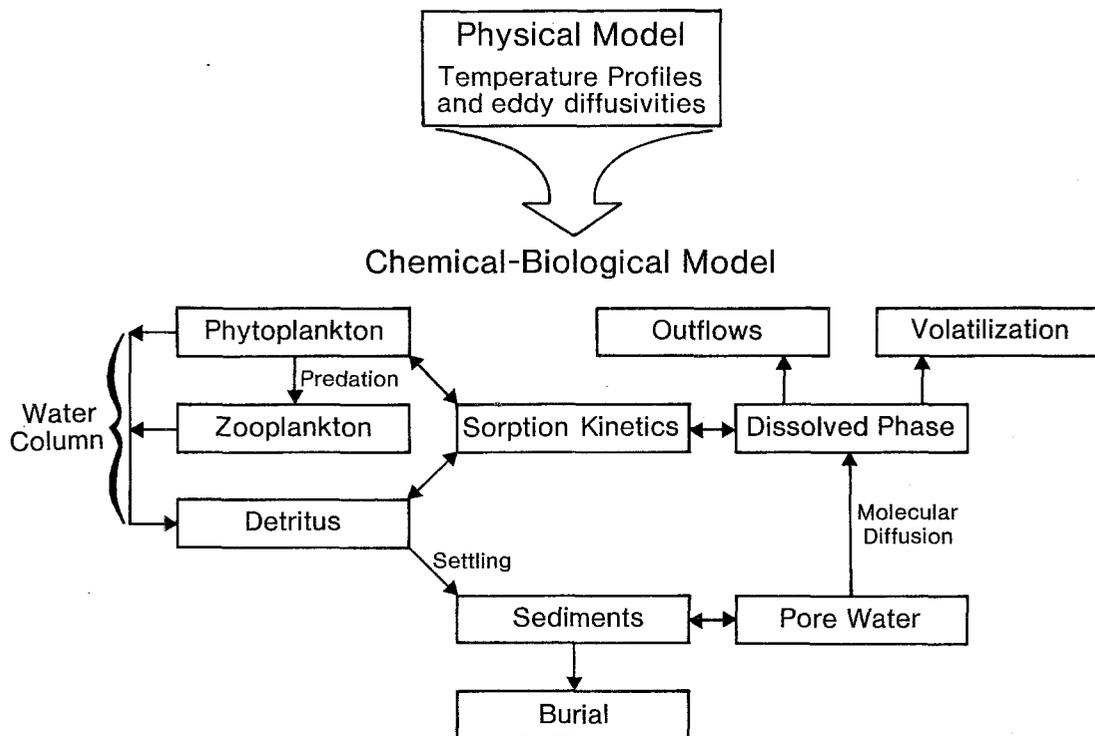


FIGURE 54.--Model conceptualization depicting the transfer of carbon and synthetic organic contaminants.

TABLE 25.--Initial conditions and parameter values for mirex calculation

| | |
|--|-----------------------|
| Total Sedimentary Mirex (PPB) | 5 |
| Total Water Column Mirex (PPB) | 0 |
| Sediment Mass Distribution Coefficient | 9 |
| Molecular Mass Diffusivity ($\text{m}^2 \text{ day}^{-1}$) | 10^{-6} |
| Settling Velocity (m day^{-1}) | 0.5 |
| Volatilization Rate for Top Meter (day^{-1}) | 0.87 |
| Photolysis Rate (day^{-1}) | 0 |
| Outflow Rate (day^{-1}) | 3.48×10^{-4} |
| Partition Coefficient | 10^6 |

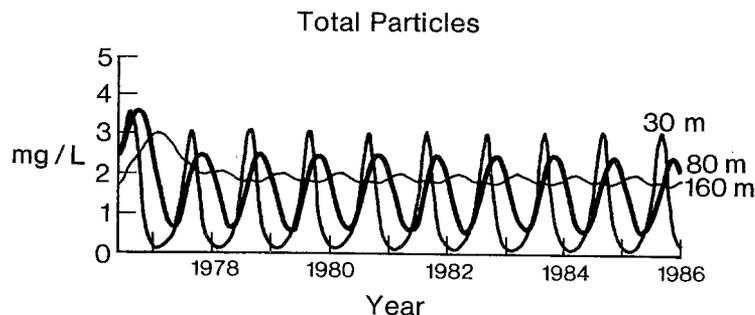


FIGURE 55--*Simulated total particle distribution for Lake Ontario.*

while with lower settling velocities, a near steady-state condition is achieved as local particle concentrations remain at nearly constant levels.

The temporal behavior of mirex associated with the individual particle groups, total particulate material and in solution are shown in figures 56-60.

Figures 56 to 60 show strong seasonal oscillations, with the largest gradients occurring in the summer and the smallest in winter. The onset of stratification limits the vertical flux of mirex to the surface waters necessary to replenish that lost by volatilization and adsorption due to particle production. The vertical gradient then increases and remains large throughout the stratification period until fall overturn when the thermocline is no longer a barrier to vertical transfer.

Concentrations span over two orders of magnitude during the summer with plankton ranging from 0.01 to 1 PPB (figures 56 and 57) and the detritus from 0.01 to 0.5 PPB (figure 58). The detritus group is the only grouping that shows subsurface peaks in concentration. No subsurface peaks are seen in the total particulate or dissolved components (figures 59 and 60), but rather they show uniform decreases in concentration with increasing distance from the

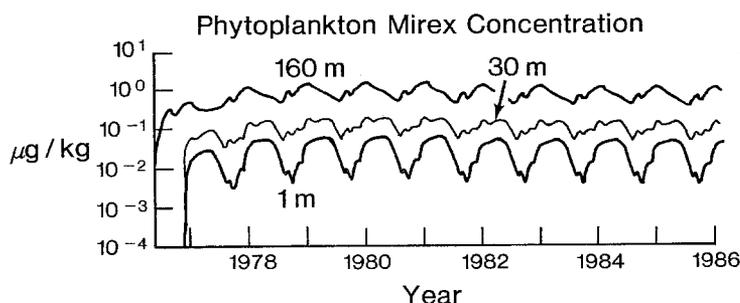


FIGURE 56.--*Simulation of phytoplankton mirex.*

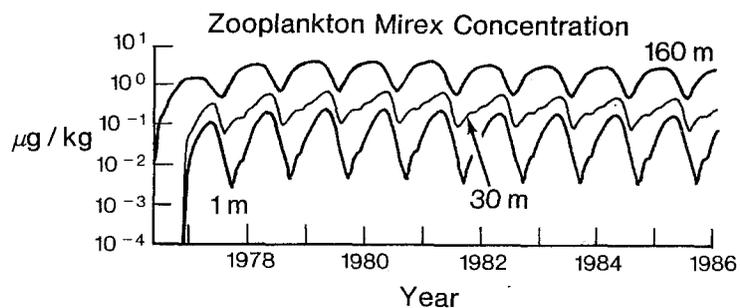


FIGURE 57.--Simulation of zooplankton mirex.

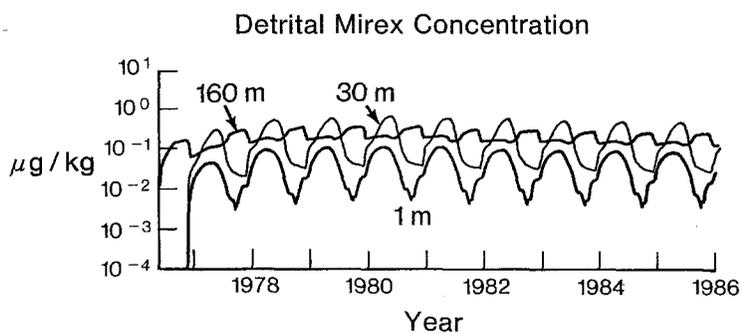


FIGURE 58.--Simulation of detritus mirex.

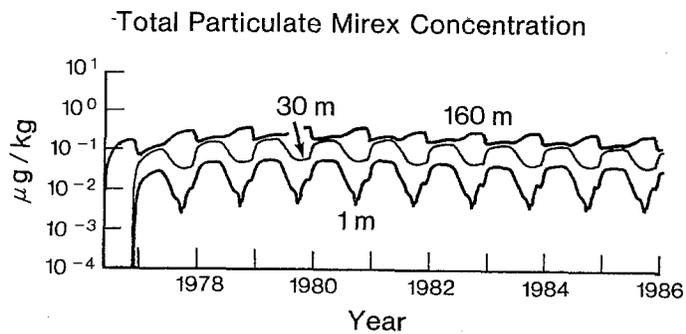


FIGURE 59.--Simulation of total particulate mirex.

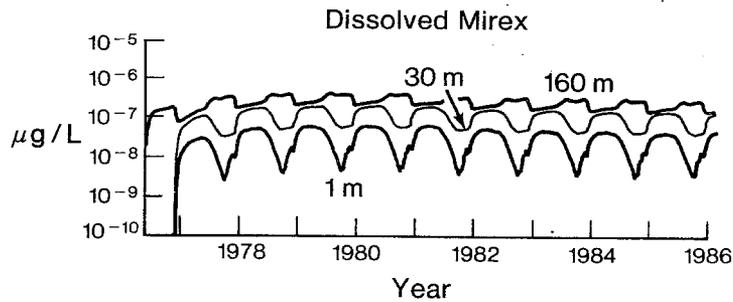


FIGURE 60.--Simulation of dissolved mirex.

sediment source. Individual particle groups, like the detritus, may show patterns that are inconsistent with expectations if concentration profiles were to be inferred from examining the total particulate profiles alone. However, no inconsistency exists when it is recognized that contaminant partitioning is assumed to equate with the total substrate concentration and not with some fraction of it. Furthermore, by assuming an equal affinity for adsorption among the groups, subsurface maxima can be explained by noting the concentration of dissolved contaminant and the composition of the total particulate material.

Total vertically-integrated concentrations are seen in figure 61. The percent total relative to the sediments peaks at approximately 0.25 percent about 4 years after the start up, followed by a slow decline to about 0.20 percent by the end of the simulation. The seasonal fluctuations demonstrate the inhibitory effect of low eddy diffusion on sediment leakage by decreasing the concentration gradient across the sediment/water interface and, therefore, reducing the mass flux of mirex into the water column.

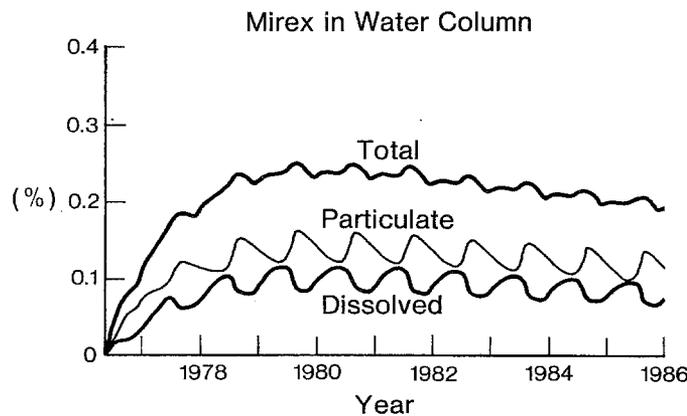


FIGURE 61.--Model approximation of percent total of water column mirex relative to sediments.

Cumulative mirex losses suggest that 99 percent is by sediment burial, 0.7 percent by volatilization, and 0.3 percent by outflow (figure 62). Burial losses dominate because of the high concentration of mirex in the sediment relative to that in the water column. After a 10-year simulation, approximately a third or 12 μg of mirex were lost owing to burial. In a more realistic situation where resuspension is taken into account, losses due to volatilization and outflow will be much higher, but will probably never exceed that due to burial.

In conclusion, the following three points can be made: (1) Less than 0.3 percent of mirex is ever present in the water column due to molecular diffusion from the sediments; (2) despite low solution concentrations the particle-associated mirex concentrations are relatively high. Background levels should range between 0.01 and 1 PPB; and (3) the effect of all mirex losses on water column concentrations is small and suggests that mirex should persist as a future source of contamination for at least the next two decades.

11. EQUILIBRIUM CONTAMINANT MODELING

A previous report (Eadie, 1981) described a model based on the concept of fugacity, which predicted the equilibrium distribution of hydrophobic organic contaminants in aquatic ecosystems. Although many synthetic organic compounds are designed and used because of their stability, they are subject to multiple environmental decomposition pathways, such as photolysis, biological decomposition, and chemical oxidation. These, along with physical processes, such as outflow and sediment burial, combine to remove the contaminant from an ecosystem. The obvious question to ask of a model is how long will it be before the contaminant concentration drops below a specified level.

There are several ways to address such questions; the approach basically comes down to the level of detail required and the level of information available. The latter is the constraining factor in the development of ecosystem models. This section describes a simplified approach in which all

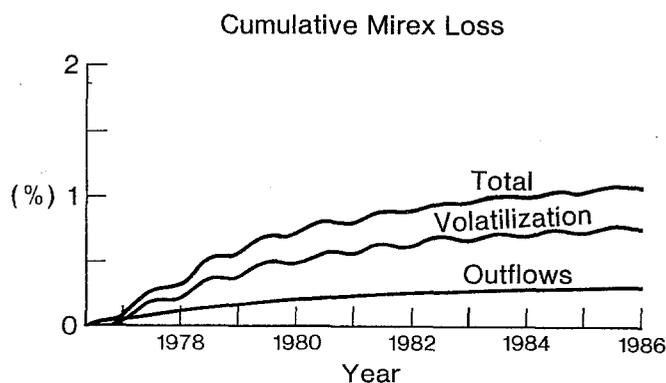


FIGURE 62.--Model approximation of cumulative percent loss of mirex from the water column.

transformations are handled as first order with respect to contaminant concentration and that provides useful insight into the fates of synthetic organic compounds in well-mixed aquatic systems.

11.1 Model Description

The model, which is based on the fugacity concept described in detail elsewhere (Mackay, 1979; Eadie, 1981), assumes all compartments are in equilibrium, but allows input and transformations. Briefly, the model calculates the fugacity or escaping tendency of the contaminant within each ecosystem compartment. At equilibrium, the fugacities in all compartments are equal. At the low concentrations of contaminant encountered, fugacity (f) is proportional to concentration (C),

$$C = fZ, \quad (43)$$

where Z is the fugacity capacity.

At equilibrium

$$f_1 = f_2 = \dots = f_i, \quad i = \text{number of compartments, and}$$

the total mass in the system (M) is

$$M = \sum C_i V_i, \quad (44)$$

where V_i = volume of the i^{th} compartment. Then from (43)

$$M = \sum f_i Z_i V_i = f_i \sum V_i Z_i; \quad (45)$$

thus

$$f_i = M / \sum V_i Z_i \quad (46)$$

and

$$M_i = f_i V_i Z_i, \quad (47)$$

where M_i is the contaminant mass in the i^{th} compartment. The concentration in the i^{th} compartment is

$$C_i = f_i Z_i. \quad (48)$$

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

- Vapor phases: PV = nRT ideal gas
 fV = nRT at low concentration
 CV = ZnRT from (1)
 Z = 1/RT from CV = n
 R = 82 x 10⁻⁶
 T is Kelvin temperature
- Liquid phases: H = P/C Henry's constant
 H = f/C at low concentration
 Z = 1/H from (1)
- Sorbed phases: Z = K_p/H,

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

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

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

- Fish: Z = 6 x bioconcentration factor H⁻¹
 log BCF = 3.5 - 0.54 log S
 factor of 6 converts wet weight to dry weight.

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

For more detail on these calculations, see Mackay (1979) and Eadie (1981). Decomposition at other removal processes (photolysis, biolysis), settling, and burial can be included in the fugacity model. All of the removal mechanisms are approximated as first-order reactions. The sum of the first-order rates for each compartment (i), period (j) is:

$$K_{ij} = \sum_{k=1}^n K_{i,j,k}, \quad n = \text{number of processes.} \quad (49)$$

Thus the total removal rate from compartment i is

$$V_i C_{i,j} K_{i,j} \text{ (mol/half year)} \quad (50)$$

For the purposes of initial analyses and flexibility, the ecosystem will represent a 1-m², 100-m-deep basin with the biological and sedimentary characteristics of Lake Michigan.

| <u>Ecosystem Compartment</u> | <u>Volume (m³)</u> | <u>Comments</u> |
|------------------------------|-------------------------------|--|
| Atmosphere | 10 ⁴ | 10-km thick |
| Epilimnion | 25 | 25-m deep |
| Hypolimnion | 75 | 75-m deep |
| Detritus | 1.5 x 10 ⁻⁴ | 1.5 ppm; 10 percent organic order |
| Biota | 5 x 10 ⁻⁶ | 50 mg m ⁻³ ; 40 percent organic order |
| Sediments | 2 x 10 ⁻² | 2 cm mixed; 2 percent organic order |
| Fish | 2 x 10 ⁻⁷ | |

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

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

Detritus settling is set at ~0.3 m day⁻¹ (Chambers and Eadie, 1981); thus, one-half of the detritus mass enters the sediment each time step and an equivalent mass of sediment is buried, leaving the mixed layer constant. For this model, the detritus mass is renewed each time step, keeping all compartment volumes constant. At the end of each time step, a mass balance calculation is made to warn of any internal inconsistencies.

11.2 Model Runs

The model was run for a mixture of PCBs as Aroclors®. The results are presented below. In the graphical output, winter conditions imply that the epilimnion was kept at 4°C for all time steps and that microbial decomposition was one-quarter and photolysis one-half of the summer case. These winter/summer scenarios were designed to approximately span the range of decomposition rates in the literature.

The environmental history of PCBs is similar in many ways to DDT. Both compounds were first developed in the 1930s and slowly leaked into ecosystems for which they were not intended. DDT values reported prior to about 1975 are

very often contaminated with PCBs because analytical techniques had not been designed to separate them.

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

Unfortunately, information on PCBs is predominantly reported in terms of commercially available mixtures, called Aroclors[®] in the United States. These are coded such that the last two digits represent the weight percent chlorine in the mixture (e.g., 1254 contains 54 percent chlorine, an average of five chlorines per molecule). Figure 63 illustrates the approximate composition of the Aroclors[®]. The modeling of these mixtures is very unsatisfying because of the range of characteristics and, consequently, environmental pathways that are "smoothed over" in this averaging process. Also, it appears that a major photodecomposition reaction is dechlorination, which produces another PCB. Improvements in ecosystem simulation models can only come when sufficient information is available to model the individual isomers.

The version of the model discussed in this report follows the movement of PCB mixtures 1242, 1248, 1254, and 1260. The model information is listed in table 26. The two temperatures and corresponding pairs of rate numbers and physical characteristics are designed to span a range that can be obtained

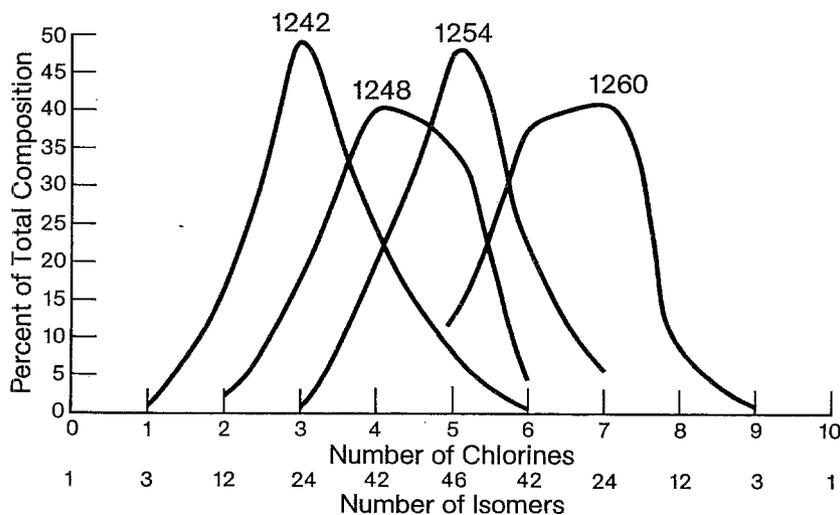


FIGURE 63.--Isometric composition of commercially available Aroclors[®]. Modified from NRC (1979).

TABLE 26.--Input parameters for PCB model

| | 1242 | 1248 | 1254 | 1260 | Comments |
|---|-------------|--------------|--------------|--------------|----------|
| "Molecular Weight" | 258 | 290 | 324 | 375 | 1 |
| Temperature (°C) | 4; 20 | 4; 20 | 4; 20 | 4; 20 | 1 |
| Solubility (g m ⁻³) | 0.20; 0.24 | 0.043; 0.054 | 0.010; 0.012 | 0.002; 0.003 | 2 |
| Vapor Pressure (mm Hg) x 10 ⁴ | 1.5; 7.2 | 1.3; 6.3 | 0.28; 1.5 | 0.14; 0.75 | 3 |
| Photolysis Rate (0.5 yr) ⁻¹ | 0.05; 0.1 | 0.03; 0.06 | 0.02; 0.04 | 0.01; 0.02 | 4 |
| Burial Rate (0.5 yr) ⁻¹ | 0.005; 0.02 | 0.005; 0.02 | 0.005; 0.02 | 0.005; 0.02 | 5 |
| Biolysis Rate (0.5 yr) ⁻¹ | 0.5; 1. | 0.2; 0.4 | 0.05; 0.1 | 0.01; 0.03 | |

- 1) From NRC (1979).
- 2) Calculated from information in NRC (1979).
- 3) Estimated from Simmons (personal communication).
- 4) From Chambers and Eadie (1981); J. A. Robbins (GLERL, pers. comm.).
- 5) Calculated from C. P. Rice (The University of Michigan, pers. comm.); Anderson (1980), Furukawa *et al.* (1978). See discussion on microbial decomposition rates for dissolved contaminant reduced by 10x (Lee and Ryan, 1979).

from the literature. The low rates (winter conditions) are combined for the first run and the high rates (summer conditions) for the second run, producing an envelope of prediction.

Individual process rates are often difficult to extrapolate from the literature. Early results from GLERL's program at The University of Michigan (M. S. Simmons, The University of Michigan, pers. comm.) provide the most realistic numbers for photolysis. These have been subjectively combined with the results of Safe and Hutzinger (1971), Ruzo *et al.* (1972), Herring *et al.* (1972), Hutzinger *et al.* (1972), and Crosby and Moilanen (1973). Variations in experimental conditions and exotic experimental procedures (from the point of view of someone trying to extrapolate to an aquatic ecosystem) make objective comparisons impossible. Thus, the photolytic rate numbers in table 26 are comparatively weak at this time.

Model output for sediments and biota are shown in figures 64 (winter conditions) and 65 (summer conditions). The winter condition is the result of

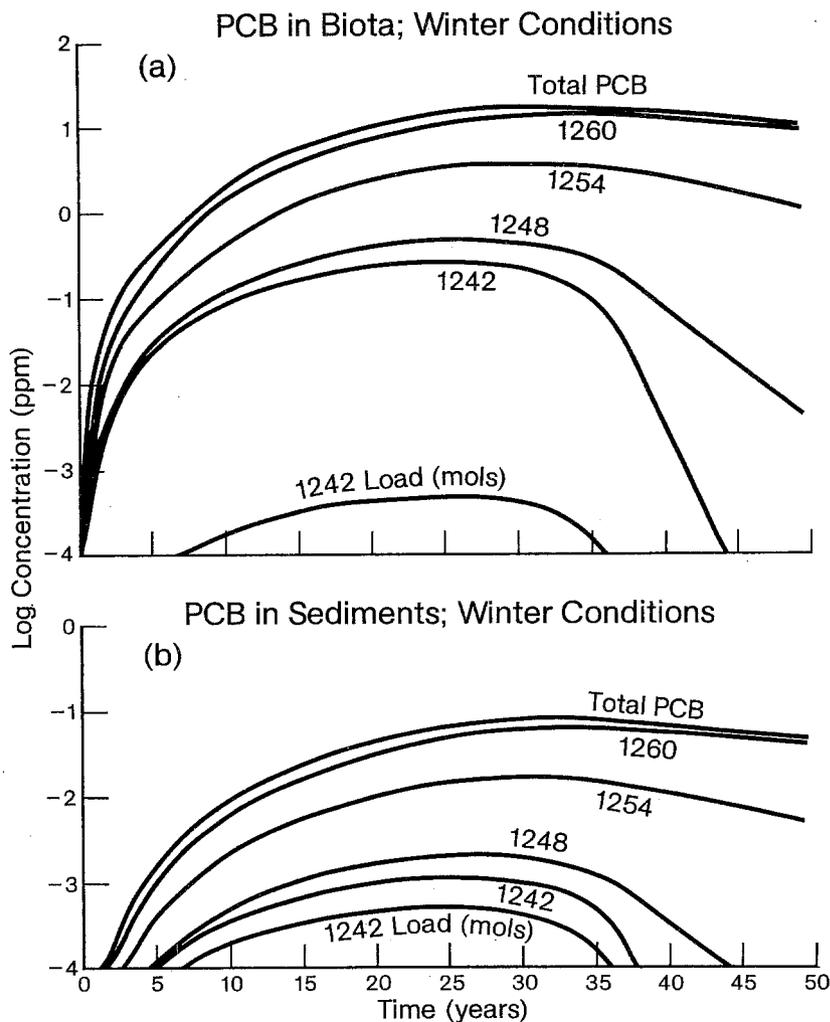


FIGURE 64.--(A) PCB mixtures in biota using the low rates in table 2. The numbers refer to Aroclors® as described in figure 6. The 1242 shape load is depicted to give a feeling for the shape of the input function. The other Aroclors® have the same load function but a lower ($0.25x$) magnitude. (B) PCB mixtures in sediments for the same run.

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

Year 35 is approximately equal to 1972. Figure 66 compares model output for the winter and summer cases with PCB data for Lake Michigan fish as summarized in Sonzogni *et al.* (1981). The model outputs can be moved up and down

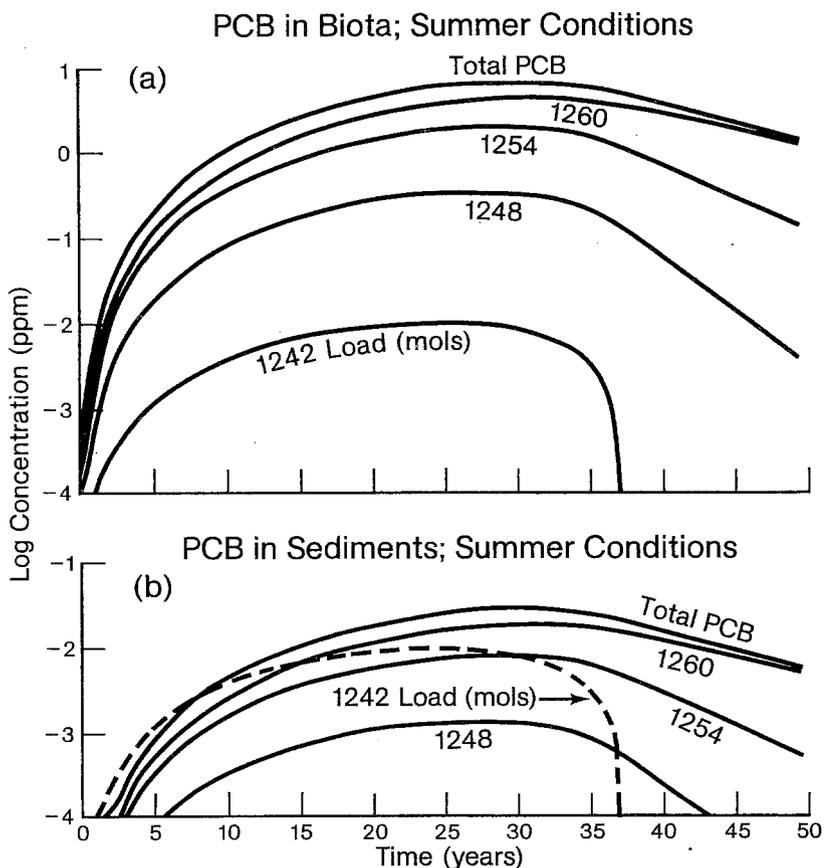


FIGURE 65.--(A) PCB mixtures in biota using the high rates in table 2.
 (B) PCB mixtures in sediments for the same run.

the page by altering the load, and the outputs will remain very nearly parallel. The agreement with bloaters and coho salmon is encouraging, considering the simplicity of the model. The lake trout data could not be simulated with a model as simple as this. Weininger (1978) proposed considerable food chain transfer from benthic organisms to lake trout and there is no food chain accumulation explicitly considered in this model.

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

The loss rates from the ecosystem are illustrated in figure 67. Aroclors® 1242, 1254, and 1260 are shown; 1248 is intermediate between 1242

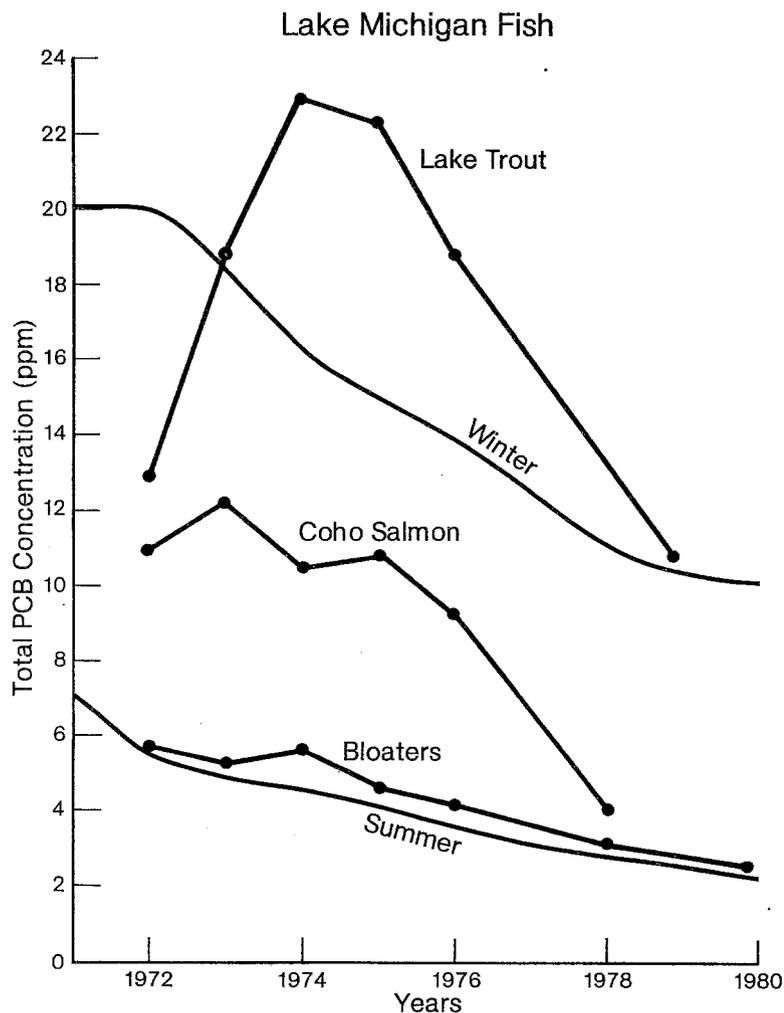


FIGURE 66.--Total PCBs in Lake Michigan fish. Data are from Konasewich et al. (1978) and IJC (1979). The model outputs for biota from the runs illustrated in figures 1A and 2B are shown as smooth curves.

and 1254, and was omitted for clarity. Atmospheric photolysis predominates, followed by microbial decomposition in the water and sediment. In the Great Lakes, burial is a slow process, which is slowed by bioturbation. The model considered a general condition of a 2-cm-mixed thickness with 0.5- to 1-mm accumulation per year. Assuming desorption occurs, the sediments can act as a source of stored hydrophobic contaminants for several decades.

12. MODELING HORIZONTAL TRANSPORT OF SEDIMENT-BOUND CONTAMINANTS

Mirex is a chlorinated hydrocarbon (C₁₀Cl₁₀) that has many applications, the primary one being an insecticide for fire ants in the southeastern region

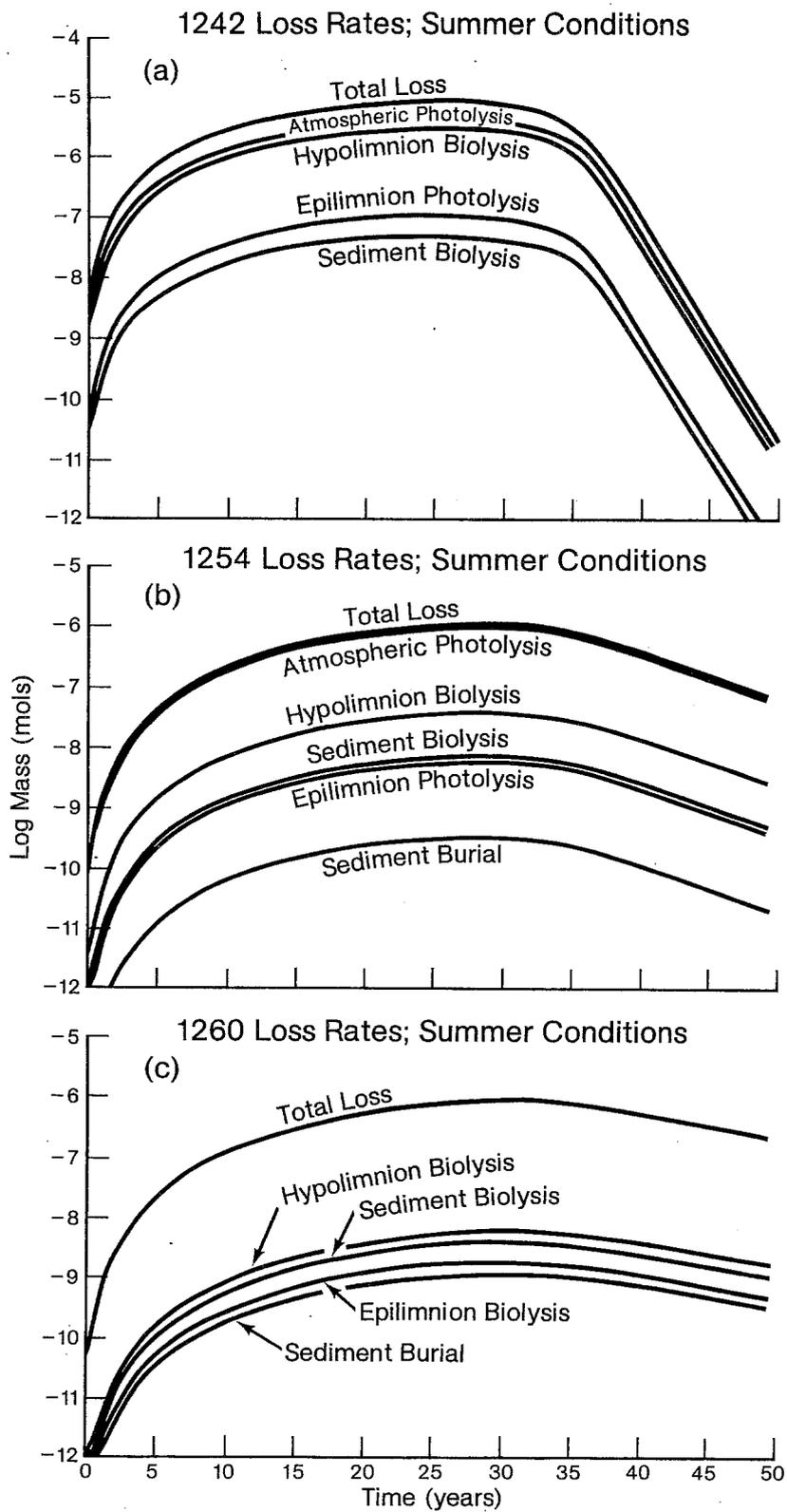


FIGURE 67.--PCB loss rates (mol per half year) from the summer scenario (figure 6). (A) Aroclor® 1242, (B) Aroclor® 1254, and (C) Aroclor® 1260.

of the United States. The compound was manufactured along the Niagara River and used in industrial processes along the Oswego River between 1959 and 1976. Both of these rivers flow into Lake Ontario, and by 1974 mirex was discovered in Lake Ontario fish (Kaiser, 1974). By 1976 both New York State and the province of Ontario had to issue warnings against Lake Ontario fish consumption, and New York soon extended the warnings to an outright ban. Summaries of this mirex problem, including history, health aspects, chemistry, quantities manufactured, applications, and fish and bird egg residues can be found in Hetling and Collin (1978) and Kaiser (1978).

The magnitude of the Lake Ontario contamination was made clearer when sediments taken during a 1968 lake-wide sampling program (Thomas *et al.*, 1972) were analyzed for mirex (Holdrinet *et al.*, 1978). These results suggested some 700 kg of mirex were mixed with the top 3 cm of sediments off the Niagara River and Oswego River mouths. These mirex-contaminated sediments extended in a path along Lake Ontario's south shore and around the eastern end of the lake.

Holdrinet *et al.* (1978) also analyzed a small number of replicate mirex samples taken in 1976. These new data were too limited to plot a distribution, but they suggested a doubling of mirex concentrations between 1968 and 1976. Production data (Kaiser, 1978) confirm that mirex was still being manufactured (and apparently escaping) until 1976.

By 1978, Canada and the United States had signed a Water Quality Agreement that required research to identify temporal and spacial trends in concentrations of persistent toxic substances such as mirex. As a result, model tests were run to determine whether the observed mirex pattern on the lake bottom was consistent with the known sources and with the lake's circulation pattern (Pickett and Dossett, 1979). A reasonable simulation of the observed pattern was obtained by allowing mirex to advect, diffuse, and settle from Niagara River and Oswego River sources in a simple circulation model. Results confirmed that the two known sources accounted for the quantity and pattern of the observed sediment contamination.

Although the above studies have provided much insight, the problems with mirex in Lake Ontario persist. Norstrom *et al.* (1978) and Norstrom *et al.* (1980) described how mirex is still migrating up the food chain and concentrating in fish and birds around the lake. The ecological impacts of this migration were described by the Great Lakes Water Quality Board (1978), and the human health aspects by the U.S. Food and Drug Administration (1978). Most recently, Scudato (1980) suggested that mirex will be a long-term threat in Lake Ontario because the sediments can act as recurring sources of the compound.

To help evaluate the above threat, we decided to simulate the horizontal movement of the mirex-contaminated sediments in Lake Ontario. To do this, we used current and water quality models to predict how resuspended mirex could move around the lake bottom over a 10-year period. Our major finding was that mirex-contaminated sediment patches tend to move around the eastern end of the lake and eventually out into the deep central basins.

12.1 Model Description

The model used in this paper was similar to the model used in Pickett and Dossett (1979). A steady-state current model was driven with the mean wind. This linear, homogeneous current model calculated vertical integrated transports for the given winds, and the effects of both bottom topography and the earth's rotation were included. Inflows were added at the Niagara River and Oswego River ($5,700$ and 180 m s^{-1} , respectively) and an outflow at the St. Lawrence River ($5,880 \text{ m s}^{-1}$).

Mirex calculations were next added to this simple circulation model so that mirex could advect, diffuse, settle, and resuspend according to:

$$H \frac{\partial C_w}{\partial t} + \nabla \cdot MC_w = A \nabla \cdot H \nabla C_w - \lambda C_w + k \left(\frac{\bar{M}}{H} \cdot \frac{\bar{M}}{H} \right) C_B \quad \text{in water} \quad (51)$$

and

$$D \frac{\partial C_B}{\partial t} = \lambda C_w - k \left(\frac{\bar{M}}{H} \cdot \frac{\bar{M}}{H} \right) C_B \quad \text{in the bottom.} \quad (52)$$

where $H(x,y)$ is local water depth (cm), $C_w(x,y)$ is mirex concentration in the water column (gr gr^{-1}), t is time (s), $M(x,y)$ is water transport ($3.5 \times 10^{-3} \text{ cm s}^{-1}$ or 3 m day^{-1}), A is a horizontal diffusivity ($1.5 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$), λ is a settling speed (0.083 cm s^{-1} or 3 m day^{-1}), k is a resuspension constant ($10^{-7} \text{ s cm}^{-1}$), C_B is the concentration of mirex in the sediments (gr gr^{-1}), and D is the depth of sediment contamination (3 cm).

Horizontal diffusivity was taken from dye experiments (Kullenberg *et al.*, 1974), and settling speed was taken to be 3 m day^{-1} because mirex was assumed to attach to fine particles.

Resuspension was allowed by adding a new term to the original model. This term depended on a constant (k) times current speed squared (kinetic energy of the water). We selected the constant by noting that suspended particles in Lake Ontario average about 3 ppm (Bell, 1980), and that observed mirex in the bottom was initially around 10 ppb (Holdrinet *et al.*, 1978). Hence resuspension would bring up 30×10^{-15} units of mirex per unit of lake water [$(3 \times 10^{-6})(10 \times 10^{-9})$]. Thus in the total volume of Lake Ontario ($1.64 \times 10^{18} \text{ cm}^3$) some 50 kg of mirex would be resuspended on particles. Hence, we selected a value of k ($10^{-7} \text{ s cm}^{-1}$), which resulted in roughly this amount of mirex resuspended in Lake Ontario water at any one time.

Using the original models with the new formulation for resuspension, we projected the movement of mirex-contaminated sediments for 10 years. This was done by starting with the observed mirex pattern in Holdrinet *et al.* (1978) and using a mean wind of 7 m s^{-1} from the west (National Climatic Center, 1975) that blew over the lake for the entire period.

12.2 Results

Figure 68 shows the distribution of mirex in the model. Since the initial conditions have all the mirex in the sediments, about 2 months are required for a balance between resuspension and settling to occur. As mentioned earlier, the amount of mirex in the water attached to particles is controlled by resuspension. The rest of the mirex (about 85 percent) is in the bottom.

In addition to the 2-month time scale mentioned above, there are also several other time scales of interest. For example, the time required for material to settle out of the lake depends on the settling speed (3 m d^{-1} in the model) divided by local water depth. This value ranges from about 3 months over the deepest regions, to 1 month over regions near the mean depth (90 m), to a few days over nearshore regions.

Opposing this settling is resuspension. Initially resuspension continues until all of the 3 cm of mirex-laden sediment is eroded. The total time for this to happen equals 3 cm divided by the resuspension constant and by the current speed squared. In regions of low currents (1 cm s^{-1}), about a year is required to erode the initial mirex-laden sediment. In regions of moderate currents the time is about a month. Finally, in regions of higher currents ($> 10 \text{ cm s}^{-1}$), only a few days are required to erode the top 3 cm of sediment.

Besides this up and down motion of mirex, there is also a net loss that occurs due to the St. Lawrence River outflow.

This outflow loss is small because only a small portion of the mirex is attached to suspended particles at any one time and thus available to be carried out the St. Lawrence River. Since the flushing time of Lake Ontario is about 10 years, and since only 15 percent of the mirex is resuspended and available for flushing, some 60 years would be required for the Lake Ontario mirex to dilute to one-third of its original value.

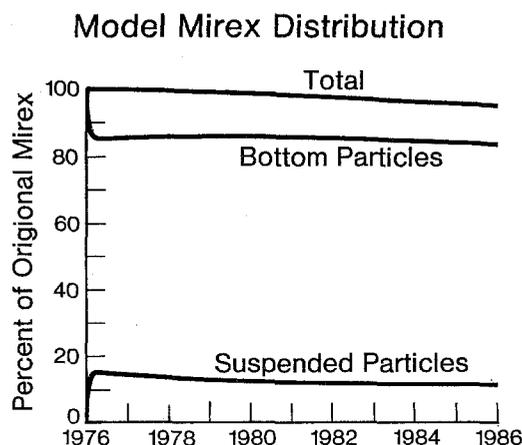


FIGURE 68.--The simulated distribution of mirex in Lake Ontario.

Figures 69 through 74 show the observed and predicted mirex patterns in the sediments of Lake Ontario. During the first few years the mirex-contaminated sediments simply move eastward along the south shore of the lake. The pattern also becomes smoother as it migrates eastward.

After 4 years, mirex is starting to accumulate in the lower current regions of the western and central basins. The mirex patch north of the Niagara Bar did not come from mirex moving directly north. Instead, this patch is accumulating from mirex moving east down the center of the lake and being deposited off the Niagara Bar.

After 6 years, the trend is continuing with accumulation into the center of the low current regions and a gradual eastward drift of the south shore

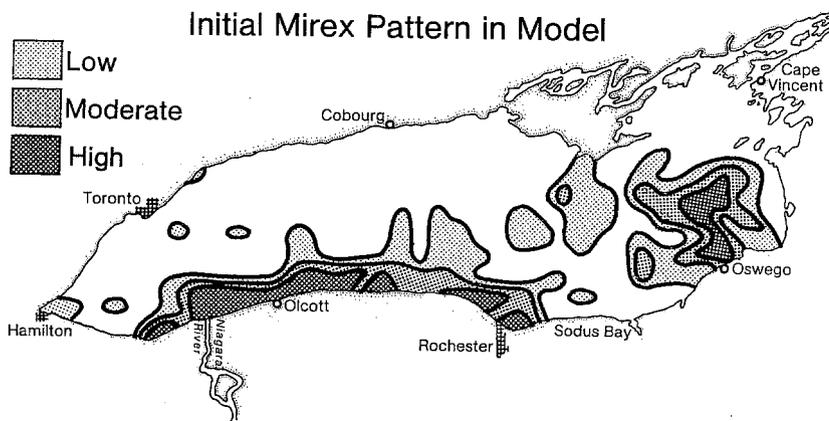


FIGURE 69.--Initial distribution of sedimentary mirex, based on the data in Holdrinet et al. (1978).

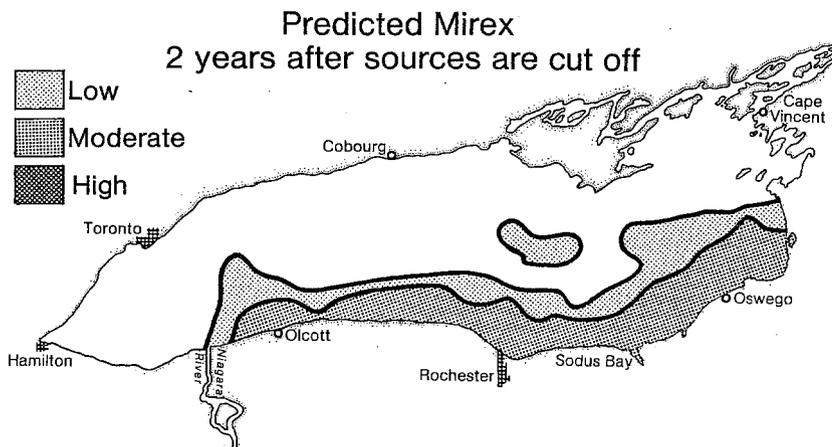


FIGURE 70.--Predicted sedimentary mirex distribution 2 years after source is cut off.

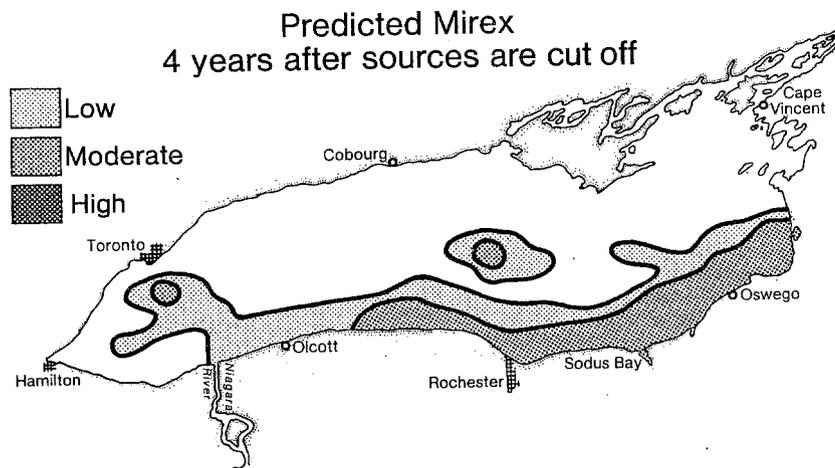


FIGURE 71.--*Predicted sedimentary mirex distribution 4 years after source is cut off.*

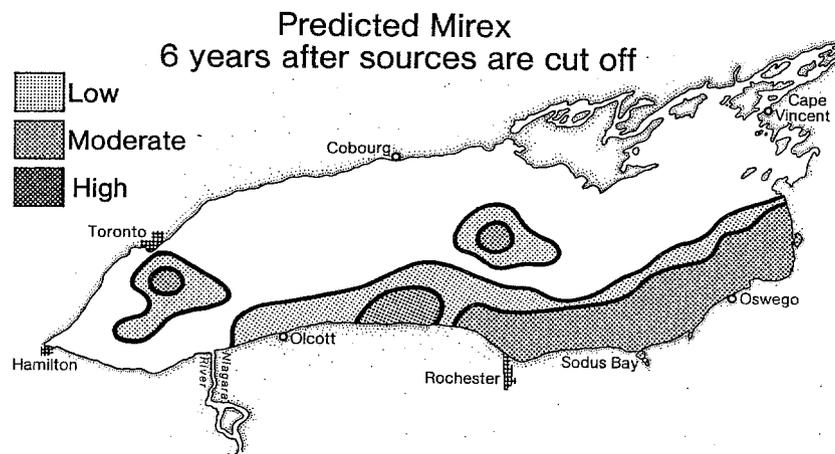


FIGURE 72.--*Predicted sedimentary mirex distribution 6 years after source is cut off.*

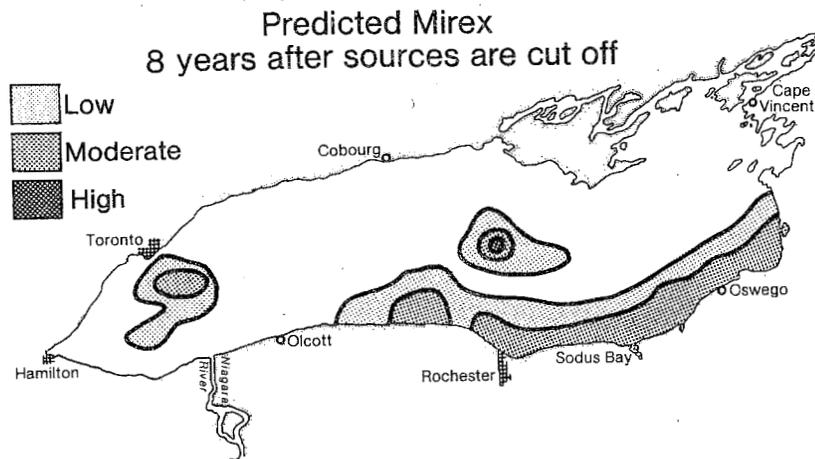


FIGURE 73.--*Predicted sedimentary mirex distribution 8 years after source is cut off.*

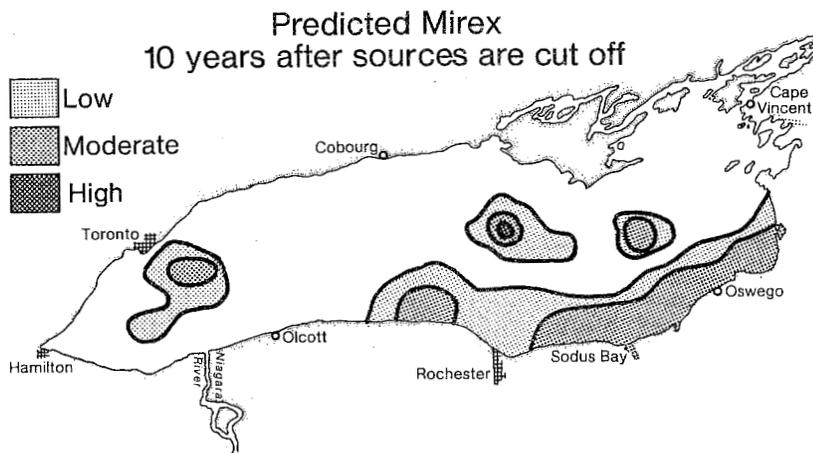


FIGURE 74.--*Predicted sedimentary mirex distribution 10 years after source is cut off.*

patch. After 8 years all the original mirex on the Niagara Bar region has moved eastward.

Finally, after 10 years, the prediction shows three patches: eastern and western deep water patches that continue to accumulate, and a southeastern patch that is a vestige of the original south shore contamination.

13. CONCLUSIONS

The above predictions suggest some general conclusions about the future of mirex in Lake Ontario. First, deep regions will accumulate mirex or any

other pollutants attached to fine sediments. The bottom concentrations in these regions, however, will be mitigated by a process ignored in this model--burial. Burial is important because some 5 million tons of fine-grained sediments are added to Lake Ontario each year (Kemp and Harper, 1976). Polluted sediments will be diluted and buried by some 2 cm of fresh, and hopefully uncontaminated, sediments per decade.

Second, the model shows little mirex ending up on the lake's north shore. Strong north shore currents and no initial load combined to keep the north shore clean.

Third, the southeastern mirex patch lasts a long time. The strong south shore currents driven by the prevailing west winds moved the initial mirex patch eastward. But as the mirex reached the eastern end of the lake, currents slowed down and turned northward, and the rate of mirex migration also slowed. Hence the southeastern mirex patch remains and only slowly bleeds mirex to the deep regions.

Fourth, hypothetical model runs showed similar final results regardless of which Lake Ontario river was assumed to leak mirex. By moving a mirex source to each river, we found that it would always move eastward, then turn and head for the deep basins. By contrast, when sources were placed in the deep basins, the mirex stayed there. Resuspension was insufficient to move the mirex. These model runs suggest that any sediment-attached contaminant from any Lake Ontario river will end up in the deep basins in a few decades.

We also tested the sensitivity of the above results to the wind by trying a variety of steady and time varying winds. We found that west winds do the major sediment movement, because they occur most frequently and set up the strongest currents.

In similar fashion, we tested a variety of resuspension formulations and values. Higher resuspension made the contaminants move faster, but the pattern was basically unchanged.

In summary, our work suggests a general pattern of movement for sediment-attached pollutants in Lake Ontario. Nearshore sources produce eastward migrating sediment patches that reach the eastern end of the lake, turn around, and eventually end up accumulating and being buried in the western and central deep basins.

Confirming evidence for this pattern comes from surveys of other sediment-attached pollutants. Studies of PCBs in Lake Ontario sediments (Frank *et al.*, 1979) show a similar south shore patch with some accumulation in the deep basins. One suspects an original Niagara River source. Mercury in Lake Ontario sediments (Thomas, 1972) also shows a patch streaming eastward along the south shore. Finally, decomposition products from the relatively old pollutant DDT (Frank *et al.*, 1979) are now found mainly in deep basin sediments.

The slow movements, small dilution, and slow burial predicted above suggest that sediment-attached pollutants in the Great Lakes will pose problems

far into the future. These results, coupled with the fact that millions of people drink the water, make the Great Lakes dangerous dumpsites for such chemicals.

14. SUMMARY

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. Research-modeling interactions enable us to make stepwise improvements in our understanding of the cycling, behavior, and fate of synthetic contaminants and to identify priority research areas.

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 will incorporate the information into our modeling program to improve our parameterizations of processes occurring in that region.

This past year 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.

This interim report discusses results of most of our current projects, which are in various states of completion. A summary of recent accomplishments in our program include:

- 1) Equilibrium models that predict the distribution of an organic contaminant based on the contaminants' 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 bioconcentration 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, and

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

In addition to the work on behavior and fate (which is the focus of our ongoing program), we are beginning a major new program on the modeling of contaminant uptake by fish. Currently we model fish as passive substrates upon which contaminants can sorb. A more realistic approach employs bioenergetics and food chain transfer that connects fish to their food source. Our work on the bioaccumulation of PAH by benthic organisms indicates that they may be an important vector for the movement of contaminants from the sediments into the food web. This process will be incorporated through our new grant to Jim Breck at Oak Ridge.

Another new area for our program are the two projects on effects of contaminants. Studies of bioturbation and mixing rates will give us information on mixing of recent sediments. These experiments are also designed to use mixing rates as a behavioral indicator of chronic stress in worms exposed to increased levels of contaminants. A second stress test for benthic organisms is under study: the lysosomal enzyme release rate. After a year or two of laboratory development, these tests will be used to estimate the condition of indigenous Great Lakes benthic organisms.

14.1 Modeling Strategy

We are structuring our modeling efforts more toward answering the most likely kinds of questions to be asked regarding toxic contaminants, such as:

- How long will the concentration of contaminant xyz in fish be above the level recommended by the FDA, IJC, EPA, etc.?
- What level of load reduction is necessary to achieve a specified concentration of contaminant xyz in fish, birds, water, etc.?
- If such a load reduction is implemented, how long will it take the system to respond?

We feel that by developing the tools to answer such questions we are addressing some of the major responsibilities of both the OMPA and GLERL.

Our long-term models will be modified to become a coupled Great Lakes model. They will incorporate resuspension input and the time steps shortened to 1 month in order to incorporate the variances associated with changing particle characteristics. Case studies of DDT, PCBs (characterized by chlorine content), cesium-137, and PAHs will be run.

We will continue to improve our detailed process model and run studies on air/water exchange and sediment/water exchange. Another component of this modeling exercise is an analysis of the sensitivity of its response to perturbations in input information and coefficients. Such error analyses enable us to examine the most sensitive areas of the model in greater detail and aid us in our research planning.

15. 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 made presentations at scientific meetings.

A list of our program documents and presentations through September 1982 follows.

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16. ACKNOWLEDGMENTS

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