NOTICE: Return or renew all Library Materials! The Minimum Fee for each Lost Book is $50.00.

The person charging this material is responsible for its return to the library from which it was withdrawn on or before the Latest Date stamped below.

Theft, mutilation, and underlining of books are reasons for disciplinary action and may result in dismissal from the University.

To renew call Telephone Center, 333-9400

UNIVERSITY OF ILLINOIS LIBRARY AT URBANA-CHAMPAIGN
EFFECT OF PHYSICOCHEMICAL PARAMETERS ON PESTICIDE DEGRADATION

ILENR/RE-EH-86/06
UNIVERSITY OF ILLINOIS LIBRARY.
AT URBANA-CHAMPAIGN
AT URBANA-CHAMPAIGN
AGRICULTURE
EFFECT OF PHYSICOCHEMICAL PARAMETERS
ON PESTICIDE DEGRADATION

Prepared by
Illinois State Water Survey
2204 Griffith Drive
Champaign, IL 61820

Principal Investigators
John A. Helfrich
Jessica J. St. Aubin

Prepared for
Illinois Department of
Energy and Natural Resources
Energy and Environmental Affairs Division
325 W. Adams
Springfield, IL 62704-1892

James R. Thompson, Governor
State of Illinois
Don Etchison, Director
Illinois Department of
Energy and Natural Resources
This report has been reviewed by the Illinois Department of Energy and Natural Resources (ENR) and approved for publication.

Printed by the Authority of the State of Illinois.

Date Printed: September 1986
Quantity Printed: 200
Referenced Printing Order: IS 36

One of a series of research publications published since 1975. This series includes the following categories and are color coded as follows:

- Energy Resources - RE-ER - Red
- Water Resources - RE-WR - Blue
- Air Quality - RE-AQ - Green
- Environmental Health - RE-EH - Grey
- Economic Analysis - RE-EA - Brown
- Information Services - RE-IS - Yellow
- Insect Pests - RE-IP - Purple
ABSTRACT

EFFECT OF PHYSICOCHEMICAL PARAMETERS ON PESTICIDE DEGRADATION

Modern agricultural practices continue to rely heavily on the use of herbicides and insecticides to maintain or increase crop yields. Past pesticide usage, especially of organochlorine compounds such as DDT, aldrin, heptachlor and chlordane, has resulted in serious environmental damage. Illinois surface waters and lake sediments have been contaminated with these compounds and their degradation products as a result of their heavy and prolonged usage. A 1979 IEPA survey (Kelly and Hite 1981) of Illinois lakes revealed dieldrin residues in 58% of the 63 lakes surveyed; heptachlor epoxide was detected in 25% of the samples. Sediment samples collected from Lakes Mattoon and Paradise in the summer of 1985 still contained dieldrin residues almost 10 years after use of its precursor, aldrin, had been discontinued. The levels of dieldrin appear to have declined more in Lake Mattoon than in Lake Paradise. It is believed that this is a result of the lower sediment redox potential and higher levels of surficial ferrous iron found in Lake Mattoon. Degradation products resulting from the decomposition of dieldrin could not be isolated. It is surmised that this is because the concentration of the degradation products is below analytical detection limits and/or the compounds have become chemically bound to sedimentary humic materials.
<table>
<thead>
<tr>
<th>TABLE OF CONTENTS</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>4</td>
</tr>
<tr>
<td>Methods and Materials</td>
<td>5</td>
</tr>
<tr>
<td>Sediment Collection</td>
<td>5</td>
</tr>
<tr>
<td>Inorganic Analysis</td>
<td>6</td>
</tr>
<tr>
<td>pH/ORP</td>
<td>6</td>
</tr>
<tr>
<td>Sulfide and Wet Density</td>
<td>7</td>
</tr>
<tr>
<td>Pore Water Analyses</td>
<td>7</td>
</tr>
<tr>
<td>Organic Analyses</td>
<td>8</td>
</tr>
<tr>
<td>Sediment Cores</td>
<td>8</td>
</tr>
<tr>
<td>Dieldrin Degradation Experiment</td>
<td>10</td>
</tr>
<tr>
<td>Instrumental Conditions</td>
<td>11</td>
</tr>
<tr>
<td>Results</td>
<td>12</td>
</tr>
<tr>
<td>Discussion</td>
<td>15</td>
</tr>
<tr>
<td>Conclusions</td>
<td>19</td>
</tr>
<tr>
<td>References</td>
<td>20</td>
</tr>
<tr>
<td>List of Tables</td>
<td>24</td>
</tr>
<tr>
<td>List of Figures</td>
<td>26</td>
</tr>
</tbody>
</table>
INTRODUCTION

Modern agricultural practices in use since the early 1950's have continued to rely heavily on the use of herbicides and insecticides to maintain or increase crop yields. As the number of acres under cultivation has increased so has the amount of pesticides applied. During 1971-72 about 34 million pounds of the active ingredient of pesticides were applied to more than 14 million acres of Illinois farmland (Metcalf and Sanborn 1975). In 1982 (Pike and Colwell 1983) farm acreage receiving pesticides had increased to more than 26 million acres and pesticide applications totaled more than 72 million pounds of active ingredient.

Unfortunately, many of the pesticides that were heavily used in the past were discovered to have devastating ecological effects only after millions of pounds of the chemicals had already been introduced into the environment. The problems surrounding past use of organochlorine insecticides, such as DDT, aldrin, heptachlor and others, are now well known (Steffey et al. 1984; MacMonegle et al. 1984; Havera and Duzan 1986). The discovery in the 1960's and 70's of the environmental impact of synthetic organic chemicals spurred an intensive research effort aimed at trying to understand the consequences of past mistakes in order
to avoid future mistakes. As an example, a USEPA study, cited by Metcalf and Sanborn (1975), recommended "a massive interdisciplinary research effort be mounted to clarify the environmental behavior of major pesticides . . .". The research called for, among other things, information on fates, routes of degradation and the nature of the ultimate breakdown products of these chemicals.

Past usage of organochlorine pesticides in Illinois, especially the cyclodiene insecticides aldrin, heptachlor and chlordane, has been very high. In the 20-year period between their introduction in 1954 and 1975 it is estimated that more than 82 million pounds of aldrin and heptachlor were applied to Illinois farm soils (Metcalf and Sanborn 1975). Wiersma et al. (1972) estimated that more than 60 million pounds of aldrin alone was applied to Illinois farmland between 1954 and 1972. As a result of the massive use of this chemical, soils in Illinois had the highest average levels of aldrin (0.13 ppm) and dieldrin (0.11 ppm), the epoxidation product of aldrin, in the nation (Wiersma et al. 1972). The last appreciable use of aldrin was in 1977; heptachlor use was discontinued after 1978 (Steffey et al. 1984).

Contamination of Illinois surface waters and sediments with organochlorine pesticides occurred primarily from agricultural runoff. In a 1979 survey of 63 lakes conducted by the Illinois Environmental Protection Agency (Kelly and Hite 1981) dieldrin was detected in more sediment samples (58%) than any other pesticide. Heptachlor epoxide, the epoxidation product of heptachlor, was detected in 25% of the samples. The highest pesticide levels were found in lakes having large watersheds under intensive row crop cultivation. Sediments from Lake Mattoon and
Lake Paradise, in east-central Illinois, were both found to have among the highest dieldrin levels in the state. Ten of the 63 lakes had dieldrin levels exceeding 19 µg/kg sediment (dry weight). The highest level in Lake Mattoon was 25 µg/kg, while the highest level in Lake Paradise was 51 µg/kg. Lake Bloomington had the distinction of having both the highest dieldrin level, 87 µg/kg, and the highest heptachlor epoxide level, 13 µg/kg, in the state. Lake Mattoon followed Lake Bloomington with the second highest heptachlor epoxide level in the state (12 µg/kg).

There is presently a significant gap in the literature concerning the ultimate breakdown products of compounds such as the cyclodiene insecticide residues, dieldrin and heptachlor epoxide, under the highly reducing conditions typically found in the sediments of reservoirs and wetlands common to Illinois. Although much work has been done in the past to determine the environmental fate of these and other agricultural chemicals, many of these studies (Metcalf et al. 1973; Sanborn and Yu 1973; Sanborn et al. 1977; Paris et al. 1975; Sharom et al. 1980a,b) have focused on aerobic aquatic systems or well drained agricultural soils. These conditions do not reflect the physicochemical conditions of sediments in which these compounds are deposited. Oxidation reactions, whether chemically, photochemically or microbially mediated tend to form more hydrophilic (water soluble) by-products that are less likely to associate with organic matter than the parent compound. In the case of aldrin and heptachlor these alterations primarily involve epoxidation, beta-oxidation, and diol formation at the $R_1CH=CHR_2$ double bond without reducing the level of chlorination (Matsumura et al. 1968).
The purpose of this project was twofold: (1) to isolate and identify degradation products of selected pesticides that have demonstrated environmental impacts, and (2) to correlate their presence and abundance with the physicochemical parameters of the sedimentary environment. Dieldrin and heptachlor epoxide were chosen for this study because: (1) previous studies (Kelly and Hite 1981) had shown their presence in relatively high amounts in the sediments of nearby municipal water supply reservoirs (e.g. Lake Paradise and Lake Mattoon), (2) the presence of these compounds and their degradation products in dredged sediments might cause environmental problems if the sediments were used for agricultural or other purposes (e.g. uptake/bioaccumulation by plants or biota), (3) the residues have been present in the sedimentary environment for a sufficient period of time (some for at least 30 yrs) that "ultimate" degradation products might be present that would probably not be observed in the much shorter period under which most laboratory experiments are run, and (4) they are representative of the class of highly stable synthetic organic compounds that have been introduced into the environment over the past 30-40 years in great abundance. Very little is known of their long-term environmental and biogeochemical behavior.

ACKNOWLEDGEMENTS

This project was funded by the Department of Energy and Natural Resources (ENR Contract No. EH21); Thomas K. Heavisides and Douglas Wagner were project managers. The authors would also like to thank the
following people for their assistance: Michael J. Barcelona, Gary R. Peyton and Thomas R. Holm for their suggestions and encouragement during the project and for review of the manuscript; Ed Garske for help with field work; Professor Bruce Rittmann for use of his centrifuge; J. Carter Cook of the University of Illinois Mass Spectrometry Laboratory for chemical ionization MS analyses; and Pam Beavers for typing the manuscript.

METHODS AND MATERIALS

Sediment Collection

Sediment core samples were collected from Lake Paradise (7/25/85) and Lake Mattoon (10/25/85) using a gravity coring device. Sampling sites were chosen to coincide as closely as possible with sites used during the IEPA lake surveys in 1979 (Kelly and Hite 1981). The Lake Paradise site coincides with IEPA site #1; the Lake Mattoon site coincides with IEPA site #2. Enough cores were obtained at each site to provide ample sediment samples for all organic and inorganic analyses.

The corer was fitted with clear polycarbonate (Cadillac Plastics) core liners (1-3/4" OD x 1-5/8" ID x 1/16" wall thickness x 26.8" long). Core liners were of three types: (1) solid, for organic and pore water analyses; (2) drilled with 1.6 cm diameter holes spaced 2.0 cm between centers in a single helical pattern along the length of the liner; and (3) drilled with holes as above but in a double helical pattern. The last two types of liners were used for measuring pH/ORP and for taking sulfide and wet density subsamples. Prior to insertion into the corer
the drilled liners were wrapped with duct tape to keep the sediment core intact. Upon removal from the corer, sediment filled cores that were to be saved for transport back to the lab were immediately sealed by taping polyethylene caps onto both ends of the liner tube. The cores were then labeled, tightly wrapped in a plastic bag to inhibit oxygen diffusion, and stored in an upright position surrounded with ice until return to the lab where they were placed in cold storage (5°C) until time of analysis.

INORGANIC ANALYSES

pH/ORP

pH and oxidation-reduction potential (ORP) were measured in the field on selected cores by inserting the electrode into the core through the holes drilled in the liner.

The refillable pH/ORP (platinum) combination electrode with saturated KCl calomel reference was designed with a spear tip and an annular ceramic junction for use in sediment (No. 5773913 10B, pHoenix Electrode Co., Houston, TX). The electrodes were calibrated at pH 4.01, 6.86, and 9.18 before use and were checked between analyses. ORP was checked at +430 mV and +190 mV (Redox calibrating solution, Schott-Gerate GmbH, D-6238 Hofheim a. Ts.). An equilibration period of ten minutes was found necessary for ORP measurement in the sediment. pH and ORP were measured and recorded simultaneously by connecting the separate leads to two pH meters (Orion model 231).
**Sulfide and Wet Density**

Sulfide and moisture content were measured in the laboratory using an undisturbed core. Sulfide was measured with an ion-selective electrode (Orion model No. 94-16-00) against a double junction reference electrode (Orion model No. 90-02-00). The electrode system was calibrated with diluted, certified 100 ppm sulfide standards (Orion Research, Inc.).

Sediment core subsamples for sulfide determinations were taken by gently inserting a 5 mL plastic syringe (Plastipak, Becton Dickinson), with tip cut off, into the sediment core through the holes in the liner while slowly pulling the plunger back to fill the syringe with sediment. Two or three milliliters of sediment thus obtained were then transferred to a 50 mL beaker containing 15 mL of sulfide antioxidant buffer (SAOB II; Orion Research, Inc.) and 12 to 13 mL deaerated, deionized water, for a total volume of 30.0 mL. All solutions were mixed 50% sample (or standard):50% SAOB II.

Sediment subsamples for percent water measurements were taken by the same technique as were sulfide samples. The samples were weighed before and after drying. Sediment-moisture content was calculated after drying 24 hours at 110°C.

**Pore Water Analyses**

A fresh core was used for determinations of iron, nitrite, and ammonium ions in pore waters. The core was subsectioned at 10 cm intervals by pushing the sediment out of the liner from the bottom using a Teflon(R) plunger. The sediment was immediately transferred to 50.8 x
152 mm polypropylene centrifuge bottles and capped. The bottles were balanced and centrifuged for 20 minutes at 500 rpm using a Damon/International Equipment Company model CU-5000 centrifuge.

The supernatant was filtered through a 0.4 μm polycarbonate membrane filter (Nucleopore Corp.). Three samples were collected for analysis: (1) iron (preserved with HCl); (2) nitrite (preserved with chloroform); and, (3) for ammonia determination (unpreserved).

Manual analysis of all pore water constituents was done on micro-liter volumes of sample due to the limited sample size. The analytical methods were modified from standard techniques, such as Standard Methods, (APHA 1985), and are detailed in the ISWS Aquatic Chemistry Section's Method Manual. Reaction vessels were 5 mL polyethylene snap-cap vials (Nalgene). Spectrophotometer determinations were performed in 1 cm semi-micro masked cells (Spectrocell Precision Glass Products Co., Oreland, PA) using a Beckman model DU spectrophotometer. EPA and/or USGS quality control samples were run along with pore water samples on each day of analysis.

ORGANIC ANALYSES

Sediment Cores

All solvents (Burdick and Jackson) and pesticide standards (Supelco, USEPA) were used as received. All glassware was washed, solvent-rinsed and heated in a muffled furnace at 450 °C for 1 hour before use.

A fresh core was used for analysis of the cyclodiene pesticide residues, dieldrin and heptachlor epoxide, and their degradation
products. Sediment sections were extruded from the liner and transferred to pre-extracted cellulose thimbles (Whatman, 43 mm x 125 mm) for Soxhlet extraction. The sediment was then weighed and extracted with 250 mL of acetone for 12 hours. Before starting the extraction, the sediment was mixed with some of the acetone in the thimble by stirring with a glass rod. Difluorobiphenyl (DFBP), a surrogate pesticide standard used to monitor analytical recovery, was then added to the sediment. After 12 hours the acetone was removed and followed by a second 12-hour extraction with 250 mL of 1:1 acetone:hexane. Upon completion of the extraction process the acetone:hexane extract was combined with the acetone extract. The thimbles were removed, dried, and weighed to determine the dry weight of the sediment.

The combined extracts were transferred to a 1-L separatory funnel and washed with 300 mL of pH 11-12 water, prepared from deionized double-distilled water. The hexane was separated from the acetone/water layer. The acetone/water extract was then reextracted with hexane three times (100, 100, and 50 mL). The hexane extracts were combined and dried by passing through a column (400 mm x 22 mm ID with glass frit and Teflon® stopcock) containing approximately 12 g of activated copper (granular, 20-30 mesh, J. T. Baker Chemical Company) for removal of sulfur interferences and 60 g of anhydrous pre-extracted sodium sulfate (Fisher Scientific Company, certified A.C.S.).

The dried hexane extracts were then concentrated by rotary evaporation (Buchi/Brinkmann, Rotavapor RE-120) to approximately 1-2 mL. The extract was transferred to a 10 mL concentrator tube and the solvent
reduced to 1.0 mL use a mini-Kuderna Danish apparatus and a Kontes tube heater. Alternatively, the sample was transferred to a 5.0 mL Reacti-Vial (Pierce Chemical Company) and evaporated to 1.0 mL under a gentle stream of high-purity nitrogen.

Florisil (PR 60/100 mesh) column chromatography was used to separate the pesticide residues from coextracted organics (USEPA 1982). The florisil fractions were concentrated by rotary evaporation and reduced to 1.0 mL under a stream of N₂. Samples were then transferred to 1 dram vials with Teflon(R)-lined septa, and spiked with the internal standard, dibutyl chlorendate (DBC) (USEPA, Pesticides & Industrial Chemicals Repository, RTP, NC).

Blank and spiked sediment samples were run with each batch of sediment extractions. Blank samples containing only solvents are used to monitor glassware and reagent interferences. Selected sediment samples (usually taken at > 30 cm depth) were spiked with known amounts of the target pesticides at the same time the DFBP was added to monitor recovery.

**Dieldrin Degradation Experiment**

A second set of sediment samples were collected with an Eckman dredge from Lake Mattoon (11/26/85) for a short-term anaerobic degradation experiment. The sediment was transported back to the lab under anaerobic conditions in a sealed glass jar. An anaerobic generator (BBL(R) GasPack(R), Becton Dickinson and Co.) was placed in the jar to help maintain a temporary oxygen-free environment. Upon arrival at the lab, the sample was transferred to a N₂-filled glove box (Labconco
Corp., model 50004) which had been purged with oxygen-free N₂ for more than 24 hours. The sediment was allowed to equilibrated with the N₂ atmosphere at room temperature for eight days in darkness. Prior to fortification with dieldrin, the sediment was analyzed for sulfide, pH, oxidation-reduction potential, ferrous and ferric iron, nitrate, nitrite, ammonia, and sulfate.

After a period of eight days equilibration in the dark under the N₂ atmosphere, the sediment was thoroughly mixed and transferred to 120 mL serum bottles in the glove box. The bottles were capped with Teflon(R)-lined rubber septa and aluminum seals. Five days later, approximately half of the serum bottles were spiked with dieldrin (USEPA, Pesticides & Industrial Chemicals Repository, RTP, NC) by syringe through the septa, at 86 μg/100 mL sediment slurry. The rest of the bottles were kept as controls. The bottles were shaken periodically to distribute the dieldrin.

Duplicate controls and spiked samples were removed from the glove box on days 8 and 64 and extracted by the same procedure as for the core samples. The entire content of each bottle was transferred to the thimbles and extracted.

**INSTRUMENTAL CONDITIONS**

Analysis of sediment extracts was performed on a Varian 3700 gas chromatograph (GC) equipped with a 63Ni electroncapture detector and a Hall Model 700A electrolytic conductivity detector. A Hewlett Packard 5790 gas chromatograph with 5970B mass selective detector (MSD) was used
for qualitative analysis. SPB 608 (Supelco) bonded phase fused silica capillary columns (30 m x 0.25 mm i.d.) were used for all analyses. The temperature program was as follows: 100°C for 4 minutes, increase to 290°C at 8°C/min, hold at 290°C for 5 minutes. The injector temperature was 200°C; MSD capillary direct interface was maintained at 280°C. The carrier gas for both GC's was ultra-high purity helium. Injection was in the splitless mode (30 sec delay).

RESULTS

The data in Figures 1 and 2 show the change in pH and the oxidation-reduction (redox) potential in sediment cores from Lake Paradise and Lake Mattoon as a function of depth. The potentials have not been standardized to the hydrogen electrode (Eh). To standardize these data add a correction factor of +0.240 V. In general, a measured redox potential (Eh) of greater than +0.2 volts at pH 7 indicates an oxidized environment. Lower values are considered to be reducing (suboxic or anaerobic) (Patrick & DeLaune 1972). By this definition these sediments are highly reducing. The measured parameters indicate that the entire sediment profile is in a highly reduced state in both lakes. The Mattoon sediments, with measured redox values generally between -260 and -400 mV, appear to be more reduced than those from Lake Paradise, which range between -218 and -242 mV. The pH values from both lakes range between 6.0 and 7.0 and exhibit essentially the same trend with depth.
The high levels of reduced inorganic species, sulfide (Figures 3 and 4), ammonium and ferrous iron (Figure 5 and 6), observed in sediment pore water also support the view that the sediments of both lakes are highly reducing. All measured oxidized species (NO$_2^-$, NO$_3^-$, Fe$^{3+}$, SO$_4^{2-}$) were either absent or present in only very low levels. The sulfide profiles were similar in pore water from both lakes. Levels were low, around 10 mg/L, at the sediment-water interface and generally increased with depth to a maximum of 20-30 mg/L at between 20 and 30 cm. Below this depth levels decreased sharply, presumably due to precipitation of ferrous sulfide. Ferrous iron (Fe$^{2+}$) and ammonium ion (NH$_4^+$) concentrations were high (10-30 mg/L) in both lakes also. The very low and irregular abundance of ferric iron (Fe$^{3+}$) was probably due to oxidation of ferrous iron during sample preparation.

Sediment carbon analyses (Table 1) show that organic carbon (OC) levels are relatively high (>3% of the total sediment mass) and that they generally comprise more than 90% of the total carbon present in the sediment. The remainder of the total carbon is composed of inorganic species, such as carbonates. The high organic carbon levels, which result from the highly productive nature of these lakes, reinforce the reducing sediment environment by providing a rich substrate for anaerobic bacterial growth.

The short-term anaerobic degradation experiment did not yield any results prior to concluding the project. No degradation was observed between day 8 and day 64 of the experiment. Although significant degradation was not expected in such a short time period, it was hoped that at the relatively high spike levels used even a small (e.g. 1%) amount
of degradation of the parent compound would yield detectable amounts of degradation products. This experiment will be continued for at least one year to monitor the degradation process.

The pesticide residue data obtained from Lake Paradise and Lake Mattoon are shown in Table 2. Only dieldrin data are available. Heptachlor epoxide concentrations could not be determined because of analytical interferences. The presence of dieldrin residue was confirmed by electron impact GC/MS. IEPA data (Kelly and Hite 1981) from the 1979 Illinois lake surveys are included for comparison. The IEPA data are from the top 3-5 cm of the sediment surface; the sediment data from this study are from core sections 1-10 cm and 10-20 cm from the sediment-water interface. The data labeled as "combined" was calculated from the total dieldrin residues determined in the two sediment core sections and the total sediment dry weight. This calculation was made to compensate for any sediment mixing and dilution effects that may have occurred since the 1979 IEPA survey.

Both lakes showed apparent reductions in pesticide residue levels from the 1979 IEPA survey. Assuming that the sediment samples from the present study and the IEPA survey are directly comparable, Lake Paradise showed a reduction in dieldrin residue of from 36% to 72% while Lake Mattoon's dieldrin burden was reduced by 70% to 91%. Despite the apparent reduction in dieldrin residue from the previous IEPA survey, however, we were unable to detect or isolate any cyclodiene pesticide degradation products from the sediment. Probable explanations for these results are discussed below.
DISCUSSION

The physicochemical parameters most closely associated with the degradation, or transformation, of chlorinated hydrocarbon insecticides are low redox potentials and the presence of ferrous iron. Glass (1972) was the first to show that the rate of DDT degradation was dependent upon redox potential and the presence of ferrous iron. He found more rapid degradation rates at -250 mV than at -20 mV ORP and demonstrated that the degradation of DDT occurs in the presence of the ferrous/ferric (Fe⁺²/Fe⁺³) iron redox system. The sediments of Lakes Mattoon and Paradise fulfill both of these conditions. The Lake Mattoon sediments, however, have a slightly lower redox potential than Lake Paradise in the upper 20 cm sediment zone (-260 to -310 mV vs -220 to -242 mV) and a higher level of ferrous iron in the upper 10 cm zone (11 mg/L vs <0.5 mg/L). These conditions may explain why Lake Mattoon exhibited a somewhat higher apparent reduction in dieldrin residue levels than Lake Paradise.

The two most common reductive pathways found in anaerobic sedimentary environments are mediated by the Fe⁺²/Fe⁺³ redox couple and by reduced iron porphyrins. Glass (1972), as previously described, was the first to propose a mechanism for the dechlorination of DDT by ferrous iron. Williams and Bidleman (1978) have shown that toxaphene can also be dechlorinated under these conditions. Dechlorination was limited to aliphatic chlorines in both of these cases. Other researchers have shown that reduced iron porphyrins are capable of dechlorinating complex chlorinated molecules, such as DDT (Miskus et al. 1965), mirex
(Holmstead 1976) and toxaphene (Khalifa et al. 1976). Klecka and Gonsior (1984), however, found that the reaction of reduced iron porphyrins with simple chlorinated hydrocarbons was limited to aliphatic molecules with three or more chlorines on the same carbon atom. Compounds such as carbon tetrachloride and chloroform were rapidly dechlorinated while lower chlorinated homologs, such as methylene chloride, 1,1,2-trichloroethane, and alkenyl chlorides, like tri- and tetrachloroethylene, were not dechlorinated.

Dieldrin and heptachlor epoxide are complex, cyclic chlorinated molecules containing 1 or 2 chlorines on aliphatic and alkenyl carbon atoms. Based on the results of Klecka and Gonsior (1984) dechlorination by reduced iron porphyrins would seem unlikely. However, toxaphene and mirex, which resemble the cyclodienes in having 1 or 2 chlorines on aliphatic carbon atoms have been shown to be dechlorinated by these systems. Khalifa et al. (1976) found that roughly one-half of the C-Cl bonds in toxaphene were cleaved by reduced iron porphyrins, and Holmstead (1976) found that mirex, which had been thought to be extremely resistant to most common oxidizing and reducing systems, was also dechlorinated to mono-, di-, tri-, and tetrahydro derivatives by iron (II) porphyrins. In both cases the degradation products were more polar and had shorter chromatographic retention times than the parent compound.

These findings suggest that the Fe$^{2+}$/Fe$^{3+}$ couple, cell-free iron (II) porphyrins, and microbial systems involving iron (II) porphyrins or other reduced systems (e.g. reduced microsome-NADPH) might mediate reductive dechlorination and/or dehydrodechlorination of the dieldrin
and heptachlor epoxide residues known to exist in the sediments of Lakes Mattoon and Paradise. Because of their extreme persistence it is unlikely that these compounds have been completely degraded to $CO_2$ or $CH_4$. Therefore, it is possible that less highly chlorinated transformation products of dieldrin and heptachlor epoxide are accumulating in the sediments of these lakes. This raises the question: why weren't degradation products observed?

There are several possible explanations for the absence of degradation products. They might also apply to the apparent decrease in parent compound concentrations as well. The explanations include, but are not limited to, dilution due to sediment burial and mixing, and decreasing extractibility due to pesticide humidification and binding with clay or organic substituents in the sediment matrix (Weber 1972; Khan 1978, 1980).

Several steps were taken to improve the recovery and detection of potentially very low levels of degradation products. To counter the effects of sediment dilution larger sediment fractions were extracted in order to achieve lower detection limits. Physical limitations of the extraction apparatus, however, prevented analysis of sediment samples larger than about 150 grams. Also, to minimize losses of degradation products and pesticide residues, some initial sediment extracts were subjected to as little fractionation and cleanup as possible. Large amounts of coextractives, however, necessitated the fractionation of the extracts on a florisil column. This improved the detection of dieldrin but the fraction containing heptachlor epoxide still contained too many interferences to allow quantitation. Recovery of dieldrin from spiked
sediments averaged about 70-80%, indicating that the analytical method was operating satisfactorily.

The high levels of coextractives also interfered with electron impact GC/MS for qualitative analysis of degradation products. The concentrations of any potential pesticide degradation products are much lower than the levels of other coextracted organic materials, even after florisil clean-up of the extracts. Electron impact GC/MS was not sensitive enough to allow detection of degradation products under these conditions. This prompted an attempt to use chemical ionization (CI) GC/MS to detect possible degradation products. Cyclodiene insecticides are reported to be very sensitive to detection by chemical ionization GC/MS, and especially to negative ion (NI) chemical ionization (Onuska 1985). Several samples were submitted to the University of Illinois mass spectrometry laboratory for GC/MS-CI and NICI analysis. Again, the results were negative. It appears that either the degradation product levels are below analytical detection limits or they have become bound to organic or mineral materials in the sediments and are not being extracted.

Adsorption to humic materials or humidification of pesticide residues and degradation products (Weber 1972; Khan 1978, 1980) may be important mechanisms for the absence of degradation products and the apparent removal of the parent compounds from the sediment. Some of these residues may have been associated with the sediment for more than thirty years since their introduction into Illinois in 1954 (Metcalf and Sanborn 1975). All of these compounds are very hydrophobic. Given the high level of organic carbon in these lake sediments one would expect
the residues to adsorb quite strongly to sedimentary organic materials. But hydrophobic adsorption alone is probably insufficient to explain the low levels observed. Although the chemistry of the cyclodiene insecticides is not highly conducive to chemical interactions with humic material, the possibility exists that some combination of reductive dechlorination, dehydrodechlorination and microbial metabolism may have altered the chemical structure of these molecules sufficiently, perhaps by the formation of more polar intermediates, so that they are capable of chemically binding to sedimentary organic carbon. Although time did not permit the characterization of the sedimentary organic matter this is a very interesting area for further investigation.

CONCLUSIONS

Dieldrin residues are still present in the sediments of Lake Paradise and Lake Mattoon almost 10 years after the use of its precursor, aldrin, was discontinued. The levels of dieldrin appear to have declined by 50% or more since the IEPA lake surveys of the summer of 1979. The decline has been greater in Lake Mattoon, which exhibited a lower sediment redox potential and higher surficial ferrous iron concentrations, than in Lake Paradise. Both of these conditions have been shown (Glass 1972) to influence the degradation rate of other organochlorine pesticides (e.g. DDT).

Degradation products resulting from the decomposition of dieldrin or heptachlor epoxide could not be isolated from the sediments. This may be due primarily to two factors: (1) the concentration of degrada-
tion products in the sediments is below present analytical detection limits, and/or (2) the degradation products may be chemically bound to sedimentary humic materials and were unextractable under the conditions used in this study.

REFERENCES


LIST OF TABLES

Table 1. Total Carbon Results for Surficial Sediments from Lake Mattoon and Lake Paradise.

Table 2. Dieldrin Residue Data (ug/kg Sediment Dry Weight) from This Study and from IEPA Lake Surveys (Kelly and Hite 1981)
Table 1. Total Carbon Results for Surficial Sediments from Lake Mattoon and Lake Paradise. Results are expressed as percent carbon.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total carbon</th>
<th>Inorganic carbon</th>
<th>Organic carbon</th>
<th>% Organic carbon of total carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake Paradise</td>
<td>3.56</td>
<td>0.39</td>
<td>3.17</td>
<td>89</td>
</tr>
<tr>
<td>Lake Mattoon (core sample)</td>
<td>2.76</td>
<td>0.12</td>
<td>2.66</td>
<td>96</td>
</tr>
<tr>
<td>Lake Mattoon (dredge sample)</td>
<td>3.17</td>
<td>0.13</td>
<td>3.04</td>
<td>96</td>
</tr>
</tbody>
</table>

Table 2. Dieldrin Residue Data (µg/kg Sediment Dry Weight) from This Study and from IEPA Lake Surveys (Kelly and Hite 1981)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lake Paradise</th>
<th>Lake Mattoon</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Apparent decrease</td>
<td>This study</td>
</tr>
<tr>
<td>0-10 cm</td>
<td>-36 to -55%</td>
<td>19.8</td>
</tr>
<tr>
<td>10-20 cm</td>
<td>-60 to -72%</td>
<td>12.5</td>
</tr>
<tr>
<td>Combined</td>
<td>-50 to -65%</td>
<td>15.5</td>
</tr>
</tbody>
</table>

* IEPA duplicate samples
LIST OF FIGURES

Figure 1. Lake Paradise, oxidation-reduction potential and pH as a function of core depth

Figure 2. Lake Mattoon, oxidation-reduction potential and pH as a function of core depth

Figure 3. Lake Paradise, moisture and sulfide as a function of core depth

Figure 4. Lake Mattoon, moisture and sulfide as a function of core depth

Figure 5. Lake Paradise, sediment pore water constituents

Figure 6. Lake Mattoon, sediment pore water constituents
Figure 1. Lake Paradise, oxidation-reduction potential and pH as a function of core depth
Figure 2. Lake Mattoon, oxidation-reduction potential and pH as a function of core depth.
Figure 3. Lake Paradise, moisture and sulfide as a function of core depth
Figure 4. Lake Mattoon, moisture and sulfide as a function of core depth
Figure 5. Lake Paradise, sediment pore water constituents
Figure 6. Lake Mattoon, sediment pore water constituents
Effect of Physicochemical Parameters on Pesticide Degradation

Modern agricultural practices continue to rely heavily on the use of herbicides and insecticides to maintain or increase crop yields. Past pesticide usage, especially of organodane, has resulted in serious environmental damage. Illinois surface waters and lake sediments have been contaminated with these compounds and their degradation products as a result of their heavy and prolonged usage. A 1979 IEPA survey (Kelly and Hite 1981) of Illinois lakes revealed dieldrin residues in 58% of the 63 lakes surveyed; heptachlor epoxide was detected in 25% of the samples. Sediment samples collected from Lakes Mattoon and Paradise in the summer of 1985 still contained dieldrin residues almost 10 years after use of its precursor, aldrin, had been discontinued. The levels of dieldrin appear to have declined more in Lake Mattoon than in Lake Paradise. It is believed that this is a result of the lower sediment redox potential and higher levels of surficial ferrous iron found in Lake Mattoon. Degradation products resulting from the decomposition of dieldrin could not be isolated. It is surmised that this is because the concentration of the degradation products is below analytical detection limits and/or the compounds have become chemically bound to sedimentary humic materials.