Fate of Organic Pesticides in the Aquatic Environment

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Symposium Chairman

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FOREWORD

ADVANCES IN CHEMISTRY SERIES was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented, their papers distributed among several journals or not published at all. Papers are refereed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications. Papers published in ADVANCES IN CHEMISTRY SERIES are original contributions not published elsewhere in whole or major part and include reports of research as well as reviews since symposia may embrace both types of presentation.

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PREFACE

Much concern has recently been expressed about the introduction and subsequent distribution of organic pesticides throughout man's environment. Some of this concern is real and genuine as it is based upon scientific evidence. However, much of the concern is based upon emotional hysteria and scientific demagogy. If restrictions or bans should be placed upon the organic pesticide, then the decision should be based upon scientific evidence and not upon emotional speculation. This symposium examines the fate of organic pesticides in one of man's environments—*i.e.*, the aquatic environment. Hopefully, some insight may be derived into the occurrence and distribution of organic pesticides throughout various natural aqueous systems so that an evaluation of environmental hazards or damage may be made.

The organic pesticide and/or a derivative probably entered natural aquatic environments concurrently with the development of the first manufacturing process. No doubt there was a waste disposal problem which led to a discharge into a river or some other body of water. Some evidence that potable, recreational, irrigational, fish, and shellfish waters were contaminated with pesticides began to appear in the literature about 1945. However, much of the early evidence was largely circumstantial as observed from physiological responses of aquatic organisms. More recently, the advent of chromatographic separation procedures and of such confirmatory procedures as nuclear magnetic resonance and mass spectrometry has led to the positive identification of organic pesticides in aquatic environments and in the attendant solid phases of bottom sediments.

The presence of a contaminant in any environment poses several questions. How was the contaminant introduced into the environment? How may its occurrence be recovered and confirmed? How is the contaminant distributed and transported throughout the environment? What is the stability of the contaminant toward the natural chemical and biological forces that would provide the opportunity for degradation? If degradation occurs, then is it complete or partial? If partial, then what are the metabolites and what is their effect on the environment?

This symposium was given the title of "Fate of Organic Pesticides in Aquatic Environments." Admittedly, the word "fate" suggests the large and difficult task of following the organic pesticide and their me-

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tabolites into every nook and cranny of the various aquatic environments. This is not the intent of the symposium as the chapters in this book testify. It is, however, the intent to gather together some scientific evidence on the distribution and stability of organic pesticides in aquatic environments.

Four major topics are covered (a) occurrence, recovery, and identification, (b) distribution and transport mechanisms, (c) stability and metabolites from chemical systems, and (d) stability and metabolites from biological systems. The first area stresses the problems of sampling, recovering, and confirming the occurrence of organic pesticides in aquatic environments. It is imperative that irrevocable evidence must be obtained before an indictment is imposed. The second topic area examines some of the mechanisms responsible for the distribution and transport of organic pesticides through aquatic environments. The mobility question is explored. The third topic area indicates the stability of organic pesticides toward such chemical degradative agents as ultraviolet radiation, inorganic oxidants, and hydrolysis. The occurrence of metabolites is stressed here. The fourth topic area examines biological systems for the accumulation and/or degradation of organic pesticides. The accumulative aspects were stressed here.

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Organic Pesticide Pollution in an Aquatic Environment

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The chemical contamination of the Great Lakes exemplifies the serious problems presented by organic pesticide pollution in major aquatic ecosystems. The evidence of DDT pollution in Lake Michigan has developed over the past decade beginning with effects on birds and climaxed by the ban of commercial fish from interstate commerce. Restrictions on the sale or use of fish contaminated by pesticides and mercury has caused significant losses to the local economy. The hazards of chemical contamination in major aquatic ecosystems is probably of much greater significance than pollution of small, localized environments. Our lack of knowledge regarding the fate of chemicals in major aquatic ecosystems has resulted in confusion and poorly defined issues regarding the hazards of chemical contaminants to human health and loss of environmental quality.

The past decade has been a period of controversy regarding chemical contamination in our environment. It began with protests against the death of songbirds in local DDT spray programs (*1*, *2*), and it continues now with an urgent concern for rapidly declining species of predatory birds (*3*). We were warned initially that certain pesticides were a potential hazard to fish and wildlife populations (*4*), and now we are warned that the global distribution of these compounds threatens the stability and utilization of our marine resources as a human food source (*5*). Our information on these subjects has often been deficient, but as time has passed, we find increasing evidence of a profound influence of organic chemical pollution on major aquatic ecosystems.

The present chemical contamination of our Great Lakes exemplifies the seriousness of this problem, and it emphasizes the vast array of social

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and economic pressures it has generated. In examining the development of this situation, it is not our intention to cast blame or to suggest that it might have been otherwise but rather to indicate the magnitude of the problems faced by a society that only is beginning to recognize the limitations of its environment.

Historical Evidence of Pollution

The story of DDT in the Great Lakes should start rightfully with the pioneering investigations of robin mortalities on the Michigan State University campus in 1957 (*6*). The near elimination of robin populations occurred over a period of about 10 years beginning with the application of DDT to control the Dutch Elm disease in 1954. Lethal concentrations of DDT found in the brain and muscle tissues were related later to the accumulation of DDT found in the soil and in earthworms consumed by the birds. This situation should have provided a strong warning of events to come, but occurring as it did during the pre-gas chromatography era, the information was considered with great skepticism, and it created only controversy. DDT applications to control Dutch Elm disease on the campus was discontinued in 1965, but recommendations for its use in Michigan cities was not dropped until 1968. It is significant that within four years after the last application on campus, the observed robin mortality had dropped to insignificant numbers. However, in the nearly eight years since the last applications, the robin populations remain in low numbers, having been replaced by seed-eating bird species which are considered a nuisance (*6*).

The potential hazard of DDT contamination in the Great Lakes had not been ignored and was predicted by many as a potential threat to resources of the region. Hickey *et al.* (*7*) reported evidence of extensive contamination of a portion of Lake Michigan and included the observation that significantly higher residues were concentrated in the higher trophic levels. Keith (*8*) found evidence of effects on reproduction in herring gulls as a result of poor hatchability of the eggs. Although the significance of these observations was not recognized widely at the time, many investigators have shown since that reproductive failure in fish-eating birds is now widespread because of the effects of DDT and DDE residues on calcium metabolism and the production of thin egg shells (*9, 10, 11, 12*).

These early observations perhaps would have had greater significance, but the fishery resources in Lake Michigan were at a low ebb, having suffered over-exploitation by commercial fishermen, the invasion of the sea lamprey, and finally by the population explosion of an invading fish species, the alewife (*13*). Within a few years the alewife population in

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Lake Michigan grew to enormous numbers resulting in massive mortalities along the beaches and threatening the tourist and recreation industry. To control the alewife and to restore a balanced and productive fishery in the Great Lakes, coho salmon from the Pacific west coast were introduced in Lake Michigan and Lake Superior in 1965. Their rapid growth and the immediate success of this initial salmon introduction surpassed even the most optimistic predictions. Nationwide attention was focused on the sport fishery, bringing so many fishermen and spectators that expansion of overloaded marinas, restaurants, and other public facilities was initiated immediately. The Michigan Department of Natural Resources with the incentive of favorable publicity and a public-supported recreation bond began investment in expanded hatcheries and stream weirs to facilitate the expansion of the salmon program. Hence, public interest in this program focused attention on pesticide pollution in the Great Lakes.

The pesticide problem was defined further by monitoring investigations by the U. S. Bureau of Commercial Fisheries which showed that DDT and dieldrin were distributed in all species of fish in the Great Lakes with the highest concentrations found in the major commercial and game species in Lake Michigan (*14, 15*). Their monitoring efforts did not show detrimental effects of the pesticides on fish populations, but the potential hazard of these pesticides to reproduction in fish was recognized from earlier studies in other locations (*16, 17, 18*).

In 1967 with the first return of mature coho salmon and the development of their eggs in hatcheries, significant mortalities of coho salmon fry did occur. Approximately 680,000 young fish died in Michigan hatcheries during the last stages of larval growth when they were just beginning to feed. Similar mortalities occurred in several other states that had obtained eggs from Lake Michigan salmon. An initial investigation showed the mortality was confined to the progeny of Lake Michigan fish in which DDT residues averaged two to five times higher than in those from Lake Superior and nearly 60 times higher than in samples from the Pacific west coast (*19*). An analysis of the salmon fry showed that DDT was concentrated highly in the lipid fractions which are retained in the last remains of the egg yolk. The timing of the mortality coincided with the period that these lipid reserves are metabolized by the developing fry. Tests for disease conditions among the dying fry were negative, and DDT was considered the most probable cause of the mortality.

During this same period, surplus adult salmon, which had escaped the sport fishery, were collected at weirs on the tributary streams and processed for commercial sale. A portion of these fish were sold also to mink ranchers as a supplement in mink food. Rations which contained up

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to 15% raw coho salmon were fed to mink during the reproductive period. Although no effects on the adult animals were noted, reproductive losses as high as 80% were reported by the fur farmers. The extent of losses depended upon the percentage of coho salmon fed and the duration of the feeding. Aulerich *et al.* (*20*) have since completed feeding tests in which mink were fed various quantities of Great Lakes fish. Their results suggest a relationship between reproductive performance of the mink and the pesticide residues (DDT and isomers or dieldrin) in the fish.

Economic Losses

In the period up to 1969, the primary issue was a concern with environmental hazards regarding pesticide effects on bird and fish populations in the Great Lakes. A legal tolerance level for pesticides in fish had not been established, and by definition the tolerance for DDT and dieldrin in fish was zero. Nevertheless, the human health consideration had not been questioned seriously, and the fish in the Great Lakes were considered safe for human consumption. A local cannery and distributor had begun to process canned and frozen salmon for distribution to midwest markets. However, in 1969 soon after the initial shipments, the U. S. Food and Drug Administration stopped releasing some canned salmon after finding samples which exceeded 0.3 ppm dieldrin. These shipments were released later, but for the first time the action established an administrative action level for dieldrin in fish (*21*).

In the same year the FDA set a precedent by declaring an interim tolerance limit of 5 ppm DDT and analogs in fish (*21*). Their action accompanied the confiscation of 39,000 pounds of frozen coho salmon taken from interstate commerce. These fish contained residues of DDT and analogs ranging from 13–19 ppm. The action not only affected the commercial sale of coho salmon, but it restricted also the sale of approximately 80% of the Lake Michigan fish crop in the commercial market with an estimated loss of three to four million dollars (*22*). Even in Lake Superior, a body of water generally considered almost pristine in nature, approximately 8% of the lake trout catch was nonmarketable under this ruling (*23*). Obviously, the economic impact has extended far beyond the market value of the crops. Commercial fishermen, suffering already from poor fishing conditions, were affected seriously, and many were forced out of the business. This was in effect a double blow since many of the commercial fishermen were from the Upper Peninsula of Michigan, an already economically depressed area.

The new FDA guideline regarding DDT in fish did not affect the sport fishery directly, but it has raised a question of ethics and confused public policy regarding human health. Although the fish cannot be sold

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in interstate commerce, the State of Michigan now distributes surplus salmon to licensed fishermen without charge. A petition by the Michigan Department of Health to raise the tolerance level in salmon to 15 ppm DDT was rejected by the FDA in 1970 because of carcinogenic properties of the compound (*23*). The influence of these actions on fishermen's attitudes is difficult to assess, but the esthetic value of a contaminated fish is diminished in the eyes of most sportsmen.

The ban of fish from the commercial market has climaxed a problem of long duration, but it has been suggested that we have yet to comprehend fully the social, economic, and biological implications of this pollution situation (*24*). It should, therefore, be a serious concern that we have learned so little about the dynamics of pesticides in the Great Lakes. The sources, rates of contamination, and degradation of pesticides in these waters largely are unknown.

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Sources of Pesticide Contamination

It is possible that important contributions of pesticides enter the Great Lakes directly from the atmosphere. It is known that pesticides move to the atmosphere from drifting spray, on airborne particulate material, and through volatilization from soil and water surfaces (*25*). Risebrough (*5*) has provided data indicating that DDT distribution in coastal and oceanic waters results from fallout of airborne particulate material. Considering the vast surface areas of the Great Lakes, the total input from the atmosphere is probably significant. As an example, Lake Michigan has a surface area of 22,400 square miles with an annual rainfall of about 33 inches.

The use of DDT in urban areas for control of Dutch Elm disease and mosquitoes probably has been a major contribution to the total burden in the Great Lakes. Although the use of DDT in Michigan and Wisconsin has been largely discontinued, substantial quantities still are entering Lake Michigan in tributary streams. In a study of the Red Cedar River, an upper tributary in the Lake Michigan watershed, Zabik (*27*) found that soluble residues of DDT in the water were close to saturation levels throughout most of the year. Considerably greater quantities of DDT were found adsorbed on suspended particles and in the sediments, with increasing concentrations found in downstream stations. Effluents from two sewage treatment plants significantly increased concentrations in the stream, particularly after spray applications in the spring. His data indicate that DDT is partitioned rapidly from the bottom sediments into the water, resulting in decontamination of the immediate stream sediments but increasing the burden flowing downstream.

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Large quantities of pesticides have been used in agriculture in the Great Lakes basin, particularly in the orchard belts near Lake Michigan. Wilson *et al.* (*27*) monitored the dieldrin input to Lake Michigan in tributaries draining 7.3 square miles of land which had been treated with dieldrin to control a Japanese beetle infestation. Water samples showed that dieldrin contributions to the streams continued for at least 21 months after treatments. During this period an estimated 11.3 pounds of dieldrin or 0.18% of the total application were contributed to Lake Michigan. This was a unique situation with data gathered before application, the application planned carefully and carried out, and the monitoring designed to measure contributions in the runoff. If we can extrapolate from this example, the magnitude of the pesticide load entering the Great Lakes can be partially understood.

The actual concentration of pesticides in Lake Michigan water is known only from limited numbers of water samples taken offshore in 1968 (*28*). DDT and its analogs were present at less than 3 ppt, and dieldrin concentrations were less than 1 ppt. If coho salmon and lake trout can develop concentrations as high as 20 ppm from an environment with such low concentrations, it would suggest that the problem will exist for a long period. Pesticide concentrations in Lake Michigan fish have not shown any appreciable changes from the first analyses in 1964 to the present (*9*, *15*). The apparent steady state concentration is probably a result of continuous input from residuals in the watershed soil and from continuous partitioning and resuspension of the bottom sediments (*29*). However, little information is available on the dynamics of pesticides in sediments of deep lakes. These data would be valuable in predicting the duration of contamination and its influence on the biota.

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Other Organic Contaminants

Continued research is needed to understand the significance of pesticide residues in fish and their effect on fish production. Our study of pesticide residues in coho salmon eggs and the survival of the hatching fry has continued for three years. The mortality, first observed in 1967 has recurred each year with the symptoms first appearing during the last stages of yolk-sac absorption. However, considerable variation in the mortality data within egg and fry samples from Lake Michigan suggest that additional factors probably are influencing the fry survival. We have recognized the presence of a number of unidentified peaks in chromatograms of the salmon egg extracts. A preliminary analysis has indicated these compounds are polychlorinated biphenyls (PCB). Armour and Burke (*30*) and Stalling (*31*) have confirmed the presence of PCB com-

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pounds in coho salmon from Lake Michigan, and Veith (*32*) has reported conclusive evidence of the presence of chlorobiphenyls in the Milwaukee River, a tributary of Lake Michigan. Veith found relatively high concentrations of chlorobiphenyls in fish within the river system and in fish from Lake Michigan. Much lower concentrations were present in fish isolated from industrial sites. The discovery of PCB residues in Great Lakes biota has suggested real or potential error in earlier reports of pesticide residues. The reports of Armour and Burke (*30*) and Stalling (*31*), however, indicate that relatively high concentrations of PCB and pesticide residues are present in coho salmon from Lake Michigan. The combination of relatively high concentrations of PCB and pesticide residues in coho salmon eggs may be particularly significant if these compounds have synergistic or even additive toxic effects on the fry, a condition which has been shown already with certain insects (*33*). Some recent work in Sweden (*34*) has suggested that PCB residues in salmon eggs may be responsible for reduced embryo survival and poor hatching success.

The problem becomes an even greater concern when we consider the potential effects upon other fish species in the Great Lakes. During the period that DDT has been used in the Great Lakes region, drastic changes in the fish populations have occurred (*13*). Many commercially important as well as noncommercial species formerly abundant in the lakes now are virtually absent or reduced drastically. Proof of an interrelationship with DDT or other chemicals is not possible at this stage, but evidence of changes in species composition and reduced abundance have occurred in smaller lake systems contaminated heavily with pesticides (*35, 36*).

Finally, in considering chemical contamination in the Great Lakes, there are many parallels between the effects of pesticides in Lake Michigan and the present mercury crisis in Lake St. Clair and Lake Erie. Although the problem has been increasing gradually for many years, the mercury contamination of these waters was not recognized until 1970 after the Minamata disaster in Japan (*37*) and evidence of significant mortalities of seed-eating birds in Sweden (*38*) had been brought to the attention of North American investigators. While the major sources of mercury contamination have been traced to industrial sites, substantial quantities of organic mercury also have been applied directly to the environment as fungicides in seed dressings and as slimicides in paper and pulp industries (*39*).

Mercury accumulation in fish in Lake St. Clair and Lake Erie has been considered a serious hazard to human health and has resulted in

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rapid regulatory action because of this health hazard. A ban on commercial fishing and an executive order forbidding sportsmen to keep or eat fish taken in these waters has had a catastrophic effect on the local economy. The greatest losses have been associated with the sports fishery, because of effects on established marinas, bait and tackle dealers, fishing guides, and miscellaneous other businesses supported by the fishery. The estimated gross business income loss for sport fishery related enterprises was 7½ million dollars for 1970 and the loss of 800 jobs. The commercial fishery loss for 1970 was estimated to be 55,000 dollars (*40*). Legislation has been proposed in the United States Congress that would provide grants to commercial fishermen and sport fishery enterprises for up to 70% of their business losses because of mercury contamination. As in the pesticide issue, the biological effects, the fate of mercury in the environment, and the total social and economic impact of this pollution is largely unknown.

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Summary

There has been a long history of chemical pollution in aquatic ecosystems around the world. The results have been illustrated often by fish or bird mortalities of limited dimensions. Much of our information on chemical pollution in aquatic systems is from such localized areas. Contrary to our earlier thinking, persistent pesticide contamination in small bodies of water may be only transient problems. The greater bottom surface area per water volume, higher flushing rates, and greater biological activity in eutrophic systems may cause more rapid decontamination. Pesticide residues in streams tend to be moved downstream particularly in association with suspended materials, to be deposited in lakes and estuaries. However, the effects and behavior of chemical contaminants in streams and small lakes may be misleading when we consider major aquatic ecosystems such as the Great Lakes and coastal marine waters. The Great Lakes constitute one of the most important freshwater resources in the world located in a region inhabitated by about a fifth of the aggregate U.S.–Canadian population. The surface area of the Great Lakes covers nearly 95,000 square miles in a drainage basin of nearly 288,000 square miles. The general chemical contamination of such a vast area can have a significant impact upon our culture, and a rapid response to pollution abatement is not likely.

Our lack of knowledge regarding the fate of chemicals in the aquatic environment has resulted often in poorly defined issues and confused public concern regarding the hazards of pesticides to human health and our environment. We already have seen evidence of increasing legislative

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activity and legal actions to restrict the use of chemicals in the environment. Despite the many unknowns, however, our need and use of chemicals will continue to increase for many years (*41*). It becomes imperative that we find the means to detect harmful properties of chemicals before they are released to the environment and methods to recover these materials from our waste effluents.

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Liquid–Liquid Extraction of Organic Pesticides from Water: The *p*-Value Approach to Quantitative Extraction

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Extraction is the first step of pesticide residue analysis of water samples. Any pesticide residue technique of water samples should include the development of a dependable quantitative extraction procedure. The pitfalls of liquid–liquid extraction as now used are explained. A theoretical approach for quantitation of the extraction step based upon the thermodynamic partition coefficient as a p-*value is proposed. The* p-*value approach is discussed to enable choosing the best solvent, water quality parameters, and solvent:water ratios for serial analysis of water samples containing pesticides.*

Liquid–liquid extraction (LLE) is usually the first step in the quantitative pesticide residue analysis of water samples. Direct analysis is usually precluded because of sensitivity and specificity analytical requirements. Therefore, any pesticide residue technique for water samples should include a dependable quantitative extraction procedure. The residue chemist should be concerned with developing reproducible quantitative analytical methodology for pesticides in the nanogram (*n*g) to microgram (μg) per liter range. Drinking water standards and stream standards for different chlorinated hydrocarbon pesticides have been suggested in the 0.1–100 μg/liter range (*1*, *2*). Present natural water pesticide background levels, however, are usually lower (*3*, *4*).

Criteria for judging the acceptability of any analytical method as a standard method have been suggested (*5*). The criteria are based upon

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the total error acceptability. Methods having a total error of less than 50% are considered acceptable (*5*). The total error equals the relative error plus two times the standard deviation divided by the true value times 100.

Pesticide residue analysis of chlorinated hydrocarbon pesticides on crops has progressed so that collaborative laboratory studies have shown a statistically acceptable total error by gas chromatographic methods (*6*). Two collaborative studies of chlorinated hydrocarbon pesticide residue analysis in distilled water by the United States Public Health Service Analytical Reference Service (*7, 8*) are unacceptable using these criteria (*5*).

These surveys by the Analytical Reference Service analyzed pesticides in fortified distilled water in the 0.1–1μg/liter range. In the first survey a method was not specified. LLE parameters used by the participants varied considerably; for example, six different solvents and solvent mixtures were used. The second survey specified the analytical procedure to include a serial extraction of acidified water samples with hexane. The second survey showed a total error of 53–168% for ten different chlorinated hydrocarbon pesticides; only the analysis for *o,p*-DDT had a total error of less than 50%. Both studies concluded that accuracy depended upon correction factors for the degree of recovery of known amounts of standards. The second study concluded also that the type of chromatographic column and detector did not affect accuracy or precision.

Reference *9* describes a collaborate survey of over 28 laboratories testing the new Tentative Standard Method for Chlorinated Hydrocarbon Pesticides in distilled water. This method calls for two successive extractions utilizing a hexane, semi-automatic extraction as described by Kawahara *et al.* (*10*) and modified by Schaefer *et al.* (*11*). Three different chlorinated hydrocarbon pesticide mixtures were tested; only three of eighteen pesticides analyzed showed a total error of less than 50%. This calculation of the total error was based upon Table 100 (*3*) which described the accuracy and precision of the new method (*9*).

These studies infer that the water residue chemist should be concerned with the LLE and cleanup steps of analysis as these are as impor-

Table I. Criteria for the Choice of Solvent for Quantitative Liquid–Liquid Extraction (*14*)

Solubility in water
Character of the solvent—*e.g.*, polarity, aromaticity
Ability to be utilized with the detection system
Volatility
Ease of solvent handling—*e.g.*, viscosity
Solvent toxicity
Solvent flammability

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tant as the chromatographic, determinative steps for precise, accurate analysis.

The ultimate choice of a liquid–liquid extraction procedure depends upon the analysis goal. Different solvents of aqueous pH values may be necessary for extracting the same pesticide when the analysis is designed for:

(a) one specific pesticide
(b) a group of pesticides
(c) a maximum number of pesticides for general screening
(d) a pesticide and its degradation products
(e) confirmational analysis of a pesticide.

At times the choice of a LLE procedure is affected by the type of determinative step. For example, chlorinated solvents are not used with an electron capture gas chromatographic detector.

Pesticides are a series of compounds considered a group because of their use. Chemically they are a diverse series of compounds with varying properties. For example, the organophosphates are a series of compounds which have in common different anticholinesterase activities. The range of polarity, hydrolysis, and oxidative stabilities are major differing attributes. Therefore LLE parameters for all pesticides will never have the same value.

The present state of the art for the LLE step of pesticides analysis is described here. Lack of knowledge about LLE of pesticides from aqueous environments is described, followed by a suggested approach for obtaining this knowledge. Recent reviews of the LLE of common pesticides from water have been presented by Faust and Suffet (*12, 13, 14*).

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Choice of Parameters for Quantitative Liquid–Liquid Extraction

Three basic criteria for developing quantitative liquid–liquid extraction techniques are:

(a) choice of solvent
(b) knowledge of the water quality
(c) type of LLE process to use—*i.e.*, serial or continuous extraction.

Table I shows criteria for choosing the solvent for quantitative liquid–liquid extraction (*14*). Many authors have reviewed these criteria for choosing the solvent (*14, 15, 16*), and they seem well known. The solvent is finally chosen to suit the desired analysis.

The effects of natural water quality parameters on quantitative liquid–liquid extraction have seemingly been neglected by many workers. The tables in References *12, 13* and *14* indicate that some water

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Table II. Water Quality Parameters Involved in Quantitative Liquid–Liquid Extraction

Classification of the type of water for analysis
- Ionic strength
- Turbidity
- Soluble organic content
- Oily organic content

Other water quality parameters
- pH
- Temperature

quality parameters are unspecified or arbitrarily chosen—*e.g.*, pH, turbidity, ionic strength, solvent:water ratios, the number of times to re-extract the sample. Table II summarizes some of the water quality parameters which affect the efficiency of the LLE step. Natural waters and wastewaters are best classified analytically by specific physical, chemical, and biological water quality characteristics. Sea water, estuarine water, and river water are classified by their different ionic strengths. Each type of water may require different ionic strength pretreatment for comparable quantitative LLE. Also a clear river water and a turbid river water may require different pretreatment before LLE.

Ionic Strength. The ionic strengths of 50% of the surface waters of the United States are less than 0.01*M* and 97% are less than 0.05*M*. This calculation is based upon surface water quality data summarized by Rainwater (*17*). In 1964 the maximum ionic strength of the water supply of 100 large cities was calculated to be less than 0.01*M* (*18*). However, the ionic strength of sea water is approximately 0.7*M*, and estuarine water varies between these two limits.

A constant ionic strength usually keeps the activity coefficients of molecules approximately constant in an aqueous solution (*15*); therefore, to compare quantitatively LLE methods, a constant ionic strength is necessary. Waters with low ionic strength can be adjusted to a constant higher value. Sea water need not be adjusted as its ionic strength is constant (*19*); estuarine water can be adjusted to the ionic strength of sea water.

The adjustment of ionic strength brings up the salting-out effect. Salting-out agents are those electrolytes that when added significantly increase the extractability of a compound from water by a solvent. The salting-out agents qualitatively orient water molecules for solute interaction (*15*). Large amounts of salt, often near saturation, are necessary to produce marked extraction enhancement. The magnitude of the salting-out effect in water depends upon the amount of added salt and the formal charge on each salt ion (*15*).

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A quantitative solution to the salting-out phenomenon has not been found, but the phenomenon is reproducible. The Setchenov Equation has most frequently been used to describe the salting-out effect of neutral molecules although the equation does not have a theoretical basis:

$$\log \gamma_A = K_{AS}(S) \quad (1)$$

where γ_A is the activity coefficient of a nonelectrolyte, (S) is the molar concentration of salt, and K_{AS} is the salting coefficient specified for A and S. Theoretical understanding of K_{AS} based upon properties of the components of solution—*e.g.*, dielectric constant, hydration of electrolytes, their concentration, and intermolecular forces—has been reviewed by Marcus and Kertes (*15*).

The effect of the ionic strength on pesticide extraction should be studied. This may produce more accurate and precise LLE procedures.

Turbidity Effect. Pesticide monitoring procedures try to extract the whole water sample as collected whether it is clear or turbid or contains large particulates (*3*, *4*). The effects of turbid matter—*i.e.*, suspended matter, such as clay, silt, finely divided organic matter, plankton and other microscopic organisms, and settleable matter—have not been delineated.

The size distribution of particulate matter has been defined in microns (μ) as dissolved ($< 0.001\mu$), semicolloidal ($0.001–1\mu$), and colloidal ($1–100\mu$). Ultracentrifugation processes can separate these size boundaries (*20*). A 0.45μ diameter millipore filter eluate has been defined as "apparently solubility" (*9*). This artificial cut off value is easy to attain. Most of the semicolloidal material in water therefore is included with the soluble fraction.

If a pesticide is adsorbed on suspended matter or settleable matter, it may or may not be extracted along with any soluble pesticide. A longer equilibrium time for extraction of turbid samples may be needed. The adjustment of the pH or ionic strength of turbid samples before extraction may cause pesticide adsorption or desorption, colloid stabilization, etc. LLE of pesticides from different turbid waters should be studied.

Soluble Organic Content. The extraction of pesticides from waters containing large concentrations of soluble organics—*e.g.*, domestic wastewater—suggests coextracted organic interferences. Most investigators have used the criterion that if the detection system showed minimum interference when compared with a reference standard, the analysis is acceptable. An efficient cleanup step should be included before quantitation for grossly polluted waters. GLC detection limits have been controlled by the capability of cleanup procedures of extracts containing large amounts of coextracted organic matter (*21*, *22*). In some cases the amount of soluble organic coextractives is possibly controlled by

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selection of solvent and water quality conditions. The exact chemical composition of organic coextractives is usually not known.

Oily Organic Content. The partition of pesticides from water into oils of petroleum origin in natural waters as surface slicks and sedimented oil have recently been reported (*23*). The extracting of pesticides from samples containing oil globules which partition pesticides is a new problem which aquatic residue chemists must solve.

Natural Organic Content-Colored Matter. The interaction of a pesticide with natural organic material, called humic and fulvic acids, has received little attention. Recently Wershaw *et al.* (*24*) showed that sodium humate stabilizes DDT in water and humic acid sorbed 2,4,5-T. LLE of water containing these materials and pesticides is yet another area to consider.

pH. The choice of the pH value for extraction depends upon:

(a) stability of the pesticide

(b) eliminating such dissociative effects of the solute as acid-base equilibria

(c) eliminating associative effects in the solvent

(d) the best extractive efficiency for the solute

(e) desired analysis.

For example, the primary criterion for the optimum pH value of LLE of organophosphates or carbamates is hydrolytic stability. The main criterion for the pH value of aqueous extraction for phenoxyalkyl acid herbicides is to eliminate any dissociative effects. The pH value should be buffered 2–3 units below the protolysis constant.

Temperature. Quantitative comparisons of the LLE steps require a constant temperature. Pesticide stability and changes in the relative solvent volumes are also affected by temperature.

Methods of Liquid–Liquid Extraction. Most methods described for LLE are the batch type (*12, 13*). This is surprising since continuous extraction has an obvious advantage over serial extraction because larger sample volumes are extracted. Kahn and Wayman (*25*) and Goldberg *et al.* (*26*) have described continuous LLE systems for lighter and heavier than water extractions, respectively. Such extractors are used with multiple chambers and internal solvent recycling. Kahn and Wayman successfully recovered chlorinated hydrocarbon pesticides with 96–100% efficiency in a 3-chamber system with petroleum ether (*25*). An average residence time of 45 minutes per chamber at a 1:1 solvent to water phase ratio was used on a 20-liter sample of less than 400 ppb concentration.

In 1965 Kawahara (*10*) introduced a semi-automatic LLE of pesticides with vortex mixing. A sample of 850-ml was stirred by a magnetic impeller with a solvent. The impeller was placed in the cap of an in-

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verted 1-liter glass bottle. Efficiency varied depending upon the solvent used and the pesticide extracted. Schaffer *et al.* (*11*) used a modification of this method to determine pesticides in two municipal raw and finished drinking waters whose source of water was the Mississippi or Missouri River. These authors used 3.5-liter samples with 10-ml of hexane and a stirring bar instead of an impeller to obtain vortex mixing. Recovery from distilled water ranged between 42–105% for 0.06–2.5 μg/liter samples of 14-chlorinated hydrocarbons pesticides. Standard Methods of Water and Wastewater 1971 (*9*) recommends this semiautomatic LLE method with two serial extractions of 10-ml hexane for chlorinated hydrocarbon extraction, although the precision and accuracy of a collaborative laboratory test of the method indicated greater than the acceptable total error (*6*).

Parameter Choice. Hermann and Post (*27*) describe the extracting of model pollutants from distilled water to be different from extracting them from natural waters. This phenomenon seems to occur because environmental samples are weathered—*i.e.*, subjected to physical, chemical, and biological changes. Pesticides are aggregated, degraded, or adsorbed on plant tissue or soil. Natural water quality is usually different from laboratory distilled water where most recovery studies are initially tested. Therefore, knowing the water quality parameters seem as important for the control of LLE efficiencies as knowing about the solvent.

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p-*Value for the Rational Choice of LLE Parameters*

Using the thermodynamic distribution coefficient for the choice of the best LLE parameters for quantitative extraction of pesticides from water is usually not done. The time to determine the distribution coefficient of a pesticide under different water quality conditions and with different solvents has seemed to justify picking these parameters arbitrarily. Then the parameters chosen are tested by fortifying, usually in distilled water. As indicated above, the arbitrary approach does not work well. A systematic procedure based upon the distribution coefficient is strongly suggested to replace the arbitrary approach. In time a Standard Method for choosing the parameters of LLE for quantitative pesticide analysis may evolve from careful comparative study of parameters.

Theory. Liquid–liquid extraction in dilute solution is thermodynamically based on the partition coefficient (*15*, *16*). Gibbs' phase rule states that:

$$F = C - P + 2 \tag{2}$$

It shows how the number of components C, the number of phases P, and the number of independent variables F (degrees of freedom) necessary

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to characterize a system are related. Gibbs' phase rule helps to predict how a LLE multiphasic system behaves and elucidates the equilibrium state. LLE is a two-phase system of three components—*e.g.*, the extraction of DDT from water by hexane. The two phases are water and hexane; the three components are DDT, water, and hexane. Therefore, there are three degrees of freedom. If two degrees of freedom, temperature, and pressure are kept constant, then only one degree of freedom, concentration, need be specified to define the system completely. The phase rule is specific for only a single molecular species. The thermodynamic partition coefficient, D equals:

$$D = \frac{\gamma_a [A]_a}{\gamma_b [A]_b} = K \frac{\gamma_a}{\gamma_b} \tag{3}$$

therefore

$$K = \frac{[A]_a}{[A]_b} \tag{4}$$

The γ's are the activity coefficients, $[A]_a$ is the concentration of the solute distributed in the solvent phase, $[A]_b$ is the concentration of the solute distributed in the water phase, and K is the extraction coefficient or distribution ratio. When γ_a/γ_b approaches 1.0, the analytical concentration of A approaches zero and K approaches D; this occurs in dilute solutions. The experimentally determined K remains constant and does not depend upon relative amounts of solutes if:

(a) chemical equilibria are minimized—*i.e.*, polymerizing or dissociating of solute species does not occur.

(b) activity coefficients in the two phases are equal, regardless of concentration

From above it is possible to develop dependable quantitative LLE parameters based upon theory.

The distribution ratio can deviate. As mentioned, a single molecular species of a compound must be maintained. For such ionizable compounds as acids, it is necessary to minimize their dissociation. The pH value must be set 2–3 units below the acidic dissociation constant. This occurs for organic hydrolysis products of organophosphate pesticides because these compounds are acidic by nature (C–O–H).

The distribution coefficient (K) is also expressed as:

$$K = \frac{E/V_n}{(1 - E)/V_p} \text{ or } \frac{E}{1 - E} \times \frac{V_p}{V_n} \tag{5}$$

where E and $(1 - E)$ are the fractional amounts of a solute partitioning into the nonpolar and polar phases, respectively. V_n and V_p are the volumes of the nonpolar and polar phases (solvent and water phases),

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respectively, after an extraction step. The general equation for unequal, unequilibrated solvents is:

$$K = \frac{E}{\alpha(1 - E)} \tag{6}$$

where:

$$\alpha = \frac{V_n}{V_p} \tag{7}$$

α is the volume correction factor for any one step of a LLE, as defined by King and Craig (*28*).

Beroza and Bowman have described the thermodynamics of LLE by amount instead of concentration (*29*, *30*, *31*, *32*, *33*, *34*). Their treatment is practical for quantitatively comparing how much solute can be extracted from one solvent phase into another under specific conditions. The comparison is based on the *p*-value, redefined by Beroza *et al.* (*34*) as the fraction of the total solute that distributes itself in the nonpolar phase of an equivolume solvent pair. This redefinition of the *p*-value is more concise than the original definition of the fraction of the total solute partitioning into the upper phase (*32*). When equal volumes of two immiscible, equilibrated phases are described, $\alpha = 1$ and Equation 6 becomes:

$$K = \frac{p}{q} \text{ or } K = \frac{p}{1 - p} \tag{8}$$

where K and p have been defined above and q is the fractional amount of solute partitioning into the polar phase of an equivolume two-phase solvent system $(1 - p)$. Equation 8 applies only where solvent volumes do not change (*29*, *30*).

The fraction extracted under any specific conditions (E) is related to the fraction extracted under equivolume conditions (p):

$$p = \frac{E}{\alpha - E(\alpha - 1)} \text{ or } E = \frac{\alpha p}{\alpha p - p + 1} \tag{9}$$

The relationship between p, E, and K for different α's is shown on Figure 1. *p*-Values are on a percentage scale, giving a water analyst direct recovery data for 1:1 solvent:water ratios with equilibrated solvents. The *p*-value for unequilibrated systems is easily translated to the theoretical amount extracted, E, for any solvent:water ratio again on a percentage basis. The accuracy and precision of an analysis is expressed on a percentage basis. Using the distribution ratio K precludes this last use.

p-Values, determined in 10,000 mgram/liter solutions, were within experimental error of those values determined at the μg–ng/liter

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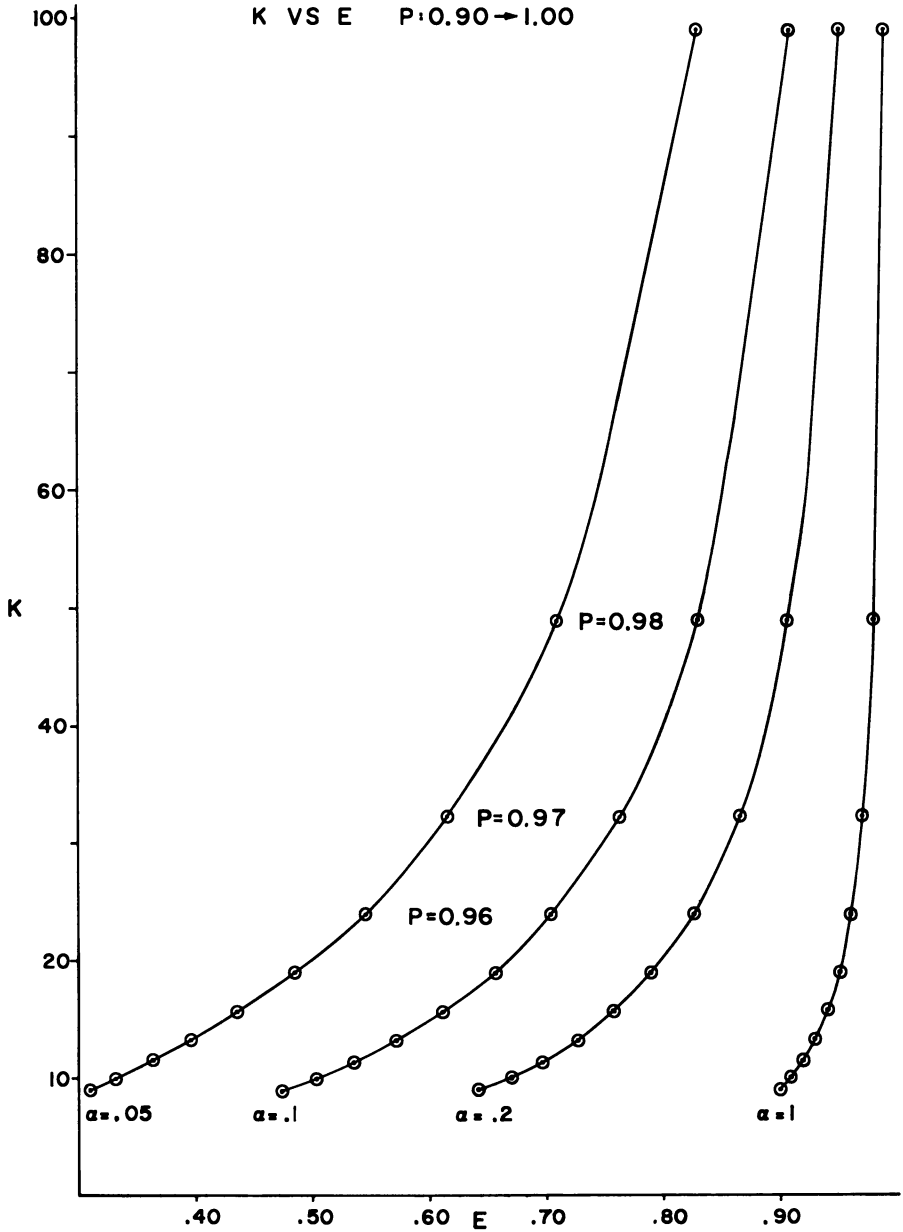

Figure 1. The relationship between p, E, *and* K *for different* α *values*

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level (*30*). *p*-Values are relatively independent of various representative food coextracts (*30*). Only when excessive amounts of coextractives were present did the *p*-values vary > 0.03. Therefore, change in a *p*-value is not expected even in the most polluted waters.

Beroza and Bowman (*29, 30, 31*) have shown the practical advantage of using the *p*-value instead of *K* to confirm insecticidal identity and cleanup of insecticides, both at the nanogram level. The *p*-value concept is also applied to optimize the LLE step of aqueous pesticide residue analysis (*35*). Using the *p*-value to optimize the LLE of pesticides from water is considered below.

***p*-Values and the Fortification Technique.** Efficiency of residue recovery from aqueous samples from a fortification technique is usually reported. Here this means adding known amounts of pesticides to water in a laboratory test before extracting and processing the sample through each step of analysis. Therefore, the fortification gives data on the efficiency of the total procedure—*i.e.*, extracting, concentration, cleanup, separating, etc.—and not only on the extracting. Each step in a residue method can cause sample loss or contamination.

Fortifying laboratory water samples approaches actually recovering field samples if a pesticide is completely dissolved and not associated with suspended matter and the other water quality characteristics are similar to natural water (pH, *T*, ionic strength). In another approach natural water characteristics are altered to laboratory fortification specification to obtain maximum efficiency and to be able to standardize extraction procedures. Different standardization procedures are needed for samples from different water environments—*e.g.*, a river water with high turbidity, a clear stream, sea water, or organically polluted lake water. Many different water quality parameters (Table II) and solvents (Table I) are possible to standardize and quantitate LLE. The best choice should be defined for each water type.

For example, Table III shows the *p*-value parameters chosen for quantitative liquid–liquid extraction of surface water (*35*). The ionic

Table III. *p*-Value Parameters Chosen for Quantitative Liquid–Liquid Extraction

Ionic Strength—0.2*M* phosphate buffer
pH—variable
Solvent—variable
Temperature—25° ± 0.5°C
Turbidity[a]
Soluble organics[a]
Oily organic content[a]

[a] Under investigation.

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strength is set at 4–20 times that of the natural ionic strength (*17*), therefore standardizing this water quality parameter. The pH value is adjusted according to the criteria previously described above. Temperature is set as a constant near laboratory temperature; thus the solvent is the prime variable to choose.

Table IV. *p*-Values for 2,4-D Extraction from Aqueous Solutions[a]

	Benzene			*Ethyl Acetate*		
	Average p-Value	*±SD*	*No.*	*Average p-Value*	*±SD*	*No.*
Distilled water	0.915	±0.008	11	0.996	±0.002	13
River water[b]	0.925	±0.007	12	0.996	±0.003	11
River water[b] (filtered)	0.911	±0.007	2	0.997	±0.0007	3
Creek water[c] (high organic load)	0.920		1	0.998		1

[a] Water adjusted to 0.2*M* ionic strength and pH = 2.00 with KH_2PO_4 and H_3PO_4; extraction temperature was 25° ± 0.5°C; less than 50 mg/liter 2,4-D in 20-ml aliquots were extracted with 2-ml of solvent.
[b] Schuylkill River water intake to Philadelphia Drinking Water Supply.
[c] Wissahickon Creek at confluence with Schuylkill River.

Table IV shows that distilled water, filtered and unfiltered river water, used as a drinking water supply, and a polluted creek water have consistent *p*-values under the set of water quality parameters described. In these *p*-value determinations the LLE extraction step is isolated when a sample is extracted from a water solution containing a pesticide at a sufficiently high concentration for direct analysis of the solvent or residual water phases (*36*).

Criteria for Quantitative Liquid–Liquid Extraction of Aquatic Samples

The ultimate goal of the LLE step is to transfer completely the pesticide from water to a solvent for subsequent qualitative and quantitative analysis at the *n*g–μg level. General criteria to achieve this goal are given in Table V (*14*). The *p*-value concept is a useful tool in the liquid–liquid extraction of organic pesticides from water for choosing the solvent and the pH value of extraction. Selecting a solvent system which yields a high *p*-value uses smaller sample volumes and/or less solvent volumes. The solvent:water ratio and number of extractions are also selected from *p*-value determinations.

The equations used to calculate the total fraction extracted (F_n) into the solvent phase for one extraction of unequal phase volumes is the same as for E (Equation 9). The calculation of multiple extractions of a different phase volumes are considered in n steps; each step has a different possible solvent:water ratio (α) (*37*).

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Table V. General Criteria for the Quantitative Extraction of Organic Pesticides from Aqueous Systems (*13*)

Choice of a solvent
Setting of aqueous conditions to stabilize the solute—*i.e.*, stop physical, chemical, and/or biological affects on the pesticide
Setting of aqueous conditions for best recovery—*i.e.*, pH, ionic strength, temperature
Choice of the smallest aqueous volume which will give a sufficient amount of pesticide for quantitative analysis
Choice of a solvent:water ratio to give maximum recovery in minimum volume and/or minimum steps
Choice of the minimum number of times to re-extract the sample and give the maximum recovery in the minimum volume and/or minimum steps
Time to attain partition equilibrium

$$F_n = \frac{\alpha_1 p}{\alpha_1 p - p + 1} + \frac{\alpha_2 p}{\alpha_2 p - p + 1} + (1 - E_1)\frac{\alpha_3 p}{\alpha_3 p - p + 1}\,[1 - (E_1 - E_2)] \tag{10}$$

$$F_n = 1(E_1) + A(1 - E_1) + B(1 - E_1 - E_2) \tag{11}$$

Two equations are written for multiple extractions of constant solvent:water ratios, where the solvent is insoluble in H_2O—*e.g.*, benzene, hexane—

$$F_n = 1 - (1 - E_1)^n \tag{12}$$

and where the solvent is somewhat soluble in water—*e.g.*, ether, ethyl acetate—

$$F_n = E_1 + (1 - E_1)\,[1 - (1 - A)^{n-1}] \tag{13}$$

where A is defined by the amount extracted in the second and subsequent step. The accuracy and precision of these equations have not been described to date.

Discussion

The difficulties and problems of LLE of pesticides from water have been outlined. A theoretical approach for accurate and precise quantitation of pesticides from natural water using p-values has been proposed. Few p-values have been reported for aqueous solvent systems; some have been determined for organophosphate pesticides (*35*). Table VI shows the p-value for the parathion system consisting of parathion, its oxon, and hydrolysis product, p-nitrophenol extracted under the conditions of 0.2*M* phosphate buffer and a pH of 3.10. At this pH value these compounds hydrolyze least. Ether is the best solvent for the LLE of the whole system. Equations 10, 11, 12, and 13 are now used to determine

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Table VI. Liquid–Liquid Extraction of Parathion System from 0.2M Orthophosphate Buffers at 25°C ± 0.5°C (35)[a]

Compound	*pH*	*Hexane*	*Benzene*	*Ethyl Acetate*	*Ether*	$CHCl_3$	CCl_4
Parathion	3.10	0.89	0.88	0.84	0.93	—	—
Paraoxon	3.10	0.77	0.99	0.98	0.99	—	—
p-Nitrophenol	3.10	<0.20	0.60	0.99	0.98	0.66	<0.30

[a] All values are the average of three determinations and are *p*-values.

the best serial LLE. Parathion has been extracted by different investigators at different water quality conditions with varied success; 1:1 ether: petroleum ether, benzene, chloroform, hexane, 1:1, hexane:ether, and methylene chloride have been used. These procedures have been reviewed by Faust and Suffet (*13*).

The solvent is finally chosen depending upon the desired analysis; for example, in a GLC procedure for studying aqueous $KMnO_4$ oxidation of parathion, small paraoxon GLC peaks next to much larger parathion peaks, 5–10 size, had to be assayed (*37*). Therefore it was desired to maximize extraction of paraoxon and minimize the LLE of parathion to quantitate both; ethyl acetate for the solvent served best. This application uses *p*-value to aid a specific LLE problem.

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3

Confirmation of Pesticide Residues by Mass Spectrometry and NMR Techniques

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Low resolution mass spectrometry (MS), especially in tandem with gas chromatography, and nuclear magnetic resonance (NMR) spectroscopy have been reviewed with respect to their application to pesticide residue analysis. Sample preparation, direct probe MS analysis, GC–MS interface problems, spectrometer sensitivity, and some recent advances in MS have been studied. MS analyses of pesticide residues in environmental samples (malathion, dieldrin, diazinon, phenyl mercuric chloride, DEF, and polychlorinated biphenyls) have been illustrated. Fragmentation patterns, molecular ions, isotope peaks, and spectral matching were important in the identification of these pesticides. The sensitivity limitations of NMR and recent improvements in sensitivity are discussed along with examples of pesticide analyses by NMR and the application of NMR shift reagents to pesticide structure determinations.

Mass spectrometry has come of age in pesticide residue analysis. The mass spectrum of an organic compound is proof of its presence in the matrix. Gas chromatography, previously the only technique available to give evidence of a pesticide residue, suffers one tremendous disadvantage—lack of qualitative accuracy. "Nothing is as ambiguous as a peak from a gas chromatograph" is an overstatement, but 90% proof of the presence of a pesticide is not enough. Nevertheless, gas chromatography is indispensable in the majority of pesticide residue analyses; it is involved in preliminary identifications or separations or is interfaced to the mass spectrometer as a separation tool. Here the mass spectrometer is the most definitive detector for a gas chromatograph.

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Infrared spectroscopy is as definitive as mass spectrometry when standard spectra are available for matching, but it has two disadvantages:

(1) Lack of sensitivity relative to MS (by a factor of 10^5)

(2) requirement for a relatively pure compound (gas chromatography–mass spectrometry tandem instrumentation allows the use of crude mixtures).

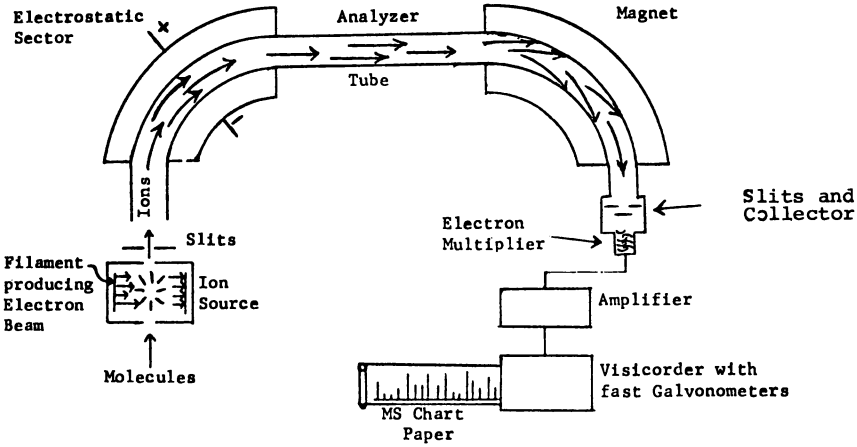

Figure 1. Block diagram of a double-focusing mass spectrometer

Production of the Mass Spectrum (*1*, *2*, *3*). Regardless of sample introduction mode, the sample must be in the gaseous state for ionization. The sample molecules are bombarded by a beam of electrons of variable energy in the ion source (Figure 1) to fragment the molecules and produce positive ions. These ions are swept through a series of slits and the analyzer tube by a strong electrostatic field. The source and tube must be maintained at a low pressure ($<10^{-5}$ torr) to minimize collisions of the ions with each other or with air molecules. The ions pass through a magnetic field where they are deflected to different degrees based on their mass/charge (m/e) ratios. By sweeping the magnetic field strength, ions of successively increasing mass are brought sequentially into focus at the collector. In a double-focusing mass spectrometer, resolution is improved by an electrostatic sector which renders the ion beam monoenergetic by velocity focusing before it arrives at the magnetic focusing sector. The electron multiplier amplifies the signal received at the collector, and the resulting signal is amplified further to drive a set of galvanometers which make a trace on a photographic chart paper.

All fragment ions of a molecule form peaks of certain intensities with positions on the abscissa of the spectrum corresponding to ion masses (mass to charge ratios, m/e). This information constitutes the mass spec-

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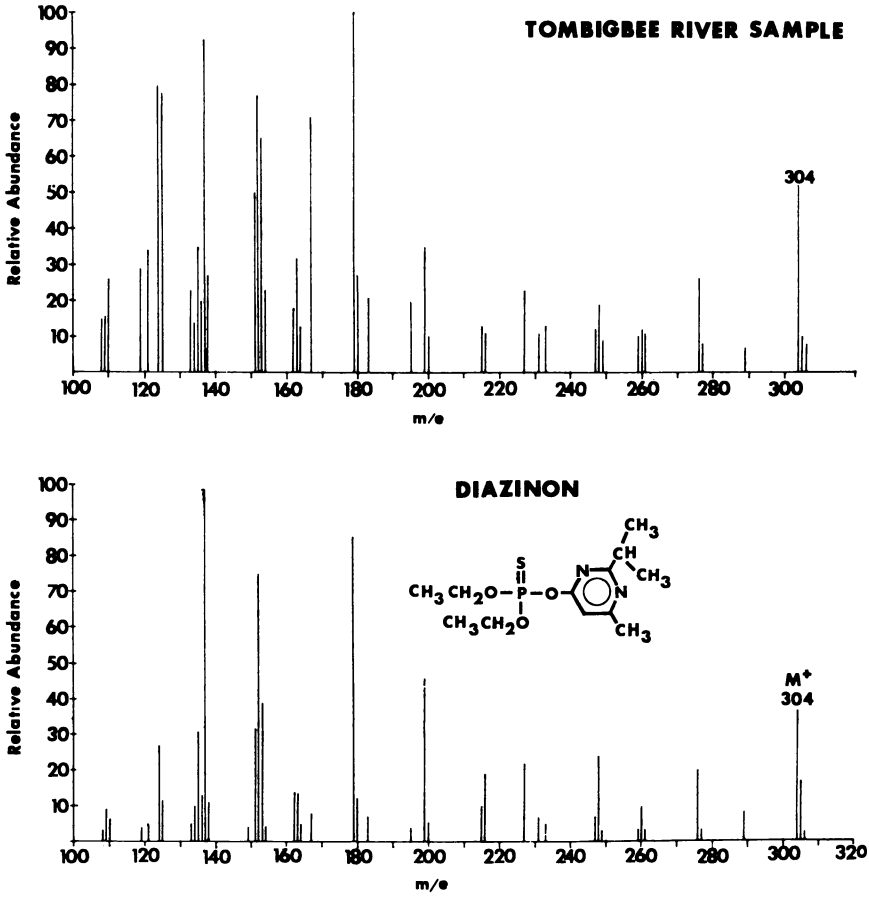

Figure 2. Mass spectra of Diazinon

trum, and comparison with the spectra of known compounds gives definitive compound identification (Figure 2). The fragment ion of greatest mass in most cases corresponds to the molecular weight of the compound (Figure 2, $M^+ = 304$), having been created by loss of one electron during electron bombardment. This ion is called the molecular ion or parent ion. The masses of important fragment ions indicate the empirical formulae of the ions and give clues to structures of parts of the molecule (Figure 3).

Direct Probe Analysis. In the direct inlet (direct probe or solids probe) MS technique, the sample is placed in a small cup and inserted into the ion source a few millimeters from the ionizing electron beam (Figure 4). The cup is heated so that solids or liquids of low volatility can be directly vaporized into the electron beam. Only 10^{-11} to 10^{-6}

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grams of sample are required, depending upon sample volatility and instrument sensitivity. The great disadvantage of the direct probe technique is that the sample first must be manually separated from the gross mixture usually found in a pesticide residue extract. Extensive cleaning is required for some samples. Three examples from our laboratory illustrate the usefulness of the direct probe sample introduction technique. (Mass spectra were measured with a Hitachi Perkin–Elmer RMU-7 double focusing spectrometer.)

Diazinon. Diazinon (*O,O*-diethyl *O*-2-isopropyl-4-methyl-6-pyrimidyl thiophosphate) was tentatively identified by gas chromatography as the cause of a fish kill in the Tombigbee River in Alabama in 1968. The water extract, previously cleaned by column chromatography for GC analysis, was chromatographed on a thin layer plate (TLC); the area of absorbent corresponding to the R_f value of a diazinon standard was scraped from the plate, extracted with methylene chloride, and filtered. The filtrate was evaporated just to dryness in a direct probe sample cup and analyzed by mass spectrometry. Absorbent from a control TLC plate was treated in an identical manner, and subtraction of the control mass spectrum from the sample spectrum left peaks corresponding to a diazinon standard (Figure 2), including the molecular ion peak (M^+ 304). There

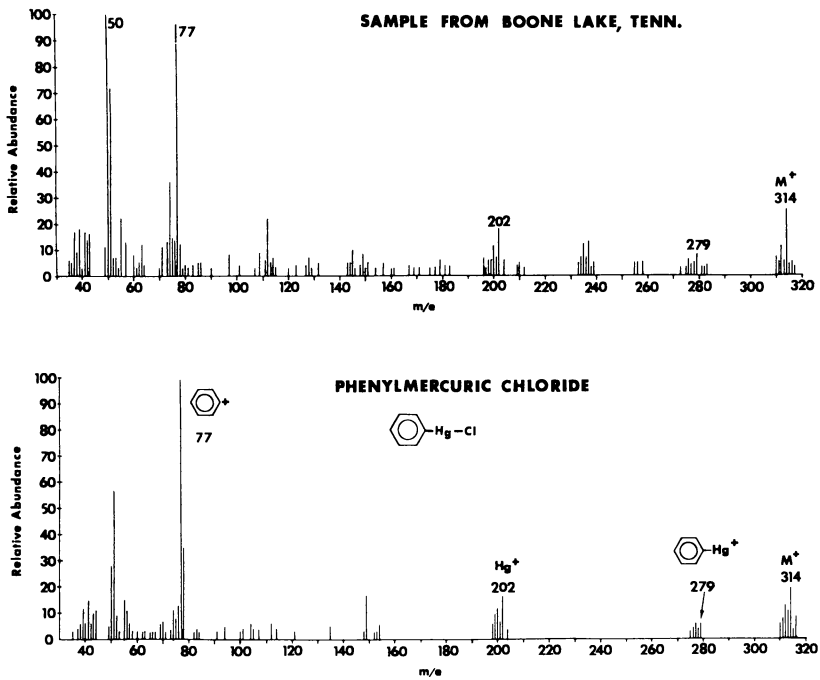

Figure 3. Mass spectra of phenyl mercuric chloride

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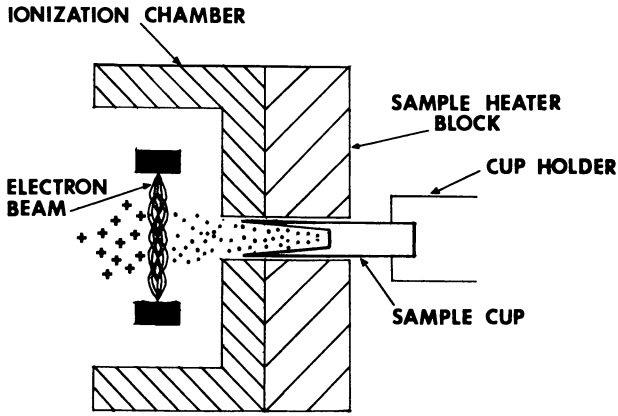

Figure 4. Direct inlet sample introduction system for a mass spectrometer

are still differences in the sample and the standard spectra; this is true for most environmental samples (Figures 3, 9, and 10a). This discrepancy is caused by several factors, among them being: (a) small changes in the amount and type of background compounds in the mass spectrometer, (b) changing conditions in the ion source, and (c) impurities in the sample.

S,S,S-*Tributylphosphorotrithioate (DEF).* During extensive fish kills in Charleston Harbor, South Carolina, in 1965, an organic thiophosphate was extracted from the water (*4*). Its mass spectrum was measured by the direct probe technique. The parent ion (M^+ 314) was 16 mass units greater than the mass of Merphos (*S,S,S*-tributylphosphorotrithioite, I), a pesticide discharged into the harbor by a pesticide manufacturer. NMR, IR, and GC analysis confirmed the MW 314 compound to be oxidized Merphos, or DEF (II). This is a classic illustration of the importance of the molecular ion in mass spectrometry. The molecular weight of a compound is the most valuable datum available for its identification.

$$\underset{\text{I}}{(CH_3CH_2CH_2CH_2S)_3P} \rightarrow \underset{\text{II}}{(CH_3CH_2CH_2CH_2S)_3P{=}O}$$

M^+ 298 M^+ 314

Phenyl Mercuric Chloride. An organomercury compound was believed responsible for a large fish kill in Boone Lake, Tennessee in 1968. Residue obtained from empty, unlabeled drums found in the lake was analyzed by MS using the direct probe method. Mercury has six isotopes of enough abundance to be observed by mass spectrometry (*5*). The mercury isotope pattern was observed in the molecular ion region of the spectrum (M^+ 314, Figure 3) where it is distorted by the chlorine isotope

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pattern in the region corresponding to loss of chlorine and in the region corresponding to loss of chlorine plus phenyl (the Hg^+ ion). A peak at *m/e* 77 corresponds to the phenyl ion. The residue was identified as phenyl mercuric chloride by matching its spectrum with a standard (Figure 3).

GC–MS Tandem Analysis. Usually MS confirmation is requested for sample extracts containing only a few micrograms of a pesticide in a gross mixture. Separating and collecting the pesticide from such a sample for direct probe MS analysis is impractical, usually impossible. Therefore, the combination of gas chromatography–mass spectrometry (GC–MS) is our routine analytical approach.

In GC–MS analyses (*6, 7*), a gas chromatograph is interfaced through a separator to the mass spectrometer (Figure 5). The effluent from the GC column may be split to allow simultaneous recording of the GC flame detector response and the mass spectra. The effluent going to the MS passes through a heated transfer line into the separator where the carrier gas, usually helium, is preferentially removed. This is necessary to lower the pressure of the effluent to that inside the spectrometer ion source, about 10^{-5} torr, and to enrich the sample in the effluent. Once in the source, the effluent gas is ionized just as any other MS sample—in this respect, the gas chromatograph is another inlet for the mass spectrometer.

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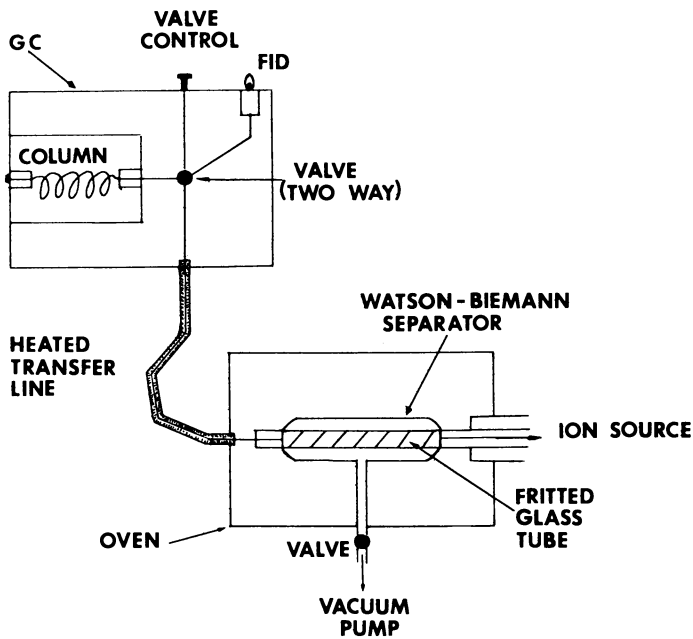

Figure 5. GC–MS interface

The mass spectrum is scanned in 1–5 seconds when using the GC–MS technique, and it is often possible to get two or three spectra of a single sample component.

Several problems accompany the GC–MS technique. Initial problems are those associated with any gas chromatographic analysis since the quality of the mass spectra is limited by the degree of separation in the chromatograph. Water and soil extracts can be chromatographed directly sometimes, but prior cleaning by column chromatography or solubility separations is usually necessary for good mass spectra. Some pesticides decompose on the metal injection port or metal columns; we have not been able to obtain a spectrum of endrin by the GC–MS technique for this reason.

Column bleed is also detrimental; bleed components that may not show up on ordinary GC detectors can produce large, masking, background peaks in the mass spectrometer, which limit its sensitivity. These components also foul the ion source. The bleed from conventional silicone or some OV-series columns is troublesome at higher temperatures. Several GC liquid phases that are much more stable at higher temperatures have become available recently. These should be excellent for GC–MS work.

SCOT (support coated open tubular) and conventional capillary columns are widely used in GC–MS analysis because of their low carrier gas flow requirements and superior resolution. Much of our GC–MS work, including pesticide analysis, is done with SCOT columns, flow rates being 5–15 ml/minute. All capillary columns limit the injection volume to 2 or 3 microliters or less.

Derivatization reagents, such as TMS and other silylation compounds (*8*), are used frequently to make materials volatile enough for GC–MS analysis. For example, diazomethane and other methylation reagents are often used for phenols and acids. These derivatives also make MS analysis by the direct probe technique possible in many cases.

Our GC–MS system uses the Watson–Biemann (*9*) separator (Figure 5). The column effluent passes through a fritted glass tube in an oven. A vacuum pump lowers the pressure outside the frit so that most of the helium carrier gas passes through the walls, enriching the sample going into the ion source. Several problems are associated with this frit. Polar sites (Si–OH groups) may adsorb polar sample molecules, causing the separator to behave similarly to a chromatographic column. This effect may cause a time lag between responses by the flame GC detector and the mass spectrometer with large polar molecules such as resin acid, methyl esters, or polychlorinated biphenyls. Often the GC column effluent is mixed partially at this point, thus decreasing the resolution. This problem may be alleviated by shortening the frit—from the usual 6 inches to

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1–3 inches—or by silanizing it for deactivation of Si–OH groups (*10*). A high separator temperature, 250°–300°C, is necessary usually with large polar molecules, such as polychlorinated biphenyls, to decrease lag time in the separator; however, these high temperatures may increase catalytic decomposition of the sample. Sample loss through the separator wall is also a problem; usually only 10–20% of the sample passes into the ion source. Finally, glass frits become fouled with use and must be replaced.

Several other types of separators are now available for GC–MS, each with advantages and disadvantages. Updegrove and Haug (*6*) give details on the various separators, as well as a discussion of many problems experienced in GC–MS analysis.

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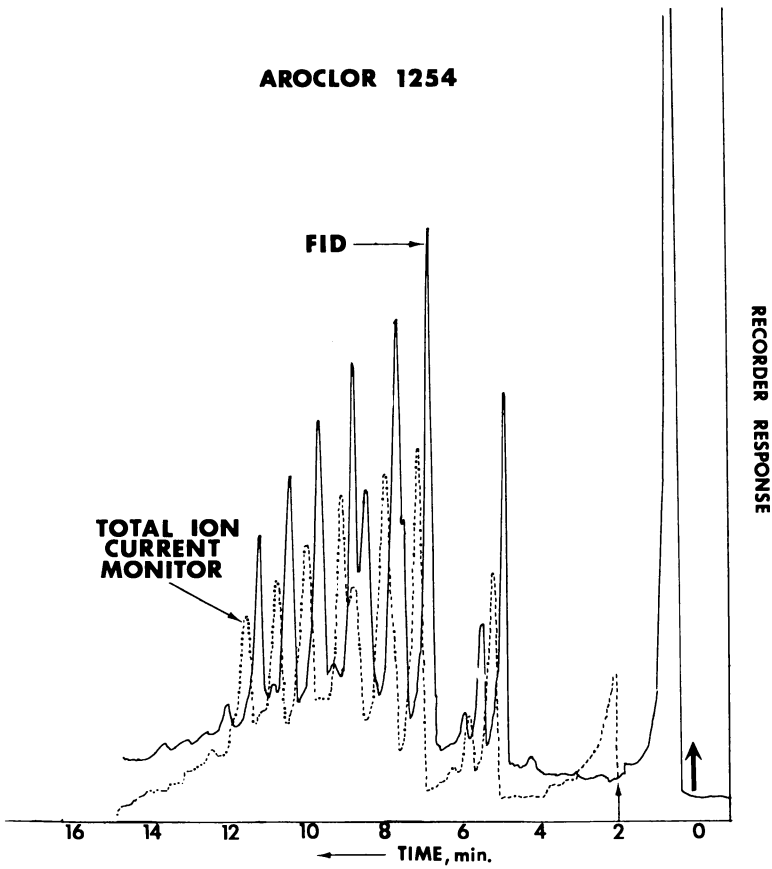

Figure 6. Dual pen recording of mass spectrometer total ion current monitor response and corresponding flame ionization detector response–Aroclor 1254. (Recorder pens are displaced slightly.)

Direct coupling of the gas chromatographic column to the mass spectrometer ion source can eliminate many of the problems discussed earlier. Although this has been done (*11*), many engineering improvements in the integrated GC–MS system are necessary before direct coupling becomes common practice.

A total ion monitor (TIM), though not part of the interface, is often useful for the GC–MS operation. The TIM is an ion detector positioned in the analyzer tube between the ion source and the magnet and is adjustable to collect a certain percentage of the total ions formed. This detector response is registered on a dual pen strip chart recorder with that of the GC flame detector (Figure 6). There may be some differences in peak ratios because of differences in detector responses to the various compounds; the mass spectra are taken at the TIM peak maxima since the ions are then most concentrated. Pesticide residue analysis by GC–MS

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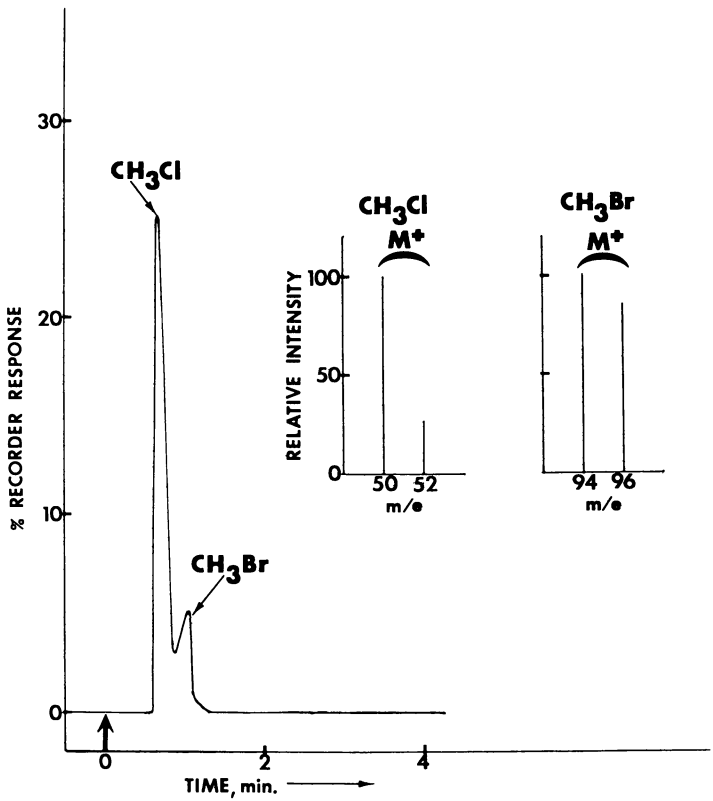

Figure 7. Gas chromatogram (FID) and partial mass spectra (GC–MS) of methyl chloride and methyl bromide in stored flour head gas

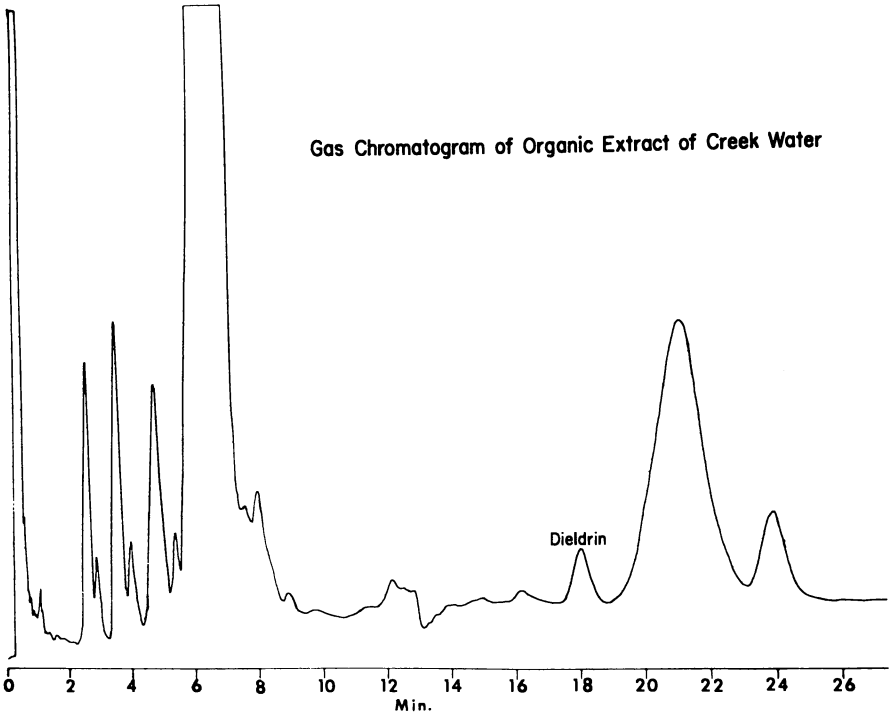

Figure 8. Gas chromatogram (FID) of a water extract containing dieldrin—ready for GC–MS analysis

is illustrated by the following examples from our laboratory. (All mass spectra illustrated in this paper were measured with a Hitachi Perkin–Elmer RMU-7 double focusing spectrometer interfaced to a Perkin–Elmer 900 gas chromatograph through a Watson–Biemann separator.)

Methyl Chloride and Methyl Bromide. GC analysis of the head gas above some stored flour detected a compound in addition to the methyl bromide normally used as a fumigant for stored grains and flour. GC–MS analysis showed the contaminant to be methyl chloride. A subambient temperature accessory on the gas chromatograph was used to separate 400 microliters (<1 microgram) of the head gas, injected *via* the regular liquid injection block, on a QF-1 SCOT column at 0°C. Figure 7 shows the gas chromatogram and mass spectra. Isotope peaks (5) were valuable in identifying these two compounds. Since chlorine occurs in nature in a ^{35}Cl:^{37}Cl ratio of about 3:1, the parent peaks of methyl chloride at m/e 50 and 52 are in a 3:1 ratio. ^{79}Br and ^{81}Br occur in almost a 1:1 ratio so the parent peaks of methyl bromide at m/e 94 and 96 should be of almost equal intensity. (The unexpectedly large difference in peak heights

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is probably a result of scanning the spectrum at a speed approaching the time limit of response of the MS signal amplifier.)

Dieldrin. Dieldrin is found often in microgram per liter concentrations in environmental samples by GC analysis. The combination of GC–MS is invaluable for confirmation in such cases. Figure 8 shows the flame detector gas chromatogram of an extract of creek water containing a textile waste with dieldrin in it (*12*). Figure 9 shows the corresponding mass spectrum of the dieldrin in the GC effluent along with a dieldrin standard spectrum, also taken by the GC–MS technique. An exact match is not observed, but enough fragment ions match to make identifying the dieldrin positive. Peaks *m/e* 79 and 108 are indicative of dieldrin, as are the chlorine isotope peaks of several of the fragment ions (*13*).

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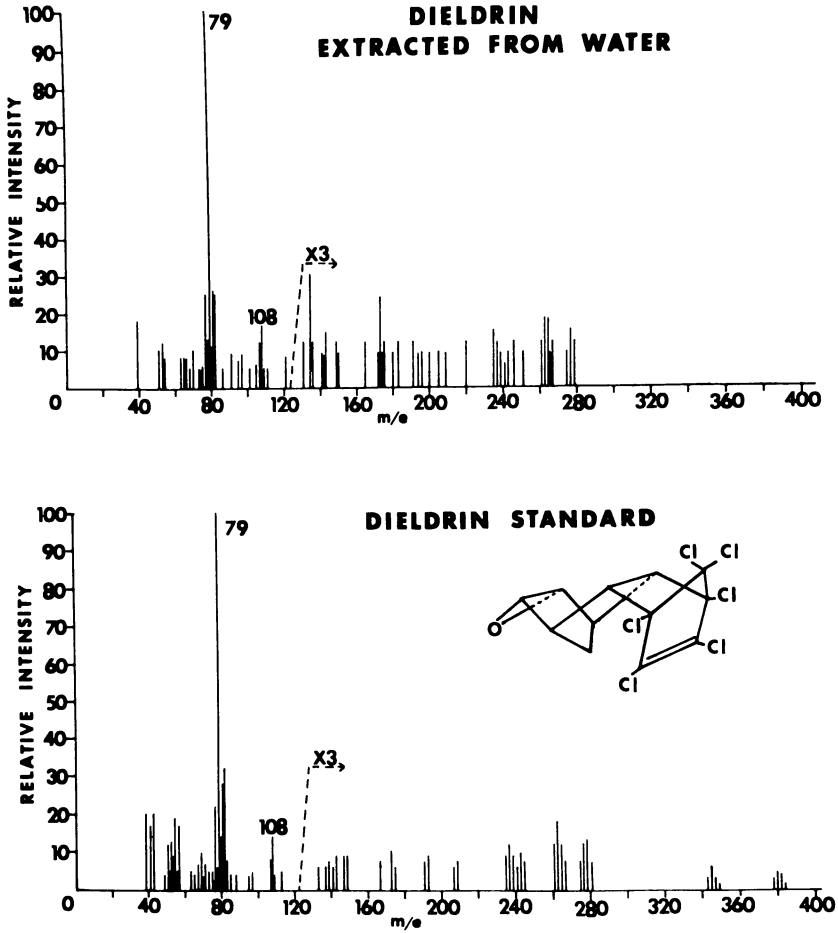

Figure 9. Mass spectra (GC–MS) of dieldrin

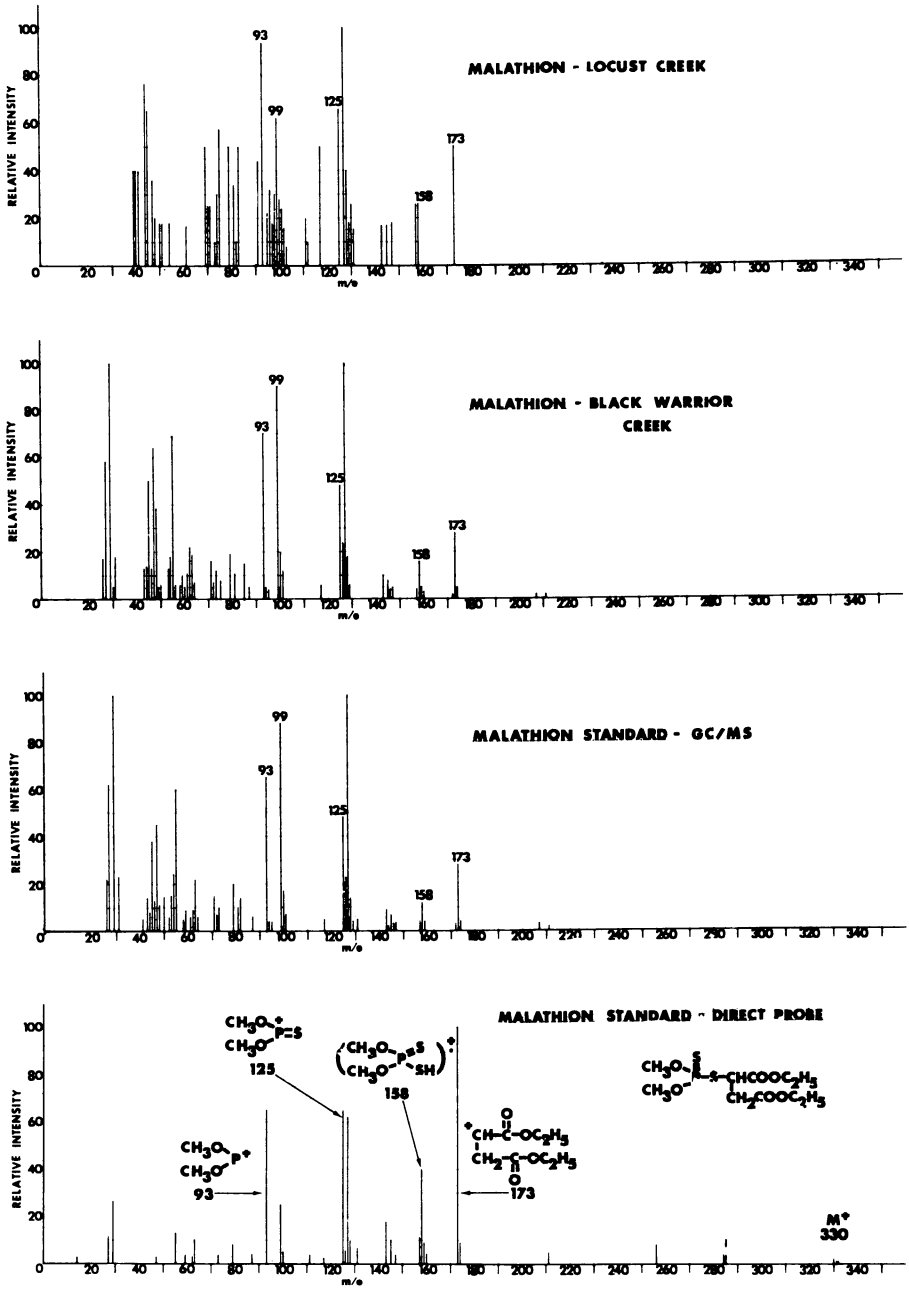

Figure 10. Mass spectra of malathion

The molecular ion cluster and the peak cluster caused by loss of one chlorine atom from the molecular ion (M–Cl) were masked in the sample spectrum by the spectra of interfering components.

Malathion. Malathion has been identified by GC in extracts of water associated with several fish kills. Confirmation was requested for one extract containing 10 μg—plenty for GC–MS analysis. An almost perfect spectral match with a standard was obtained (Figures 10b, c). Another case provided a real challenge. Figure 10a shows the spectrum; less than 1 μg of malathion was injected into the GC for GC–MS analysis. Although the spectral match is not as good as in the other case—many extraneous

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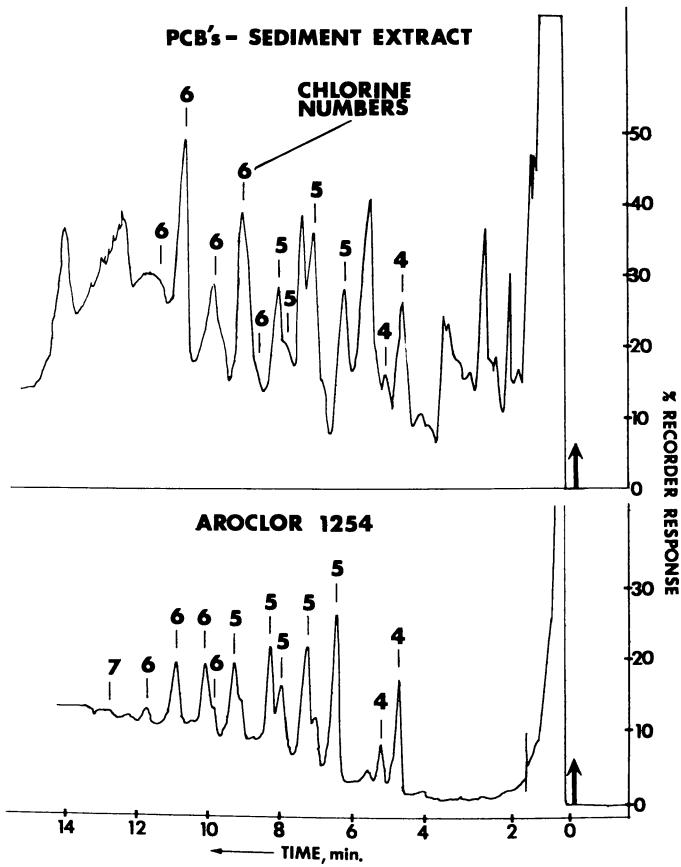

Figure 11. Gas chromatograms (FID) of polychlorinated biphenyls from the environment and in an Aroclor standard. (GC conditions are the same.)

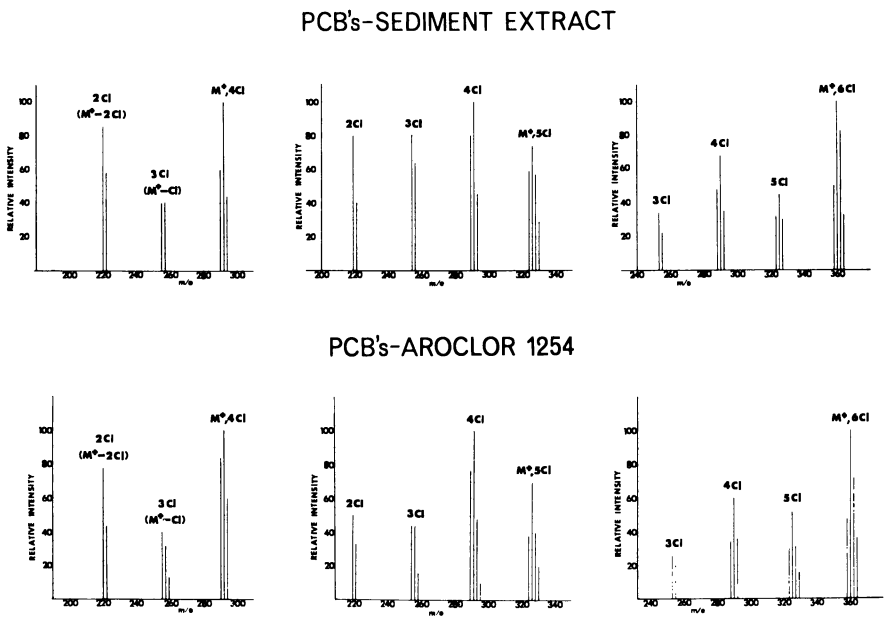

Figure 12. Partial mass spectra (GC–MS) of some of the PCB's of Figure 11 showing the number of chlorine atoms on each ion

peaks remain even after subtracting background—strong peaks at *m/e* 173, 158, 127, 125, 99, and 93 confirm the presence of malathion (*14*).

Significant differences in peak intensity ratios are observed often between mass spectra obtained by the GC inlet mode and those obtained *via* the direct probe. Figure 10d was obtained using the direct probe with standard malathion. By this method, a small parent ion is observed —it is not in the GC–MS spectrum—and peak *m/e* 173 becomes the base peak instead of *m/e* 127. Also, *m/e* 99 is much smaller and *m/e* 158 is larger than in the GC–MS spectrum. Such differences are attributable usually to different sample pressures in the ion source; the greater the concentration of sample in the source, the more likely are ion–ion and ion–molecule reactions. Spectra taken at different points of the same gas chromatographic peak will differ slightly since the concentration of the corresponding sample in the ion source varies with time.

Polychlorinated Biphenyls (PCB's). Aroclors, manufactured by the chlorination of biphenyl, are distillation fractions containing 20 or more PCB isomers. They are used widely in industry and have become ubiquitous pollutants of the aquatic environment (*15*). By using GC–MS methods PCB's have been found in bald eagles (*16*) and in human adipose tissue (*17*). Bonelli (*18*) has used a GC–MS–computer system to analyze for PCB's in sewage effluents and fish. We have used mass spectrometry

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several times to confirm the presence of PCB's, identified tentatively by electron capture GC, in water and mud samples. The flame detector chromatograms of the extracts are invariably complicated, but the specificity of the mass spectrometer allows unequivocable identification of submicrogram amounts of PCB's.

In one case, a Florida Bay sediment extract, cleaned on a florisil column, was analyzed for Aroclor 1254. The GC flame detector pattern is shown in Figure 11. Eleven of these peaks were shown by MS to be PCB's. Their retention times and chlorine numbers (number of chlorine atoms per PCB molecule, as determined by MS) correspond with those of an Aroclor 1254 standard, also shown in Figure 11.

Mass spectra showing several chlorine isotope clusters for some of the PCB's from the sediment are compared with corresponding spectra from an Aroclor 1254 standard in Figure 12. The parent ion was observed in all the PCB's. The major fragmentation path is loss of successive chlorine atoms from the parent molecule. Each such loss gives a cluster of isotope peaks whose intensity ratios depend on the number of chlorine atoms still present on the fragment. These isotope ratios are definitive; as seen in Figure 12, isotope ratios in the sample spectra are comparable with those in the Aroclor standard. The overall fragmentation patterns are also roughly the same in the sample and the standard.

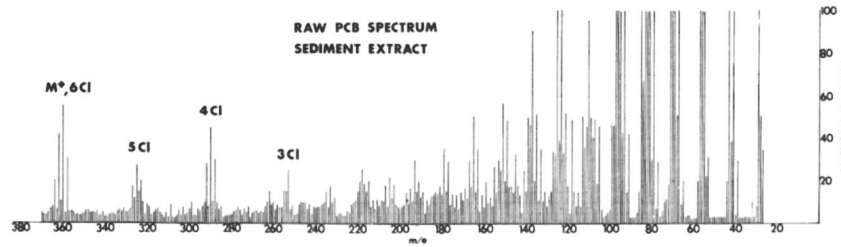

Figure 13. A mass spectrum (GC–MS) of a PCB in an environmental sample extract before background subtraction and normalization. The parent ion (M+) and fragment ions containing three, four, and five chlorine atoms gave discernable peaks.

Much of the work in mass spectrometry of pesticides is involved with data reduction. Figure 13 shows the raw spectrum of one of the 6-chlorine sediment sample PCB's shown in Figure 11 (scanned from high to low mass)—the m/e values had to be counted manually. A background spectrum had to be subtracted and the remaining peaks normalized to the base peak, or most intense ion peak, before plotting the corresponding partial PCB spectrum of Figure 12. From the sample chromatogram of Figure 11, we see that the individual mass spectra are not a result of single components; background spectra taken just before or

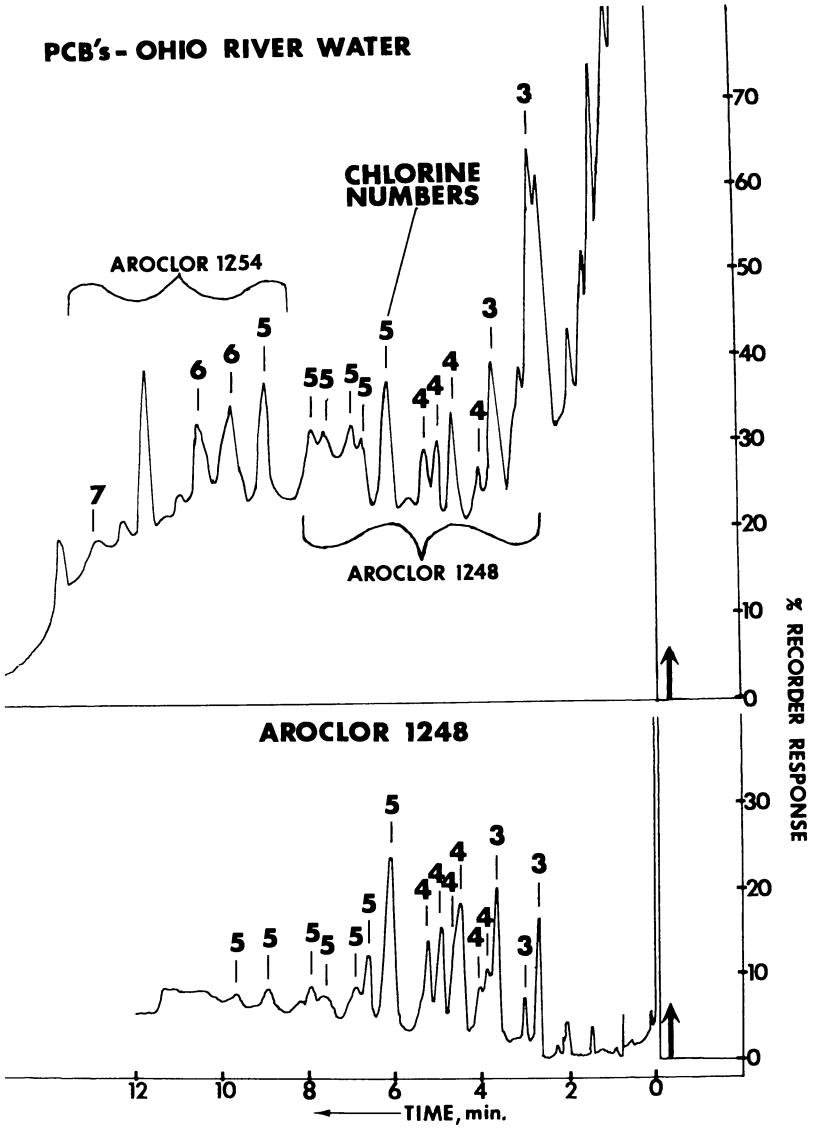

Figure 14. Gas chromatograms (FID) of PCB's in a river extract and in an Aroclor standard. (GC conditions are the same.)

just after the peak elutes must be subtracted to get spectra of the individual PCB's. Background is caused by overlapping or underlying sample components, column bleed, or spectrometer pump oil. Data reduction by computers (discussed later), promises to be a great boon for mass spectrometry.

Figure 14 shows the GC flame detector chromatogram of a water extract from an Ohio river. Mass spectra of the components eluting from the GC showed 15 to be PCB's. The retention times and chlorine number of the first eleven of these correspond to an Aroclor 1248 standard, also shown in Figure 14. However, the last four PCB peaks appear to be from Aroclor 1254 (*cf.* Figure 11). These four components are in relatively large concentrations, as they are in the 1254 standard, and the standard Aroclor 1248 contains only trace amounts, if any, of 6-chlorine and 7-chlorine PCB's.

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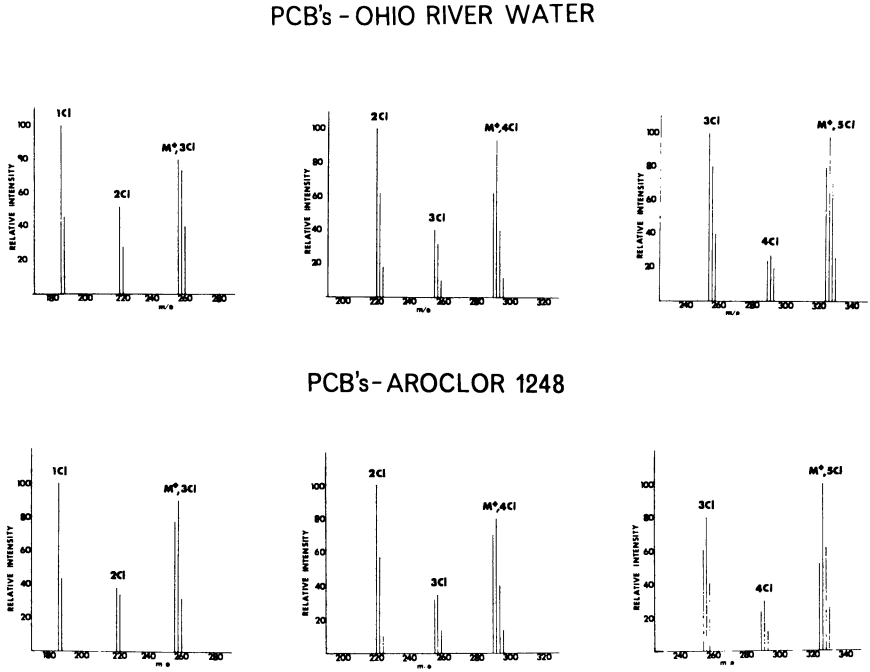

Figure 15. Partial mass spectra (GC–MS) of some of the PCB's of Figure 14 showing the number of chlorine atoms on each ion

Mass spectra showing the clearly definable chlorine isotope clusters of some PCB's from the river sample are compared with corresponding spectra from an Aroclor 1248 standard in Figure 15.

Only 6 micrograms of Aroclors were present in the total sample according to electron capture GC analysis. The sample chromatogram of Figure 14 represents an injection of about 2 μg of these Aroclors. Approximately 0.1 μg of an individual PCB gave a good spectrum.

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High Resolution Mass Spectrometry. Most spectrometers used for pesticide analysis can separate ions only well enough for their nominal mass to be determined. This is adequate for most purposes, but a tremendous amount of specificity can be gained by high resolution mass spectrometry (usually $M/\Delta M > 10{,}000$ @ 10% valley) (*19*). Knowing the empirical formulae of certain ions is helpful in identifying completely unknown compounds or when studying the mechanisms of fragmentation of known molecules. This is true for the parent ion of an unknown. The separation offered by high resolution mass spectrometry (HRMS) allows calculation to four decimal places of the masses of the parent and fragment ions from the molecule, a degree of accuracy that eliminates all but one or two possible empirical formulae for these ions.

Organochlorine and organophosphorus pesticides have been identified in synthetic mixtures by HRMS (*20*), and the high resolution mass spectra of several organochlorine pesticide standards have been determined (*13*). One technique used for survey analysis of polychlorinated biphenyls in environmental samples is tuning the HRMS to search for a single distinctive ion, one containing certain chlorine isotopes.

HRMS is expensive and complex, and sensitivity is sacrificed for resolution. Rarely is enough of an aquatic pollutant, especially a pesticide residue, available for analysis by HRMS. However, advancements are rapid; GC–HRMS analysis with on-line computer calculation of empirical formulae of each ion of each GC eluant (*21*) is now possible. Kearns (*19*) has discussed computer analysis of high resolution mass spectra.

Computer Applications in Mass Spectrometry. In the analysis of an environmental sample by low resolution GC–MS, 100 or more mass spectra, including background spectra, are obtained from the oscillographic recorder. Manually counting the mass numbers before any identifying can be done and normalizing and subtracting background from each spectrum before it can be matched exactly with a standard are exceedingly time consuming. On-line computerization of this process is helpful (*22, 23*), and several integrated GC–MS–computer systems are now on the market, although few have been field tested. Most of these computer systems are programmed to perform the above operations, including the plotting of bargraph spectra. Other software features usually include the plotting of a reconstructed gas chromatogram, subtraction of background and overlapping spectra from spectra of interest, and a print-out or mass chromatogram (*24*) of selected peaks which are distinctive for particular compounds.

On-line computerization has the advantage that the computer can interact closely with the GC–MS. For example, the computer can monitor the gas chromatogram and record mass spectra as the compounds elute.

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In a quadrupole mass spectrometer (discussed below), the computer enhances system sensitivity by integrating ion current signals at specified mass positions, thus increasing signal–noise ratio. Bonelli (*18*) used a computer-controlled quadrupole GC–MS to analyze for traces of PCB's in the environment.

Biros interfaced a small time-averaging computer (Varian C-1024) with a GC–MS to scan and average repetitively a small portion of the mass spectrum (such as the molecular ion region), subtract background peaks, normalize, and plot the partial spectrum. This was done for several chlorinated hydrocarbon pesticide standards (*25*) and for heptachlor epoxide in human liver tissue (*26*).

Computer-stored data banks of low resolution mass spectra are being established as references for identifying unknown organic compounds. By this method, comparing an unknown mass spectrum with 10,000 reference spectra can be accomplished in a few minutes (*27*). Such reference files will be extremely useful in identifying the myriads of unknown organic compounds, including pesticides, now being found in industrial and municipal waste effluents and in the natural aquatic environment. However, spectral variations may cause difficulties in spectral matching; different spectrometers and varying operating conditions can produce different intensity patterns for the same compound.

Quadrupole and TOF Mass Spectrometers. The popularity of quadrupole mass spectrometers is increasing; quadrupole GC–MS systems are commercially available and have been used for pesticide residue analysis (*18*). They have linear mass presentation and fast scan speeds and are adaptable to computerized data reduction and computer controlled operation. Quadrupoles have the disadvantage of lower resolution and mass range (both about 750 amu) than magnetic instruments. They show also a more pronounced decrease of relative sensitivity with increasing mass number (mass discrimination), tending to produce apparent differences in fragmentation patterns from those of magnetic instruments. Wiesendanger (*28*) has explained quadrupole principles, operations, characteristics, and applications.

TOF (time-of-flight) mass spectrometers are also increasing in popularity and have been successfully coupled with gas chromatographs. In fact, the first successful on-line identification of GC effluents by MS was with a TOF (*29*). TOF spectrometers are sensitive instruments. They are by far the fastest scanning of the three major spectrometer types—50,000 lines per second. This feature makes it the only mass analyzer available for fast reaction research. The TOF also has a stable mass scale and can be computerized readily. However, resolution and mass range of the TOF instrument are low—about 500 amu. This may limit its application for pesticide residue analysis; however, mass spectra of organophos-

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phorus (*14*) and carbamate (*30*) pesticide standards have been measured by TOF. Damoth (*31*) has discussed principles and applications of TOF spectrometry and compared TOF, quadrupole, and magnetic instruments.

Ionization Processes. In a conventional mass spectrometer ion source, ions are created by bombarding the sample gas with electrons of 70 ev energy. Several other ionization processes are used for special purposes. The simplest departure from the conventional is to lower the bombarding electron energy, usually to 20 ev or less (*32*). As the energy is lowered, fragmentation of the sample molecule is less severe and a less complicated spectrum results. Because its relative intensity is enhanced, the parent ion is easier to identify. This is an important advantage in pesticide residue analysis; however, because less total ionization occurs at lower energies, the sensitivity is less than at 70 ev.

Chemical ionization (CI) mass spectrometry (*33*) is new and rapidly growing and has many possible applications, including pesticide residue analysis. In CI mass spectrometry, a reagent gas, usually methane, is ionized by electron impact in the MS source. The ionized methane reacts with free methane to form mostly CH_5^+, which in turn reacts with the sample gas, mostly by simple protonation. The pseudo-molecular ions (MH^+) thus formed often dominate the spectrum. Advantages of CI mass spectrometry include: (a) sensitivity comparable with electron impact spectrometry, (b) simplified spectra with parent ions often predominating, and (c) application to GC–MS where methane is used as the carrier gas (*34*). This latter advantage carries a bonus—*i.e.*, since the carrier gas is the reagent gas and must be at a pressure of about 1 torr in the ion source, no separator is necessary. The entire GC effluent can be transferred directly to the ion source, thus avoiding sample loss. Several MS companies are actively researching applications in this area, and a CI source will probably be available soon on commercial instruments.

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NMR Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy and mass spectrometry complement each other; mass spectrometry provides molecular weight data, while NMR spectroscopy provides stereochemical information based on the various kinds of protons present in a molecule and their relation to one another. A major advantage of NMR spectroscopy is that the sample is not altered or destroyed. NMR spectroscopy has two major limitations with respect to pesticide residue analyses—it is much less sensitive than mass spectrometry, infrared or ultraviolet spectroscopy, or gas chromatography; and moderately pure (95%) compounds are required usually. Since pure materials are required, environmental sam-

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ples must be cleaned for NMR analysis. This entails preliminary separation techniques such as column, thin layer, or gas chromatography. The sample is dissolved then in an appropriate deuterated or aprotic solvent and spiked with an internal reference standard (usually tetramethylsilane).

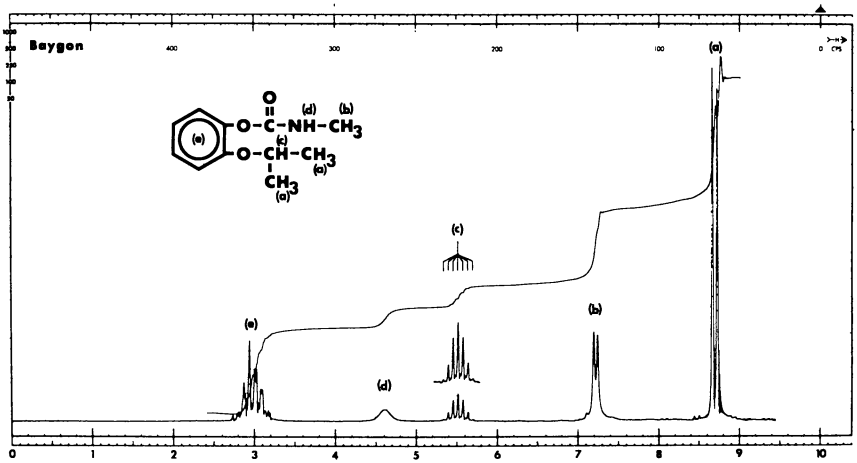

Figure 16. The 100 MHz NMR spectrum of Baygon in $CDCl_3$

Spectra of Standards. Interpretation of NMR spectra is enhanced when spectra of known similar compounds are available for comparison. Since few pesticides have been included in NMR spectral catalogs, we recorded and interpreted spectra of four important classes of pesticides and some of their degradation products:

1. Organophosphorus pesticdes
2. DDT and related compounds
3. Carbamate pesticides
4. Chlorinated polycyclodiene pesticides

Spectral interpretations are discussed, and the chemical shifts and coupling constants are presented in tabular form (*35, 36, 37, 38, 39*). A reference catalog of the 100 MHz spectra themselves is also available (*40*). An example of our spectral data is Figure 16, where the spectrum of Baygon shows signals for the five different kinds of protons in this molecule. Of particular interest is the septet of one proton intensity arising from the methinyl proton; this signal is used later in the discussion to determine the limits of sensitivity of NMR spectroscopy.

Samples from the Environment. *Oxidation Product of Merphos.* The compound from the Charleston Harbor extract (*4*) and a reference standard of merphos (I), known to be discharged into the harbor by a pesticide manufacturer, produced similar NMR spectra, but the low-field multiplet (produced by the 6 methylene protons on the carbons bonded directly

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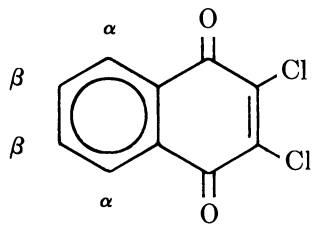
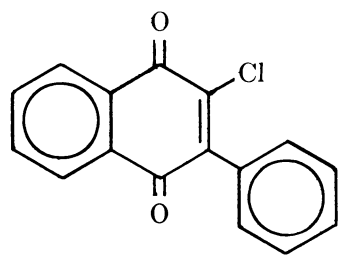
to the sulfur) in the spectrum of the unknown was shifted downfield from that of the standard. A reasonable explanation for this paramagnetic shift would be the addition of an electronegative moiety (such as =O) to the phosphorotrithioite molecule (I). Comparison of the NMR spectrum of the extracted compound with that of an authentic sample of S,S,S-tributyl phosphorotrithioate (DEF, II) showed that they were identical compounds.

Phygon. White and co-workers (*41*) observed that the concentration of Phygon (III) in benzene decreased with time under ordinary laboratory conditions with a corresponding increase in the concentration of degradation products. The most abundant degradation product was collected by gas chromatography; its NMR spectrum contained three aromatic proton signals with relative areas of 2:2:5. The NMR spectrum of Phygon has only two 2-proton signals from the α- and β-protons, respectively. Mass spectrometry showed that only one chlorine atom remained in the product. NMR, MS, and IR evidence indicated the addition of a phenyl group to Phygon and supported structure IV. Confirmation of this hypothesis was attained by synthesizing 2-chloro-3-phenyl-1,4-naphthoquinone (IV) and comparing the NMR, MS, and IR spectra of this product with the photoconversion product.

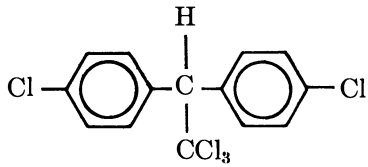


III

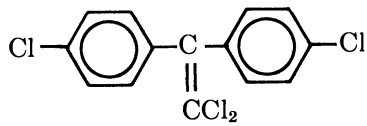


IV

DDT and DDE (42). The liver tissue of rats fed a diet containing DDT and the adipose tissue of a human, who had been exposed occupationally to DDT, were extracted and analyzed by NMR spectroscopy for DDT (V) and DDE (VI).



V



VI

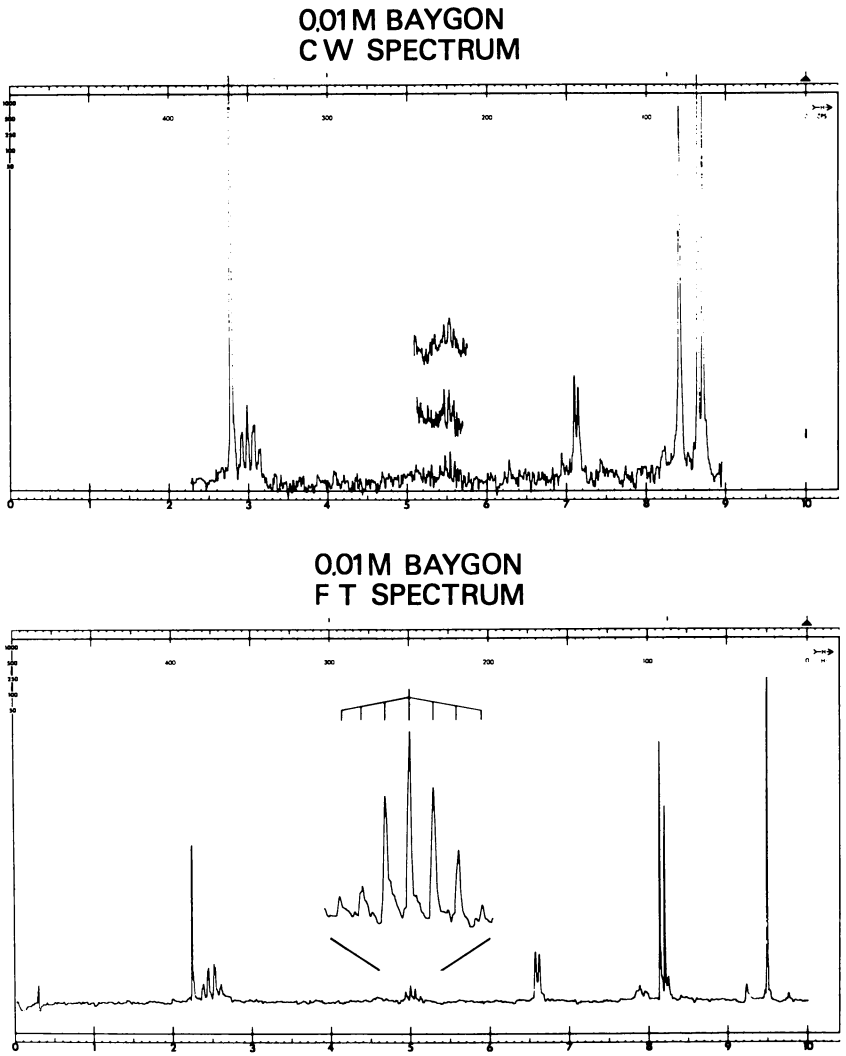


Figure 17. The 100 MHz continuous wave (CW) and Fourier transform (FT) spectra of 1 mg of Baygon in 0.5 ml of $CDCl_3$

The tissues were digested in perchloric acid and extracted, and the extract was chromatographed on a Florisil column. The fractions containing the pesticide residues were concentrated to near dryness, dissolved in 0.15 ml carbon tetrachloride, and placed in microcells. The NMR spectra were scanned 250–325 times, using a small time-averaging computer to obtain signal enhancement of the aromatic proton signals. These signals were separated sufficiently so that relative amounts of V and VI could be cal-

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culated. Other examples of NMR applications to environmental samples have been summarized in a recent review on this subject (*43*).

Advances in NMR. *Sensitivity.* Usually 1–10 mg of a sample is dissolved in about 0.5 ml of solvent. However, when less than 1 mg of sample is available, microcells can be used, reducing the volume and amount of sample required by one-third to one-fourth. Improved sensitivity through signal enhancement can be obtained by time averaging; the spectrum is scanned repeatedly, and the signals are logged in digital form in a small time-averaging computer. On command the spectrum is displayed in analog form on an oscilloscope or permanently recorded using the NMR spectrometer's pen recorder system. The signal enhancement is equal to the square root of the number of scans; a signal enhancement of 10× would require 100 scans. The main disadvantage of this method is the time required (250–500 seconds per scan) to obtain signal enhancements of 10× or more.

A recent refinement of time-averaging signal enhancement is Fourier-transform (FT) NMR spectroscopy. With an FT-accessory spectra can be accumulated in the memory banks of a small computer at the rate of one or more per second, reducing the data accumulation time by factors of 250–500.

Figure 17 is a comparison of the continuous wave (CW) and FT-spectra of 1 mg of Baygon in 0.5 ml $CDCl_3$. In the CW-spectrum the signals of all but the 1-proton septet and the 1-proton multiplet are dis-

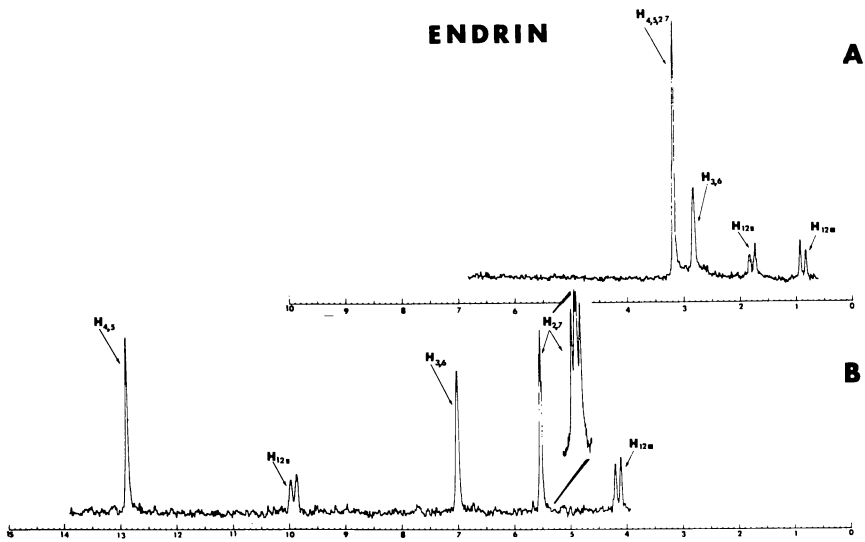

Figure 18. The 100 MHz NMR spectra of (A) endrin (0.14 M) without $Eu(DPM)_3$ and (B) with 0.07 M $Eu(DPM)_3$ in CCl_4

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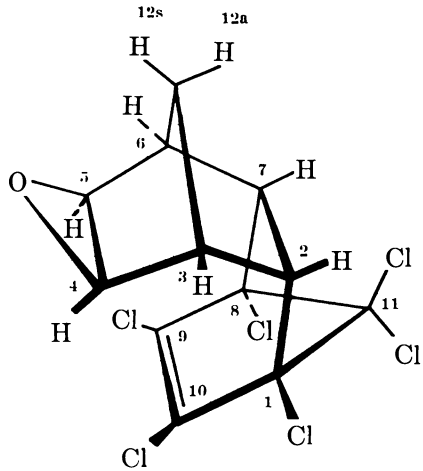
tinguishable. The FT-spectrum, after 250 pulsed scans, has reduced background noise, and the 1-proton septet is clearly distinguishable—the inset shows an expansion of this signal.

Usable FT-spectra of 0.1 mg of Baygon in 0.5 ml $CDCl_3$ were obtained after 2,750 pulsed scans (46 minutes)—the same number of scans using CW–NMR at 250 and 500 seconds per scan would have taken 8 or 16 days, respectively. At this sensitivity, weak sample peaks can be observed, but often peaks from impurities in the solvent are magnified also, and they may obscure some of these sample peaks. Accumulation of the same number of pulsed scans on a solvent blank and modification of the computer program to subtract this background from the sample data would eliminate this problem. More scans and use of a microcell should enable one to obtain spectra on 0.01 mg of sample or less. This enhanced sensitivity should do more to widen the use of NMR for pesticide residue analysis than any other innovation in NMR spectroscopy. Perhaps even GC–FT–NMR will become a reality in the future.

NMR Shift Reagents. NMR spectra of pesticides and their degradation products are often complex and may contain overlapping signals that obscure much of the spectrum. Recently discovered NMR shift reagents help alleviate this problem. We found the new NMR shift reagent tris(dipivalomethanato)europium [$Eu(DPM)_3$] helpful in making chemical shift and structural assignments of the epoxy derivatives of the chlorinated polycyclodiene pesticides and their degradation products (*44*). $Eu(DPM)_3$ associates with the epoxide oxygens and induces large paramagnetic shifts of the signals of protons in adjacent and distant rings. The NMR spectra of endrin (VII) and dieldrin (VIII) are similar in most



VII

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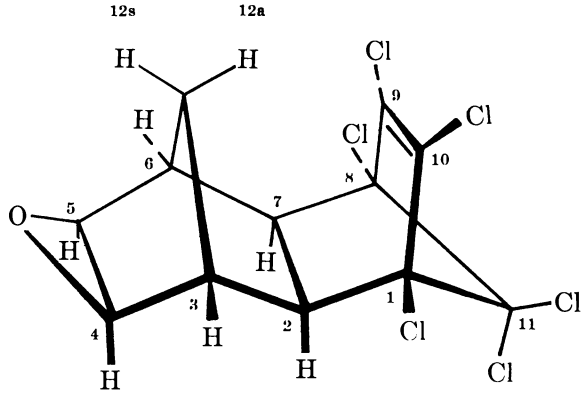
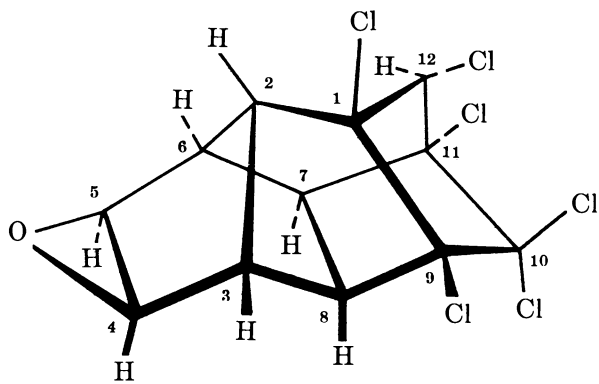


VIII

respects, but one definitive feature of the endrin spectrum (*45*) is the $H_{2,7}$ signal (a pair of doublets). This characteristic of the endo–endo ring fusion is obscured by the overlap of the $H_{2,7}$ and the $H_{4,5}$ signals of endrin in CCl_4 (Figure 18A). Addition of $Eu(DPM)_3$ to the endrin solution shifts the $H_{2,7}$ and the $H_{4,5}$ signals downfield (Figure 18B), but the latter shift is approximately four times greater. These two signals are then well separated, and the splitting of the $H_{2,7}$ signal can be observed at a 250 Hz sweep width. Dieldrin, which possesses an endo–exo ring fusion, does not contain dihedral angles conducive to the above couplings, and its $H_{2,7}$ protons resonate as a sharp singlet (*45*).

Another advantage of the NMR shift reagents is that structural information can usually be derived from the magnitude of the chemical



IX

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shift produced from addition of the shift reagent to the sample. The inverse relationship between the distance of a proton from the europium and the magnitude of its paramagnetic shift was used to determine the stereochemistry of the C-12 proton of photodieldrin (IX). We found that H_{12}, which migrated during photorearrangement, is syn to the epoxide. This configuration was confirmed by decoupling experiments that show that H_{12} is coupled to H_6—the "bowsprit" and "flagpole" hydrogens on a six-membered ring rigidly held in a skew-boat conformation (*44*).

Acknowledgments

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Interaction of Organic Pesticides with Particulate Matter in Aquatic and Soil Systems

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Organic pesticides occur in detectable amounts in many parts of the environment. An understanding of the fate and behavior of biologically-active substances in the total environment is a necessity for the chemicals to be used safely and for new products to be developed which will not produce adverse effects. The interactions of organic pesticides with particulate matter in surface waters and soil systems according to the chemical properties of the compounds and their reported behavior in these systems are discussed below. The particulate matter includes various clay minerals, soil organic matter, charcoal, and other specific adsorbents that were utilized to help identify adsorption mechanisms. Pesticides were classified according to ionizability, molecular size, functional groups present, water solubility, and vapor pressure. Adsorption included ion exchange, dipole interactions, and other physical adsorption mechanisms.

The fate and behavior of organic pesticides in the biosphere has concerned scientists almost from the time that the chemicals were discovered. In 1945 Carollo (*1*) was concerned about the effect on soldiers as a result of DDT in natural water supplies. He formulated biological methods to detect the pesticide. Forrest *et al.* (*2*) found in 1946 several toxic metabolites of DDT in soil systems. Four years later Chisholm *et al.* (*3*) and Fleming (*4*) found that DDT was persistent in soils and that it had accumulated in amounts of 137–194 pounds per acre under trees that had been sprayed to control Dutch Elm disease. Soon other investigators

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found that DDT and other pesticides had accumulated in soils in high amounts (*5, 6, 7*). In the early 1950's DeWitt (*8*) reported that feeding DDT to quail reduced the hatchability of their eggs and the viability of the chicks. About the same time Foster *et al.* (*9*) reported that DDT and several other pesticides had accumulated in the soils to the detriment of some crop plants. Several investigators implicated DDT and other pesticides with the death of fish and other aquatic life (*10, 11, 12*) and many began finding deleterious effects on the ecosystem as a result of using pesticides. After Rachel Carson (*13*) described the adverse effects of pesticides in her book, "Silent Spring," the problem finally received much public attention. Since then many popular and scientific books and governmental reports have been published concerning pesticides in the biosphere (*14, 15, 16, 17, 18, 19, 20, 21, 22*). The material which is discussed below concerns the interactions of a variety of pesticides with diverse particulate matter in aqueous and soil systems.

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Particulate Matter

Natural surface waters range from clear spring water through yellow to black swamp water containing dissolved organic substances and reddish colored river and lake waters containing high amounts of iron. The pH of these waters ranges from as acidic as 3.0 to as alkaline as 9.6 (*23, 24, 25, 26*). The waters contain dissolved and suspended particles; the particles vary from individual ions, pairs of ions, or complexes made up of several ions in the dissolved state to colloidal aggregates from 0.005–2.0μ in diameter and suspended solids which are larger than 2.0μ. The colloidal and suspended particles are classified into the following size categories: clay = below 0.002 mm (2 micron), silt = 0.002–0.02 mm, fine sand = 0.02–0.20 mm, and coarse sand 0.2–2.0 mm. The particles are inorganic and organic substances originating from municipal, industrial, and agricultural wastes and soil erosion. Tons of particles result from decomposing of natural plants and animals living in waters. Suspended solids from municipal and manufacturing wastes amount to approximately 8 and 18 billion pounds per year, respectively (*27*). The municipal wastes are primarily organic substances and dissolved minerals. Manufacturing wastes come primarily from four major industry groups—paper, organic chemicals, petroleum, steel—and are composed of inorganic substances—*e.g.*, metallic particles from grinding and milling processes—and organic substances—*e.g.*, carbon particles as soot and ashes, cellulose fibers, oil, bits of plastics and rubber, and assorted debris. However, the greatest volume of wastes entering surface waters of the United States are suspended solids carried by soil erosion. These sedimentary materials accumulate to more than 700 times those derived from total

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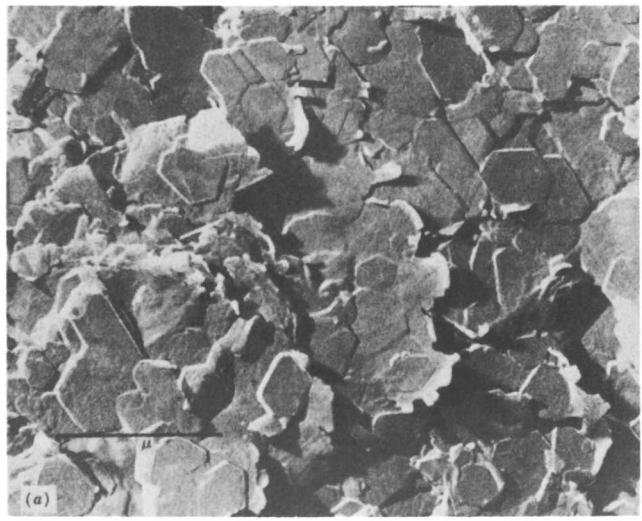
sewage discharges (27). They are washed into streams and rivers from croplands, unprotected forest soils, overgrazed pastures, strip mines, roads, or bulldozed urban areas. Soil erosion on agriculturally developed land is at least five to ten times that for natural cover, and exposure resulting from construction and land development increases the rate a hundred fold.



R. E. Grim, "Clay Mineralogy," McGraw–Hill

Figure 1. Electron micrograph of well-crystallized kaolinite clay particles (28)

Suspended materials in surface waters, stream bottom deposits, and soil systems are composed of sand, silt, and clay particles which are normally coated with thin films of organic and inorganic colloids, metallic oxides, and microbial growth. Sand particles are more or less rounded, irregularly angular, or even flat, depending upon the amount of abrasion and weathering that they have received. Silt particles are similar in shape to sand particles, but they are much smaller. Clay particles, however, are flat, platelike, or mica-like. They result in the fine texture, high water-holding capacity, and stickiness of mineral soils. Figure 1 shows an electron micrograph of well-crystallized kaolinite clay particles. Not all clay minerals have the hexagonal flake-shape of kaolinite. Some are elongate and tubular in shape; others are lath-shaped crystals, and some appear to be fluffy amorphous aggregates (28).

Several components make up the mixture of material referred to as soil clay. These include various hydrous silicates and oxides and the

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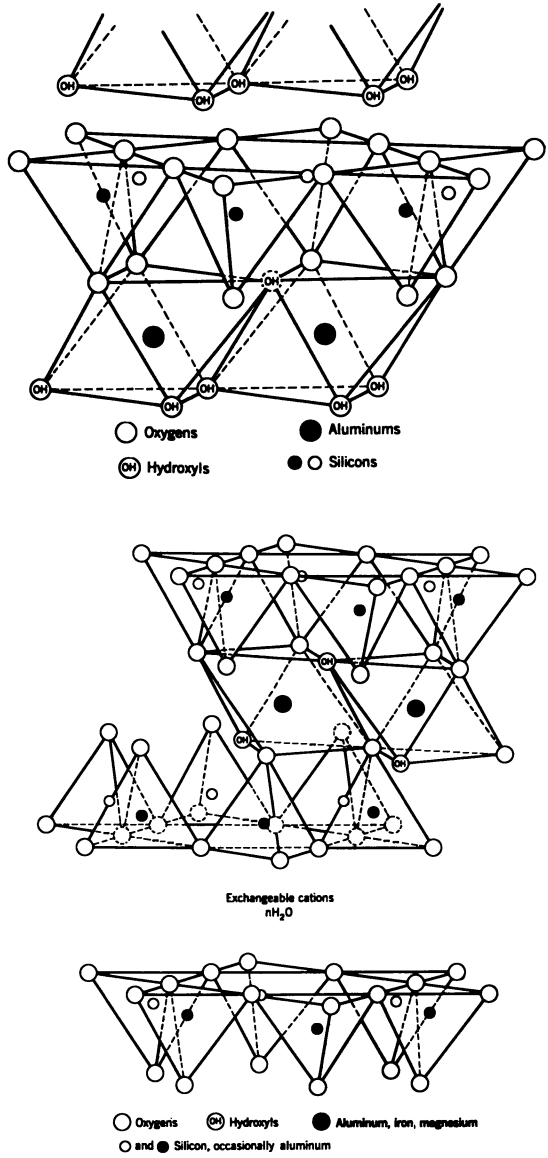

Figure 2. Diagrammatic sketch of structure of (top) 1:1 kaolinite and (bottom) 2:1 montmorillonite clay minerals (28)

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important layer silicates. The layer silicates are formed structurally from two basic units:

(1) an infinite, 2-dimensional sheet of silica tetrahedra—all three basal oxygens are shared between adjacent tetrahedra

(2) an infinite, 2-dimensional sheet of aluminum or magnesium octahedra—*i.e.*, aluminum or magnesium in octahedral coordination with six hydroxyls.

An example of the alternating tetrahedral and octahedral sheets is shown in Figure 2 for a 1:1 clay (top) and for a 2:1 clay (bottom). The layer silicate structural types are formed by condensing tetrahedral and octahedral layers in a ratio of 1:1 or 2:1—*i.e.*, the apical oxygens of the silica sheet replace hydroxyls in the octahedral sheet. According to structural considerations of ionic crystals, these oxygens are shared between a silica tetrahedron and two aluminum octahedra (or one tetrahedron and three magnesium octahedra). A tetrahedral sheet–octahedral sheet ratio of 1:1 characterizes the kaolinite minerals. Basic layer units are held together by hydrogen bonding between adjacent planes of oxygens and hydroxyls. The bonded layers do not readily separate, so the dimensions of the unit cells are relatively constant. Kaolinite minerals are common soil clays, particularly in acid soils.

In other layer silicates the tetrahedral sheet–octahedral sheet ratios are 2:1—*i.e.*, an octahedral sheet sandwiched between two tetrahedral sheets (Figure 2, bottom). The 2:1 ratio characterizes the micas, vermiculites, and montmorillonites (smectites). During crystal growth of 2:1 clays individual unit layers are superimposed and held together by van der Waals forces between adjacent planes of oxygens. The relatively weakly bonded layers are readily separated by water molecules. Such clays therefore can swell upon wetting and shrink upon drying. Montmorillonite is probably the best known member of this mineral type and soils containing high amounts of it characteristically develop large cracks during drought periods.

Usually during crystal growth, the tetrahedra are not solely occupied by silicon or by aluminum or magnesium. Aluminum may substitute for some of the tetrahedral silicon atoms, and iron, lithium, manganese, chromium, and other ions of suitable size may occupy a part of the octahedral sites. This isomorphous replacement of ions unbalances the overall charge of the crystalline lattice. An excess negative charge develops which is balanced by cations that are retained on the external layer silicate surfaces. These cations—*e.g.*, sodium, potassium, calcium, and others—are more or less exchangeable, depending on the nature of the replacing cations, the nature of the adsorbed cations, and the magnitude and distribution of the structural charge. They are held between unit layers and bond the layers together. The total number of exchangeable

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cations that a clay can retain is its cation exchange capacity (CEC). Competitive ion studies indicate that the surface charge on the layer silicates is expressed as discrete adsorption sites rather than as a charge smear (*29, 30*).

Besides the CEC resulting from isomorphic substitution, electric charges develop at the edges of clay crystals from broken bonds. These charges are positive or negative, and they contribute to the exchange capacity of the clay mineral. Negative charges are believed to result from exposed hydroxyl groups which dissociate with pH changes and are termed pH-dependent charges as opposed to charges originating from isomorphic substitution which are considered to be independent of pH.

In the 1:1 clays exchangeable cations are adsorbed only on the exterior surfaces, but in 2:1 clays the cations are also adsorbed on the interior surfaces between the tetrahedral sheets, along with the water molecules. The area between the silicate sheets is also known as the interlayer or basal spacing. For some of the 2:1 clays, potassium atoms are located between the neighboring tetrahedral sheets and because of the close geometrical spacings, potassium holds the sheets tightly together through multiple electrostatic bonds. Consequently these clays do not shrink or swell and are termed the nonexpanding 2:1 clays. Expanding 2:1 clays have a much greater specific surface area and CEC than the nonexpanding 2:1 clays. Some characteristics of selected clay minerals are given in Table I.

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Table I. Characteristics of Some Common Clay Minerals

Characteristics	*Montmorillonite*	*Vermiculite*	*Illite*	*Kaolinite*
Type of layering	2:1	2:1	2:1	1:1
Type of swelling	expanding	limited expanding	non-expanding	non-expanding
CEC (meq/100 grams)	80–120	120–200	15–40	2–10
Specific surface (m^2/gram)	700–750	500–700	75–125	25–50
C axis basal spacing in ethylene glycol (A)	17	14	10	7.2

Vermiculite, which is formed in most soils from the weathering of micas, has a higher structural charge than the other clay minerals in Table I. Calcium and magnesium plus water of hydration generally occupy the interlayer region. These cations are readily exchangeable to other solution cations, and the limited-expanding interlayer region (4–5 A) permits organic cations and polar organic molecules to enter with or instead of water, providing the organic molecules are not too large.

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Montmorillonite clay minerals are generally less well-crystallized and of much smaller particle-size than the others given in Table I. Under natural conditions various cations occupy the exchange sites, including calcium, magnesium, sodium, and aluminum. The interlayer region is variable (10–20 A) and readily accepts water and other polar molecules. Sodium-saturated montmorillonite exhibits unrestricted expansion in water, whereas the maximum interlayer spacing of the calcium-saturated mineral in water is 9.5–10.5 A.

All of the clay minerals given in Table I may occur in the clay fractions of soils. They often occur in mixtures, but frequently one mineral predominates. Kaolinite and vermiculite generally characterize acid soils of the Southeastern United States. Illite and other clay-sized micas are common in the Northeast and the Midwest. Montmorillonite occurs commonly in the neutral and alkaline soils of the Midwest and Western states. However, any and all of the clays can and do occur throughout soils of the United States, depending on the natural parent material and the formation conditions. Other details concerning clay minerals are described in the works of Grim (*28*), Marshall (*31*), and Bear (*32*).

The exchangeable cations are most highly concentrated in the immediate vicinity of the clay surface and decrease with distance from the surface. The charged surface and the associated oppositely charged ions are collectively known as the double layer. The cation swarm from the surface out into the bulk of the medium, which is usually aqueous solution, is considered diffuse following a more or less exponential distribution.

The adsorbed ions are hydrated somewhat with water molecules on the clay surfaces. These cations are replaced according to their valence and hydrated size. The water on the clay surface is less dense and more ordered than normal water and has an ice-like structure. An example of the water net configuration at clay surfaces is shown in Figure 3.

The interactions of water at clay surfaces has recently been reviewed by Low (*33*). He reported that water adsorbed on clay surface is more ordered than that in bulk solution. Exchangeable ions on the clay surface affected the heats of wetting and adsorption of water. When large or multivalent cations were present, there appeared to be little or no order in the adsorbed water. The specific volume, viscosity, and freezing resistance of adsorbed water was directly related to its structural development. Consequently, the magnitudes of these properties decrease continuously with distance from the mineral surface. Nowhere was the structure of water so rigid that ions could not diffuse through it. Low stated that although adsorbed water has a precise molecular arrangement and is ice-like, the structure is not that of ice (*33*).

Studies by Mortland *et al.* (*34*) suggested that residual water on the interlayer surfaces of expanding clay minerals is dissociated more

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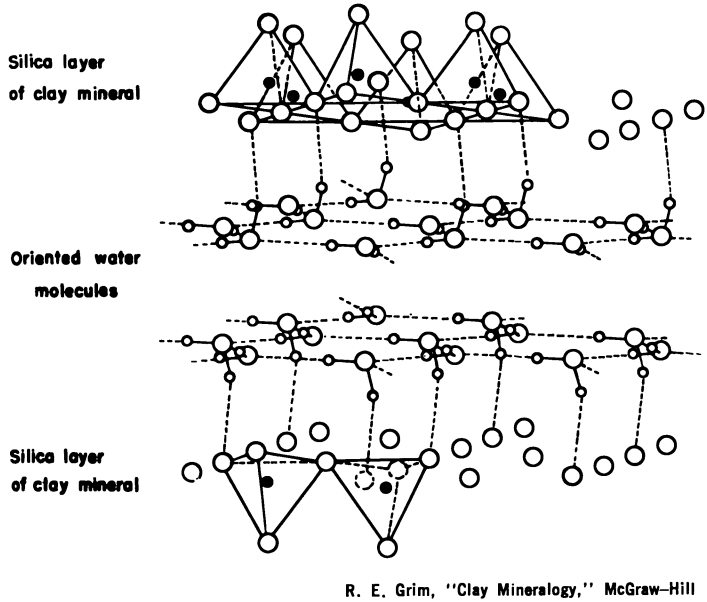

Figure 3. Configuration of water net at clay surfaces (28)

than free water. The acidity at clay surfaces in aqueous systems is greater than that in the suspension. Studies by Harter and Ahlrichs (*35*) showed that when the suspension pH was 6, 5, 4, and 3 organic acids adsorbed to clay surfaces dissociated as if they were in pH environments of 4.5, 4.0, 3.2, and 2.5, respectively. Therefore water on the surface of clay minerals is more acidic than in the bulk solution.

Besides the mineral particulate matter in surface waters and soil systems, there are organic substances occurring as dissolved solids, undecayed plant and animal tissues, and the myriads of humic substances present in soil organic matter. This humic material is called humus and is generally considered to consist of two main groups (*36*). Group one (decomposing plant and animal components and products of resynthesis in bacterial cells) consists of various nitrogenous and non-nitrogenous organic compounds belonging to well-known organic chemical groups—*e.g.*, enzymes, proteins, carbohydrates, organic acids and sugars, fats, waxes, resins, lignin, pigments, vitamins, antibiotics, and hormones. These compounds make up approximately 10–15% of the total organic matter in soils.

Organic nitrogen compounds which make up 20–50% of the total nitrogen in most surface soils are in bound amino acids and sugars. Less than 1% of the organic nitrogen in soils occurs as purine and pyrimidine bases. More than 30 amino acids have been detected in soil, including

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basic amino acids—*e.g.*, arginine, histidine, methylhistidine, lysine, and ornithine—acidic amino acids—*e.g.*, aspartic, glutamic, and cysteic—and neutral amino acids—*e.g.*, glycine, serine, valine, alanine, leucine, isoleucine, tyrosine, threonine, proline, methionine, and cystine. Amino sugars, such as glucosamine and galactosamine, occur in soils in significant amounts. Several purine and pyrimidine derivatives, including adenine, guanine, xanthine, hypoxanthine, cytosine, uracil, and thymine, have been found in soils or soil preparations. Other organic nitrogen compounds have been detected in soils or soil products. These include trimethylamine, ethanolamine, choline, histamine, creatinine, allantoin, cyanuric acid, α-picoline-γ-carboxylic acid, urea, asparagine, and glutamine. Also, enzymes—*e.g.*, amylases, catalases, glycosidases, invertase, nuclease, proteases, phosphatases, and urease—occur in soils in small amounts.

Organic phosphorus compounds, primarily inositolhexaphosphates (probably more than 50% of all organic phosphates), occur in soils. The parent cyclic polyol, inositol, exists in numerous stereoisomeric configurations, of which *myo-*, *scyllo-*, *neo-*, and *dl*-inositol have been isolated from soils as phosphate esters. The hexaphosphate of myoinositol (*myo*-IHP), phytic acid, occurs in plant tissues. It often occurs as phytin, the calcium magnesium salt. Esters of *myo*-IHP are readily adsorbed in acidic soil solution by clay minerals and finely divided hydrated oxides of iron and aluminum. Organic sulfur compounds present in soils probably occur primarily as amino acids—*e.g.*, cysteine, cystine, and methionine.

Approximately 5–15% of the soil organic matter is carbohydrate. Carbohydrates which have been isolated from soils includes monosaccharides—*e.g.*, hexoses (glucose, galactose, mannose, and fructose) and pentoses (arabinose, xylose, ribose, fucose, rhamnose), disaccharides (sucrose, cellobiose, and gentiobiose), oligosaccharides (cellotriose); polysaccharides (cellulose, hemicellulose), amino sugars (glucosamine, galactosamine, and *N*-acetyl-D-glucosamine), sugar alcohols (mannitol, inositol); sugar acids (galacturonic, glucuronic), and methylated sugars (2-*O*-methyl-D-xylose, 2-*O*-methyl-D-arabinose, 2-*O*-methylrhamnose, and 4-*O*-methylgalactose). Free carbohydrates constitute less than 1% of the total sugars and are present chiefly as monosaccharides. Approximately 10–20% of all carbohydrates have been extracted as polysaccharides, primarily cellulose, and the nature of the remaining 70–80% of soil carbohydrates is still obscure.

The nature, origin, and properties of the second group of humic materials are not yet fully understood (*36*). They comprise approximately 85–90% of the soil humus. The active portion of soil humus is made of various humic acids and small amounts of stable free radicals.

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The humic acids vary in water solubilities and in the types of functional groups present. They are believed to be responsible for the cation- and anion-exchange properties exhibited by soil organic matter.

About one-third of the humus is removed from soil by extracting with alkali. After neutralizing alkaline extracts, humic acid is precepitated, and polymeric fulvic acid remains in solution. Both acidic substances contain chemically bound nitrogen, phosphorus, and sulfur. Molecular weight estimates indicate a range of 5000–100,000 for humic acids and 2000–9000 for fulvic acids with considerable overlap. Humin is that fraction of soil organic matter which cannot be readily extracted with cold alkali. It is a chemically heterogeneous fraction and consists of relatively unchanged organic material not immediately soluble in alkali and of humified material.

Humic acids are usually polymers of aromatic compounds. The extent of aromaticity and whether aliphatic and alicyclic structures are also incorporated is not well understood. Carboxyl, phenolic hydroxyl, alcoholic hydroxyl, carbonyl, and methoxy groups are present, but the relative proportions of each are not consistent and vary with soil type, horizon, and method of isolation of the fraction. Oxygen is present in ether linkages. The nitrogen content of humic acid varies from 0.4–5%. Humic acid is a heterogeneous fraction even after purifying extensively to remove inorganic material, carbohydrates, and nitrogenous compounds. Some soils (Rendzina and mull humus) yield lignohumate humic acid, while others (moss humus and Podzel) are predominantly flavonoid. A hypothetical structure of a humic acid molecule is given in Figure 4. Additional details concerning soil organic matter are given by Bear (*32*), Kononova (*36*), McLaren and Peterson (*39*), and Eglinton and Murphy (*38*).

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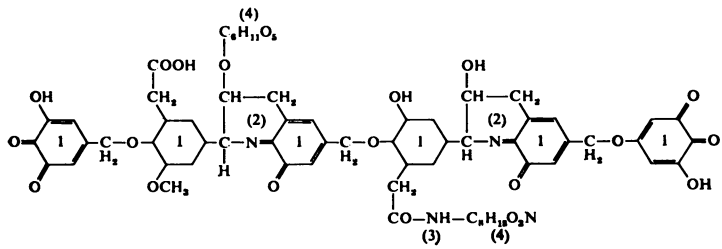

Figure 4. The structure of a hypothetical humic acid molecule: aromatic rings (1), nitrogen in cyclic form (2), nitrogen of peripheral chains (3), and carbohydrate residues (4) (36)

Classification of Pesticides

The variety of organic pesticides used presently represents many different classes of organic chemicals. The types of interactions of these compounds with the different particulate matter in aqueous and soil systems are probably enormous. Therefore, I have tried to categorize the majority of the pesticides into various groups according to their significant chemical properties and reported behavior in soils and waters. Natural occurring botanical insecticides—*e.g.*, rotenone, pyrethrins, and nicotine —will not be included here since these compounds have not been found to persist in the ecosystem. The chemicals are grouped and discussed below.

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Ionic Pesticides

Cationic Compounds. Cationic pesticides readily dissolve and dissociate in aqueous solutions to form cationic species. Physical and chemical properties for several cationic pesticides are given in Table II. The herbicides, diquat and paraquat, are the only compounds that have been studied much concerning reactions with soil colloids. Morfamquat is a herbicide related to diquat and paraquat; chlormequat and phosphon are plant growth regulators. Phenacridane chloride is a fungicide, and Hyamine is a germicide. The remaining compounds were included for comparative purposes.

Brian *et al.* (*39*) reported that diquat was water soluble (0.7 gram/ml 20°C) and that it was an effective contact herbicide which was completely adsorbed in the soil.

Diquat and paraquat are readily adsorbed from aqueous solutions by soil particles (*40, 41, 42, 43, 44, 45, 46, 47*), montmorillonite (*30, 41, 48, 49, 50, 51, 52, 53, 54, 55, 56*), kaolinite (*41, 50, 52, 53, 54, 55*), vermiculite (*29, 30, 49, 56*), biotite (*29, 30*), muscovite (*29, 30*), phlogopite (*29*), muck (*46, 48, 51*), and cation exchange resins (*48, 57*). Only small or insignificant amounts were adsorbed by charcoal and anion exchange resins (*48, 51, 53*). The compounds were adsorbed to cation exchange substances through cation exchange reactions for diquat by clay minerals (Equation 1).

$$\text{Diquat}^{2+} + 2\ \text{Na-clay} \rightleftharpoons \text{Diquat-clay} + 2\ \text{Na}^{+} \qquad (1)$$

The reaction goes strongly to the right as the large organic cations are preferentially adsorbed and small inorganic cations are displaced. The organic cations are displaced from organic matter, cation exchange resins, and vermiculite and kaolinite clay minerals by extracting with inorganic and organic salt solutions (*41, 47, 49, 53, 55, 56, 57, 58*). Only small amounts are extractable from montmorillonite clays using inorganic salt

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Table II. Properties of Cationic Pesticides

Common Name or Designation	*Trade Name*	*Chemical Name*	*Molecular Weight*	*Water Solubility 20°C, %*
Diquat	Ortho diquat	6,7-dihydrodipyrido[1,2-a:2′,1′-*c*]pyrazidiinium dibromide	344	70
Paraquat	Ortho paraquat	1,1′-dimethyl-4,4′-bypyridinium dichloride	257	70
Chlormequat	Cycocel	(2-chloroethyl)-trimethylammonium chloride		74
Morfamquat	Ceroxone	1,1-bis(3,5-dimethylmorpholinocarbonylmethyl)-4,4′-bipyridylium dichloride		
Methylene blue		3,7-bis(dimethylamino)-phenazathionium chloride	374	4
Phosphon	Phosfon	tributyl-2,4-dichlorobenzyl phosphonium chloride	398	high
Hyamine	Hyamine 10-X	di-isobutyl cresoxyethoxyethyldimethylbenzyl ammonium chloride, monohydrate	480	high
Phenacridane chloride	Acrizane	9-(*p*-*n*-hexyloxyphenyl)-10-methylacridinium chloride	406	high
Et. Pyr. Br.		1-ethylpyridinium bromide	188	high
Pyr. Pyr. Cl.		*N*-(4-pyridyl)-pyridinium chloride	193	high

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solutions (*41, 49, 53, 55, 56*), but a portion of the compounds is displaced if solutions of large divalent organic cations are used (*55*).

X-ray diffraction studies showed that diquat and paraquat were adsorbed in the interlayer spacings of montmorillonite clay with the planes of the pyridine rings parallel to the silicate sheets (*see* paraquat in Figure 5) (*30, 53*). Adsorption of one compound over another was related to the charge separation on the ions and the surface charge densities of various adsorbents (*29, 30, 55, 57*).

Adsorption of diquat and paraquat by kaolinite, vermiculite, and organic matter decreased herbicide availability but did not completely reduce it (*40, 46, 50, 52, 54, 58, 59, 60, 61*). Adsorption of the compounds by montmorillonite clay completely prevented them from being used by organisms (*40, 50, 52, 54, 58, 61*). Small amounts of diquat have been displaced and made biologically available from montmorillonite clay by

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using the nonphytotoxic organic cation *N*-(4-pyridyl)-pyridinium chloride but only when the diquat concentration in the clay was extremely high and equivalent amounts of this cation were used (*62*).

Recent studies (*63*) showed that ^{14}C-diquat retained on the internal surfaces of montmorillonite clay in aqueous soil–nutrient suspensions was not degraded by microorganisms over a one year period and that the herbicide was extracted in its original form at the end of the experiment. The chemical is tightly adsorbed in the interlayer spacings of montmorillonite and probably persists indefinitely in its original form, although in a biologically inactive state.

Other studies (*64*) done in the greenhouse showed that paraquat applied to a loamy sand at rates of 50, 100, and 200 lb/acre was readily absorbed in toxic amounts by blueberry plants. Bioassays with cucumber seedlings showed that the herbicide persisted in the soil long after the blueberry plants had been removed.

Diquat and paraquat are nonvolatile compounds, and they did not escape as vapors from aquatic or terrestrial systems (*41*, *58*). The two herbicides were readily decomposed photochemically when exposed to sunlight or ultraviolet light (*50*, *58*, *65*, *66*), but they were not photodecomposed when adsorbed onto particulate matter (*50*).

Diquat and paraquat applied to aquatic systems were effective in controlling pond flora and did not directly affect pond fauna (*45*, *67*). The absence of herbicidal activity to aquatic fauna was attributed to inactivation by adsorption on bottom muds and the subsequent lack of biological availability (*45*). The phytotoxic effects to pond flora probably occurred through absorption into the plant tissues of herbicides adsorbed on leaf surfaces. Other details concerning the behavior of diquat and

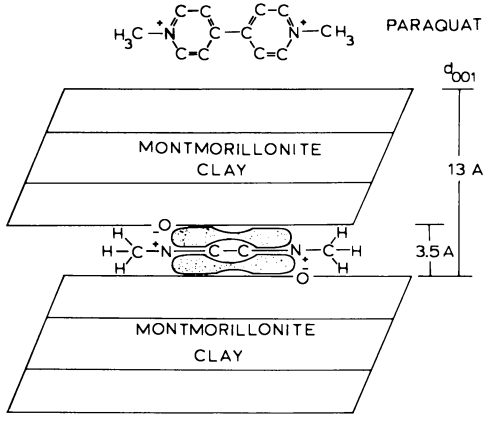

Figure 5. Adsorption of paraquat on interlayer spacings of montmorillonite clay

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paraquat are reviewed by Akhavein and Linscott (*68*), Calderbank (*69*), and Funderburk and Bozarth (*70*).

Adsorption isotherms for eight cationic compounds in aqueous suspensions with Na-montmorillonite, Na-kaolinite, and soil organic matter are shown in Figure 6. The isotherms in Figure 6 (top and center) are H-shaped, as defined by Giles *et al.* (*71*), and occur when the solute has high affinity for the solid. Since the solutes are completely removed from solution at the low concentrations, these points lie directly on the ordinate. The high affinity of the cationic species for the negatively charged clay surfaces was expected.

Diquat and paraquat were adsorbed by montmorillonite and kaolinite to approximately the cation exchange capacities (CEC) of the clay minerals (90 and 3.2 meq/100 grams, respectively). This agrees with previous findings (*30*, *53*, *55*, *56*).

On montmorillonite, divalent cations were adsorbed more than the monovalent species, and larger cations were adsorbed more than smaller ones (Figure 6, top). Desorption studies with inorganic salt solution showed that no diquat or paraquat was released when fewer herbicial cations were adsorbed than the CEC of the clay and that from 5–23% were released when they were adsorbed in excess of the CEC (*49*, *53*, *55*, *56*).

Recent desorption studies (*63*) showed that only 2% of the hyamine and methylene blue were released from montmorillonite by three extractions with 0.1*M* $BaCl_2$. Approximately 20% phosphon and pyridyl pyridinium chloride and 80% of the ethyl pyridinium bromide were released when the same extraction was used.

Adsorption of the organic cations on kaolinite and organic matter can be categorized into three groups. On kaolinite, hyamine, methylene blue, and phenacridane chloride (Group 1) were adsorbed in approximately similar amounts, which were in excess of the CEC of the clay (Figure 6, center). Diquat and paraquat (Group 2) were adsorbed to the CEC of kaolinite. Ethyl pyridinium bromide, phosphon, and pyridyl pyridinium chloride (Group 3) were adsorbed to a maximum of about 2 meq/100 grams or approximately two-thirds of the CEC of the clay mineral. Desorption with three extractions of 0.1*M* $BaCl_2$ released approximately 10, 80, and 100% of the three groups of compounds, respectively (*63*).

Adsorption of the cationic compounds on organic soil colloids resulted in isotherms which were L-shaped (Figure 6, bottom). Giles *et al.* (*71*) suggest that L-shaped adsorption isotherms are the most common type and occur when the adsorbent has a moderately high affinity for the solute. They are characterized by a curvilinear response at all concentrations used. The isotherms often seem to level off at a certain adsorption maximum. Adsorption of the cations was accompanied by a

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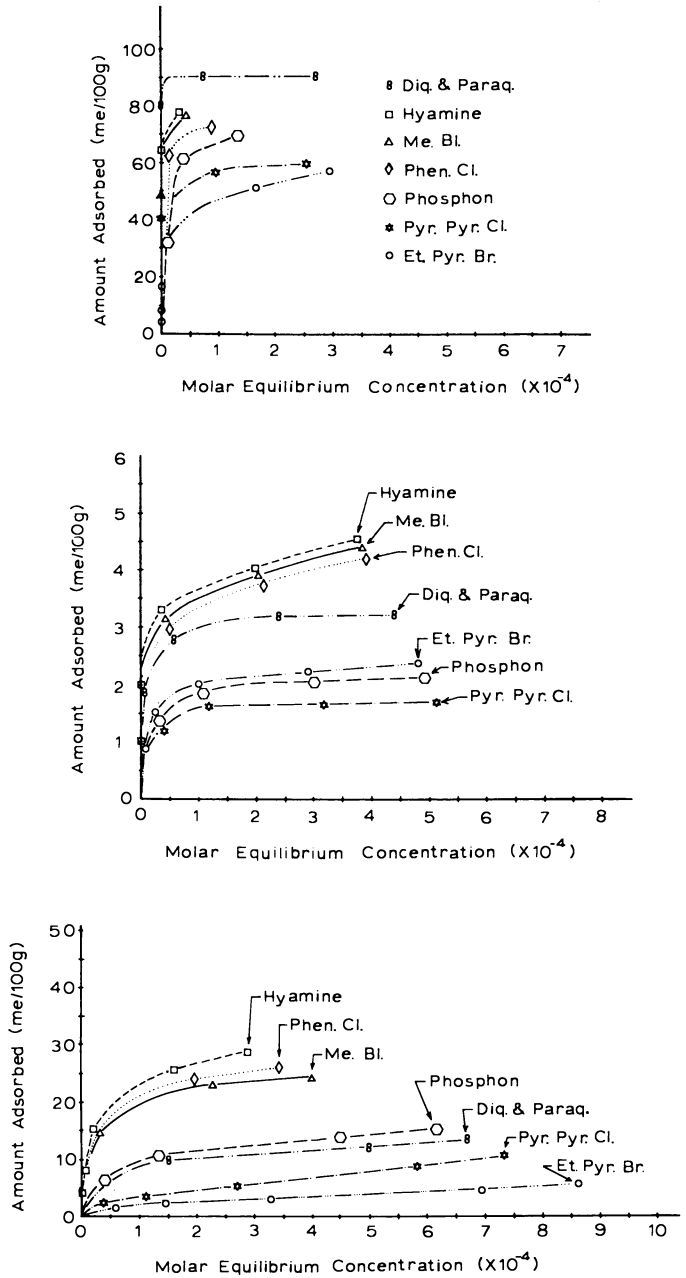

Figure 6. Isotherms for adsorption of several cationic pesticides on (top) Na-montmorillonite, (center) Na-kaolinite, (bottom) soil organic matter (63)

large decrease in the pH of the aqueous systems indicating that the primary mechanism involved was cation exchange probably at ionizable acid groups (*63*). An example of the diquat retention by ionizable carboxyl groups of organic soil colloids is shown in Figure 7. Analogous adsorption of diquat and paraquat occurs at ionizable $—SO_3^-$ groups on strong acid cation exchange resins (*57*).

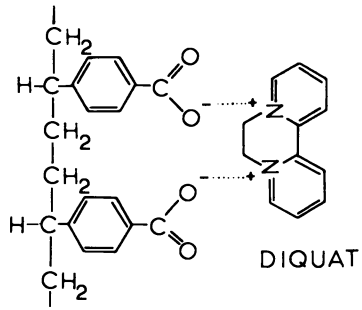

Figure 7. Adsorption of diquat at ionizable carboxyl groups of soil organic matter or weakly acidic cation exchange resins

Hyamine, phenacridane chloride, and methylene blue (Group 1) were adsorbed most by the organic matter, followed by phosphon, diquat, and paraquat (Group 2), and pyridyl pyridinium chloride and ethyl pyridinium bromide (Group 3) (Figure 6, bottom). The three groups of compounds were desorbed with three extractions of 0.1*M* $BaCl_2$ in amounts similar to those obtained when kaolinite was the adsorbent (*63*). It seems that adsorption forces other than just ion exchange are involved in the retention of the compounds of Group 1 by the organic colloids.

Basic Compounds. Pesticides such as the *s*-triazines and triazoles behave as weak bases in aqueous solutions (*72, 73*). They readily associate with hydrogen to form protonated species as shown in Equation 2, and the amount of each species in solution is governed by the equilibrium expression in Equation 3:

$$R + H^+ \rightleftharpoons RH^+ \quad (2)$$

$$pK_a = log\ [RH^+]/[R] + pH \quad (3)$$

where: R = molecular species, H^+ = hydrogen ions, RH^+ = cationic species, $pK_a = -\ log$ acidity constant, and pH = $-\ log\ H^+$ ions.

Properties of some basic pesticides are given in Table III. All of the compounds are herbicides except for hydroxypropazine which is a non-

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phytotoxic metabolite of the 4,6-bisisopropylamino-*s*-triazines and menazon which is an aphicide. The pK_a values represent the pH level at which half of the species in solution is present in the cationic form and half is in the molecular form. Since ionic species are more soluble than molecular species, basic pesticides have higher solubilities at low pH levels than they do at neutral pH levels (Table III). Information concerning the properties of the *s*-triazines has been published (*74, 75, 76, 77*).

A review of the fate and behavior of triazine herbicides in soils has recently been published and provides information concerning these compounds (*78*). Interactions among *s*-triazines and soil colloids have been discussed by the author for clay colloids (*77*) and soil organic matter (*79*). New references or those not included previously will be discussed here.

The interactions of amitrole with soil colloids is discussed in papers by Ercegovich and Frear (*80*), Naylor (*81*), and Sund (*82*) and in recent reports by Nearpass (*83, 48*) and Russell *et al.* (*85*).

Early investigators (*86, 87, 88, 89, 90*) working with *s*-triazine herbicides noted that the compounds adsorbed and moved differently on various soil types. Organic matter and clay minerals were the soil factors related most highly to inactivating the compounds; similar findings were reported for amitrole (*80, 82, 91*). Later workers observed that the adsorption and activity of *s*-triazines in soils depended upon pH (*51, 53, 92, 93, 94, 95*), soil temperature (*53, 93, 96*), soil moisture (*87, 97, 98, 99, 100, 101*), molecular structure (*95, 96, 100*), and the concentration and species of other ions in the system (*92, 95, 102, 103*). Recent investigations have confirmed and elaborated on these reactions of *s*-triazines and triazoles with various types of clay minerals (*77, 84, 85, 104, 105, 106, 107*) and organic soil colloids (*79, 83, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117*).

Examples of the pH dependent adsorption of *s*-triazines by clay colloids and by organic soil colloids are shown in Figure 8. Both isotherms are L-shaped (*71*) showing that adsorbed species are in equilibrium with species in solution at each pH level.

H-shaped (*71*) isotherms occurred only when hydrogen saturated montmorillonite or strongly acid cation exchange resins were used (*53, 57*). For hydrogen-saturated montmorillonite clay, a hydrophobic adsorbent–adsorbate complex was formed (*53*). In both cases adsorption was attributed to the complexing of the basic triazine molecules with hydrogen ions on the adsorbent surfaces. The triazines were released when acids, bases, or salt solutions were added to the systems. For strong acid exchange resins the triazines were released in the hydroxy form after having been hydrolyzed on the resin surfaces (*57*). Sund (*82*) also

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Table III. Properties of

Common Name or Designation	*Trade Name*	*Chemical Name*
Atrazine	AAtrex	2-chloro-4-ethylamino-6-isopropyl-amino-*s*-triazine
Propazine	Milogard	2-chloro-4,6-bisisopropyl-amino-*s*-triazine
Simazine	Princep	2-chloro-4,6-bisisopropylamino-*s*-triazine
SD-15418	Bladex	2-chloro-4-(1-cyano-1-methyl-ethylamino)-6-ethylamino-*s*-triazine
Ametryne	Evik	2-methylthio-4-ethylamino-6-isopropylamino-*s*-triazine
Prometryne	Caparol	2-methylthio-4,6-bisisopropyl-amino-*s*-triazine
Desmetryne	Semeron	2-methylthio-4*n*-methylamino-6-isopropylamino-*s*-triazine
Terbutryne	Igran	2-methylthio-4-ethylamino-6-*tert*-butylamino-*s*-triazine
Atratone	Gesatamin	2-methoxy-4-ethylamino-6-isopropylamino-*s*-triazine
Prometone	Pramitol	2-methoxy-4,6-bisisopropylamino-*s*-triazine
Hydroxy Propazine	"Degradation product"	2-hydroxy-4,6-bisisopropylamino-*s*-triazine
Menazon	Saphos	S-(4,6-diamino-*s*-triazin-2-ylmethyl)-*O,O*-dimethylphosphorodithioate
Amitrole	Amino Triazole	3-amino-*s*-triazole

found complete adsorption—*i.e.*, H-shaped isotherms—of amitrole by a strongly acid exchange resin.

Figure 9 illustrates better the influence of pH and molecular structure on the adsorption of *s*-triazines by clay and organic matter. Maximum adsorption occurred near the pK_a of each compound, suggesting that basicity was a significant factor in their adsorbability by particulate matter. Adsorption of other basic molecules by cation exchange adsorbents, including atrazine by a carboxyl resin (*118*), amitrole by montmorillonite (*84*) and organic matter (*83*), and purines and pyrimidines by montmorillonite (*119*), exhibit similar responses.

Adsorption of the basic *s*-triazines by cation exchange adsorbents has been postulated to occur through various mechanisms including:

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Basic Pesticides

	Water Solubility 20–25°C, ppm		*Vapor Pressure mm Hg 20°C*
pK_a	*pH 3*	*pH 7*	*($\times 10^{-6}$)*
1.68	31	35	0.3
1.85	4.8	4.8	0.029
1.65	5.8	5.0	0.0061
1.1		160	0.01 @ 30°
3.93	404	194	0.84
4.05	206	40	1.0
4.0		501	1.0
4.07		58	0.96
4.20	1900	1600	2.9
4.28	1000	677	2.3
5.20	326	41	
3.8		250	
4.17		280,000	

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(a) physical adsorption and hydrogen bonding of molecular species
(b) ion exchange adsorption of cationic species
(c) complexing of the basic molecules with hydrogen ions on the exchange surfaces (*53, 55, 57, 79, 95*).

The adsorption processes which occur between basic pesticides and solid particulate matter in aqueous systems are depicted in the following equations:

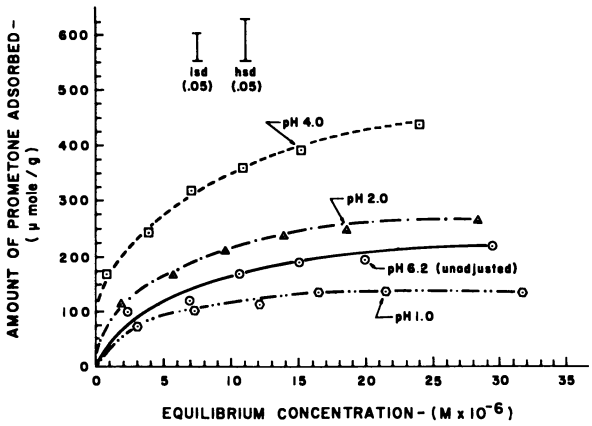
$$R + X\text{-solid} \rightleftharpoons RX\text{-solid} \quad (4)$$

$$RH^+ + X\text{-solid} \rightleftharpoons RH\text{-solid} + X^+ \quad (5)$$

$$H^+ + RH\text{-solid} \rightleftharpoons H\text{-solid} + RH^+ \quad (6)$$

$$H^+ + X\text{-solid} \rightleftharpoons H\text{-solid} + X^+ \quad (7)$$

$$R + H\text{-solid} \rightleftharpoons RH\text{-solid} \quad (8)$$



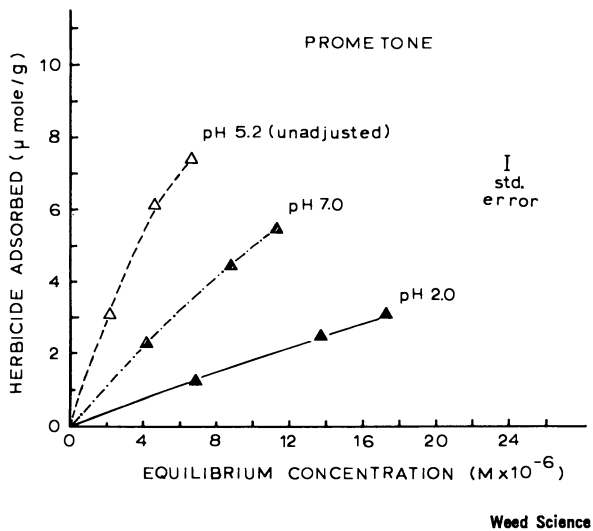


Figure 8. Isotherms for adsorption of prometone on (top) montmorillonite (95) and (bottom) soil organic matter (79)

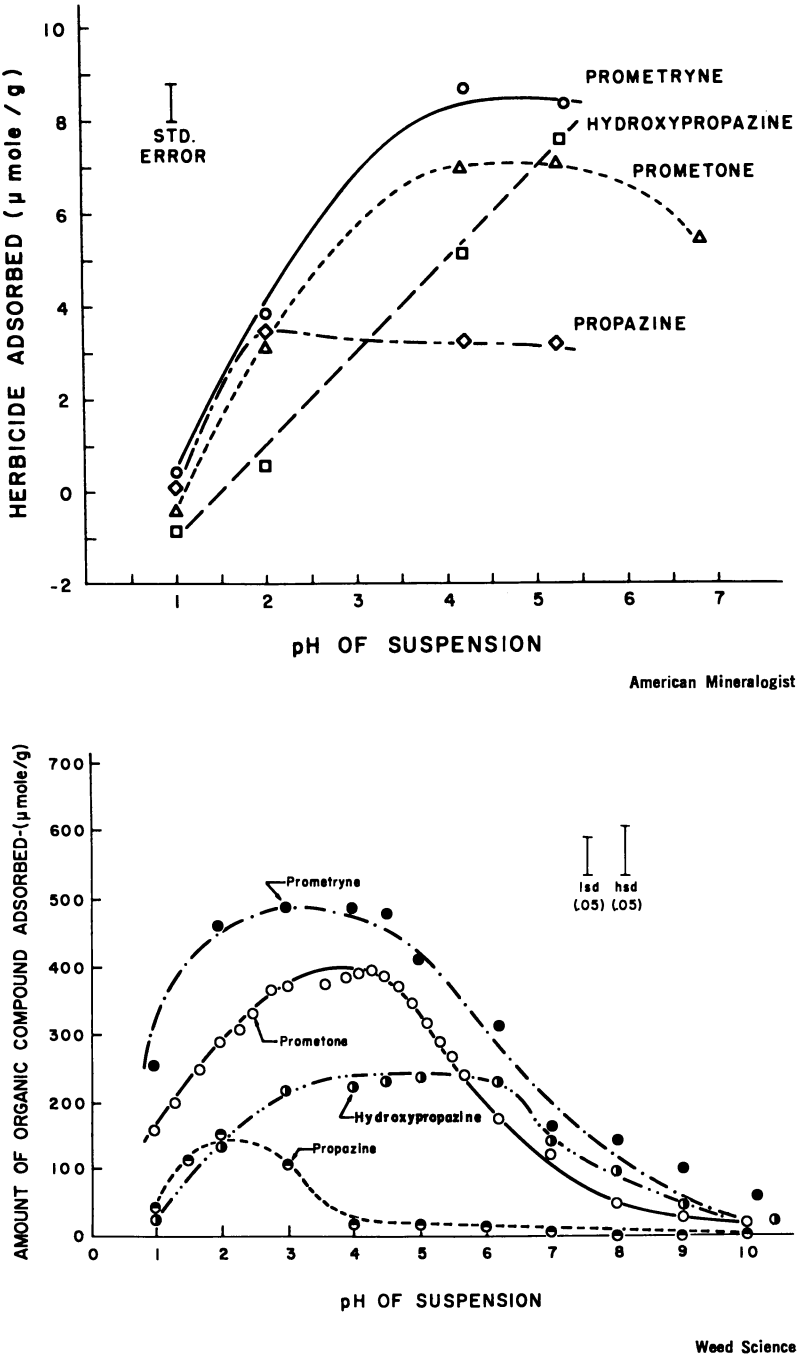


Figure 9. Effect of pH on adsorption of four related s-triazines on (top) Na-montmorillonite (95) *and (bottom) soil organic matter* (79)

where: R = basic pesticide in molecular form, RH^+ = cationic species of pesticide, *X*-solid = particulate matter with *X* = exchangeable cations other than hydrogen—*e.g.*, Na^+, K^+, 1/2 Ca^{2+}, etc.—and H-solid = particulate matter on which hydrogen is the exchangeable cation. The particulate matter is composed of clay minerals, organic soil colloids, exchange resins, mixtures of these constituents, and probably other materials.

Equation 4 represents the physical adsorption of molecular species to solid particular matter. This process occurs in neutral pH systems and at particulate surfaces which are relatively neutral in reaction. Water molecules but not exchangeable cations are displaced from the particulate surfaces.

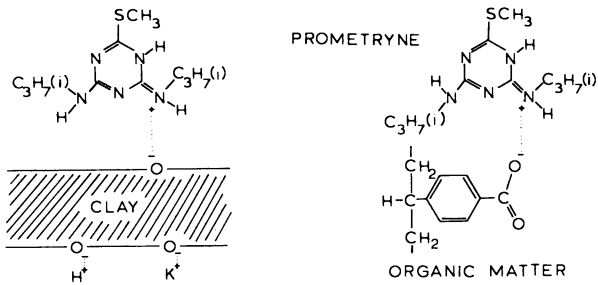


Figure 10. Ionic adsorption of prometryne cations to clay and organic matter surfaces

Equation 5 shows how cationic species are ionically adsorbed and exchanged for exchangeable inorganic cations on the solid surfaces. Examples of the adsorption of prometryne by clay and organic matter are shown in Figure 10. This occurs when the pH of the system is acidic and protonated species are present according to the reaction shown in Equation 2. As H^+ ions in solution increase, reactions depicted by Equations 2 and 5 are driven to the right, and adsorption by the solid increases, as when the pH decreases from 7 to 5 for prometone in the systems shown in Figure 9. This depends on the pK_a of the compound involved, as for propazine (pK_a = 1.85) in Figure 9 (top), which does not adsorb appreciably until the pH decreases from 4 to 2.

When excess acid is added to the system, H^+ ions (actually hydronium ions) compete for adsorption sites (Equation 6) and displace the pesticide cations back into solution as shown in Figure 9 where the pH decreases from 4 to 1 for prometone. Again the process depends upon the pK_a of the compound; for example, propazine cations are not released until the pH decreases from 2 to 1 (Figure 9). When strongly acid exchange resins were used, the *s*-triazine cations released were in the hydroxy form, having been hydrolyzed at the resin surfaces (*57*).

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Hydrogen ions added to the system also replace other exchangeable cations on the solid surfaces (Equation 7). Adding inorganic cations—*e.g.*, Na^+ and K^+—drives Equations 5 and 7 to the left, releasing the basic pesticides and H^+ ions into solution. Organic cations, such as diquat and paraquat (Table II), similarly release the triazine cations (*55, 57*).

When basic pesticides are added to hydrogen saturated particulate matter, the molecules are complexed directly onto the solid surfaces according to Equation 8.

Besides showing how pH affects adsorption of *s*-triazines, Figure 9 also depicts differences in adsorption which are attributed to molecular structural effects. Adsorption of approximately 30 compounds were compared and showed that the more basic compounds were adsorbed more than less basic ones and that steric and solubility factors also influenced the adsorption processes (*79, 95, 120*). For compounds substituted in the 2-position, adsorption of the *s*-triazines decreased in the order: $-SC_2H_5 > -SCH_3 > -OCH_3 > -OH > -Cl$. Substitutions made in the 4- and 6-positions indicated that dialkylamino compounds were adsorbed more than monoalkyl substituted compounds and that adsorption decreased in the order: C_4H_9 (tert) > C_4H_9 (sec) > C_2H_5 > C_3H_7 (i) > CH_3 > $C(CH_3)_2CN$.

Other physical adsorption processes, suggested to occur between *s*-triazines and particulate matter surfaces, include hydrophobic bonding through van der Waals forces and charge transfer complexes (*110, 111*).

X-ray diffraction studies showed that the *s*-triazines and amitrole are adsorbed in the interlayer spacings of expanding clay minerals (*53, 80, 106*). The compounds are exchangeable with other cations (*62, 95*) and are not biologically unavailable (*46, 116*), as were the cationic herbicides, diquat and paraquat.

Field experimentation on soils modified by adding montmorillonite clay or soil organic matter showed that these additives greatly reduced the phytotoxicity of soil-applied prometryne (*121*). The effects occurred too soon after application to be attributed to microbiological processes and were attributed to adsorption of prometryne by the clay and organic matter.

The *s*-triazines, especially the chloro-substituted compounds, are chemically hydrolyzed in aqueous and soil systems. Hydrolysis depends upon pH, being more rapid under highly acidic or alkaline conditions, and the reactions are catalyzed on highly acidic surfaces (*57, 105, 106, 118, 122, 123, 124, 125*).

Some *s*-triazines in aqueous and organic solvents in vitro were readily photodecomposed by ultraviolet and infrared radiation including sunlight, but photodegradation was negligible when the compounds were applied to soil surfaces (*89, 126, 127*). The chloro- and methylthio-*s*-triazines

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were photodecomposed somewhat, but the methoxy-substituted compounds were not photodegradable.

Another process where *s*-triazines are lost from aquatic and soil systems includes volatizing. Volatility depended upon the vapor pressures of the compounds (*126*, *128*) and the pH of the system (*129*). Compounds with vapor pressures greater than 1×10^{-6} mm Hg at 20°C (Table III) vaporized considerably from systems at neutral pH levels. Compounds with vapor pressures ranging from $0.3–0.84 \times 10^{-6}$ mm Hg at 20°C (Table III) evaporated less. Compounds with vapor pressures less than 0.3×10^{-6} mm Hg at 20°C were relatively nonvolatile. Volatility of the compounds was much lower when they had been applied to and adsorbed by soil surfaces instead of metal surfaces (*128*).

Recent studies by Talbert *et al.* (*130*) confirm these findings. Prometryne volatilized much more from metal surfaces than from soil surfaces, and volatilization increased at higher soil moisture and temperature levels than at lower levels.

Even the more volatile compounds—*e.g.*, prometone—did not vaporize at all when such compounds were applied to surfaces in aqueous solution at pH levels of 2–3 (*129*). Ionic species vaporized less than molecular species. Since prometone was present primarily in the ionic form in the acid system, this was probably the case here.

The pH-dependent adsorption and hydrolysis of basic pesticides in soil systems affect the biological availability of these compounds. DeVries (*92*) noted that aluminum sulfate, applied to simazine-treated soils, decreased the activity of the herbicide while lime increased activity. For lime, the increased activity was attributed to calcium toxicity. Leefe (*131*) measured greater damage to strawberries from simazine on soils which were limed as compared with unlimed soils. He attributed the lower activity on the acid soils to increased hydrolysis of simazine. Weber *et al.* (*116*) showed that soil pH greatly affected the phytotoxicity of soil-applied prometryne in model soil systems containing montmorillonite clay or organic matter. The much lower activity which occurred in systems at pH 4.5, as compared with systems at pH 6.5, was attributed to increased adsorption by clay and organic soil colloids. Best *et al.* (*132*) recently obtained analogous results in limed *vs.* unlimed field studies. Atrazine and prometryne were much more phytotoxic when applied to soils limed to pH 7.0 than when applied to unlimed soils at pH 5.0. The compounds were also much more mobile in the soil under the limed conditions. The investigators suggested that the higher activity of the herbicides on limed soils resulted from lower adsorption by the soil colloids.

Acidic Compounds. Included in the group of pesticides designated as acidic compounds are those chemicals which possess carboxyl or phe-

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nolic functional groups and which ionize in aqueous systems to yield anionic species as shown in Equations 9 and 11, respectively. The reactions are governed by the respective ionization constants given in Equations 10 and 12.

$$\text{R-COOH} \rightleftharpoons \text{R-COO}^- + \text{H}^+ \quad (9)$$

$$pK_a = \text{pH} - \log[\text{R-COO}^-]/[\text{R-COOH}] \quad (10)$$

$$\text{R-OH} \rightleftharpoons \text{R-O}^- + \text{H}^+ \quad (11)$$

$$pK_a = \text{pH} - \log[\text{R-O}^-]/[\text{R-OH}] \quad (12)$$

where: R-COOH = molecular species of acids, R-COO^- = anionic species of acids, H^+ = hydrogen ions, pK_a = − log acidity constants, pH = − log H^+ ions, R-OH = molecular phenol species, and R-O^- = phenate anions.

Chemical properties of some acidic pesticides are shown in Table IV. The chemicals are all herbicides except for TIBA, DMSA, and MH, which are plant growth regulators. They range in acid strengths from the strong acid TCA to the relatively weak acid MCPB. The first five compounds in Table IV are members of the chloro-phenoxy acids. The next five are substituted benzoic acids. Compounds starting with fenac and ending with MH are assorted acids, and the last four compounds are substituted phenols.

All of the following acidic pesticides are mobile in aquatic and soil systems:

(a) phenoxy acids (*133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144*)

(b) benzoic acids (*98, 137, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158*)

(c) phenylacetic acids (*42, 148, 151, 158*)

(d) picloram (*48, 159, 160, 161, 162, 163*)

(e) endothall (*42*)

(f) aliphatic acids (*139, 143, 164, 165*)

(g) naptalam (*143, 165, 166*)

(h) MH (*167*)

(i) phenols (*151, 165, 168, 169, 170, 171, 172*).

Wherever mobility of the herbicides was studied in differing soil types, the compounds moved most readily in coarse-textured (sandy) soils and least readily in fine-textured (clay) and organic soils. The organic matter content of the soil was the soil factor related most highly to the relative movement of the acid pesticides (*141, 142, 143, 152, 156, 161, 162, 164, 165, 169, 170, 173, 174, 175*).

Adsorption studies with acidic pesticides and various adsorbents showed that the compounds were readily adsorbed in large amounts by

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Table IV. Properties of

Common Name or Designation	*Trade Name*	*Chemical Name*
2,4-D	Weedone 638	2,4-dichlorophenoxyacetic acid
2,4,5-T	Brush Killer	2,4,5-trichlorophenoxyacetic acid
MCPA	Methoxone	(4-chloro-*o*-tolyloxy)acetic acid
MCPB	Thistrol	4-(4-chloro-*o*-tolyloxy)butyric acid
Silvex	Kuron	2-(2,4,5-trichlorophenoxy)propionic acid
Chloramben	Amiben	3-amino-2,5-dichlorobenzoic acid
Dicamba	Banvel D	3,6-dichloro-*o*-anisic acid
Tricamba	Banvel T	3,5,6-trichloro-*o*-anisic acid
2,3,6-TBA	Benzac	2,3,6-trichlorobenzoic acid
TIBA	Floraltone	2,3,5-triiodobenzoic acid
Fenac	Fenac	2,3,6-trichlorophenylacetic acid
Benzadox	Topicide	Benzamidooxyacetic acid
Picloram	Tordon	4-amino-3,5,6-trichloropicolinic acid
Endothall	Endothall	7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid
Naptalam	Alanap	*N*-1-naphthylphthalmic acid
Dalapon	Dowpon	2,2-dichloropropionic acid
TCA	TCA	trichloroacetic acid
DMSA	Alar	*N*-dimethylamino succinamic acid
MH	MH-30	1,2-dihydro-3,6-pyridazinedione
Dinoseb	Premerge	2-*sec*-butyl-4,6-dinitrophenol
DNOC	Sinox	4,6-dinitro-*o*-cresol
Ioxynil	Certrol	4-hydroxy-3,5-diiodobenzonitrile
Bromoxynil	Brominil	3,5-dibromo-4-hydroxybenzonitrile

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anion exchange resins (*45, 51, 53, 57, 147, 176, 177*). Adsorption occurred through anion exchange reactions as shown in Equation 13.

$$\text{R-COO}^- + Y\text{-Resin} \rightleftharpoons \text{R-COO-Resin} + Y^- \qquad (13)$$

where: R-COO^- = pesticide anion, Y-Resin = anion exchange resin, and Y = exchangeable anions such as Cl^-, OH^-, NO_3^-, etc.

The reaction is readily reversible as 100% of the 2,4-D adsorbed by a strongly basic anion exchange resin was desorbed with three extractions of 1*M* NaCl (*53*). Resulting from the negatively charged surfaces of soil colloids and the anionic species of acidic pesticides predominating in neutral aqueous systems, these compounds are not adsorbed in significant amounts (*46, 51, 137, 145, 147, 152, 156, 175, 178, 179, 180*). In adsorption studies where the solution pH was controlled, negative adsorption

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Acidic Pesticides

pK_a	*Water Solubility 20–25°C, ppm*	*Vapor Pressure mm Hg 35°C (× 10^{-6})*
2.80	650	
2.84	238	
3.11	550	
4.80	44	
~3.0	140	low
3.40	700	very low
1.93	4500	
~1.5	sl. sol.	
~1.5	8400	negligible
~1.5	sl. sol.	
3.70	sl. sol.	
~4.7	19,000	
1.90	430	0.62
~4.0	10,000	negligible
~4.0	200	low
1.84	450,000	0
0.63	1,300,000	0
~4.0	sl. sol.	
~4.0	6000	~0
4.40	52	>1.0
4.35	130	1.0–52.0
3.96	1.8	negligible
4.08	130	negligible

(repulsion) of acid anions by clay colloids occurred at neutral or basic pH levels (*53, 102, 103*) whereas positive adsorption of molecular species occurred in strongly acid systems (*51, 102, 103, 104, 175*). Small amounts of acidic pesticides were adsorbed on clay colloids at pH levels where molecular and anionic species occurred in relatively equal amounts (near the pK_a of each compound) (*51, 102, 103, 175, 179, 180*). Adsorption of molecular species through physical adsorption forces was probably the primary adsorption mechanism, but adsorption of anionic species also occurred with kaolinite and illite clay minerals and hydrous metallic oxides. These soil constituents possess some anion exchange properties (*102, 103, 145, 175, 179*). The acid herbicides, 2,4-D and chloramben, have been adsorbed onto dry clay surfaces by withdrawing the water from the system, leaving the chemicals behind to adhere to the silicate

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surfaces (*181*). The investigators suggested that the pesticides would adsorb to clay particles under field conditions because the chemicals are sprayed onto the dry soil surface. Although adsorption does occur, it is weak and probably of short duration since the application of a small amount of moisture (rainfall or heavy dew) would quickly move the chemicals into the soil.

Moderate amounts of acidic pesticides were adsorbed to organic soil colloids, such as are present in muck soils, (*51, 143, 147, 175, 179*) and to charcoal (*53, 57, 147, 182, 183*). For both adsorption depended upon pH, being greater under acid conditions where the pesticides were adsorbed in the molecular form. The compounds were readily desorbed from the adsorbents with water (*51, 57*). Adsorption probably occurred through hydrogen bonding or weak physical adsorption.

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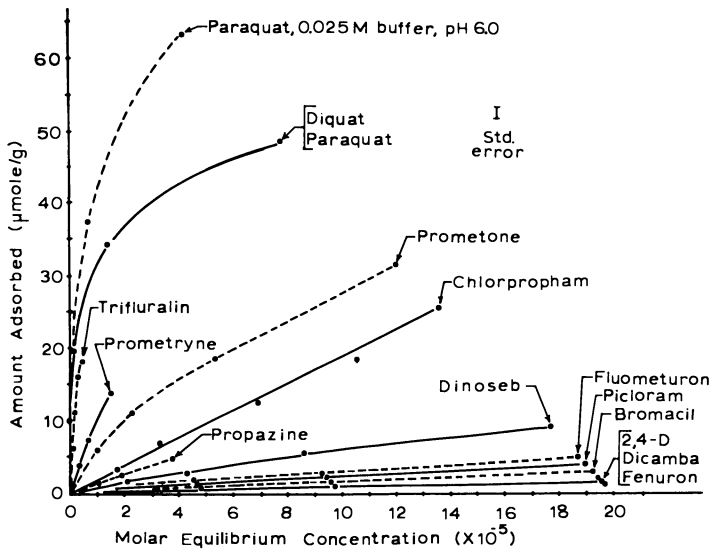

Figure 11. Isotherms for adsorption of 14 herbicides by soil organic matter (100 mg of adsorbent was used for all compounds, except for trifluralin in which 10 mg was used) (63)

Figure 11 shows the relative adsorption of 14 different herbicides by soil organic matter. The acidic herbicides, dinoseb, picloram, 2,4-D, and dicamba, were adsorbed in relatively low amounts compared with the basic and cationic herbicides, and the adsorption amount was inversely related to the water solubilities of the acidic compounds (Table IV). The weakly acidic phenol, dinoseb ($pK_a = 4.40$), was adsorbed more than the stronger acids, picloram ($pK_a = 1.90$), 2,4-D ($pK_a = 2.80$), and dicamba ($pK_a = 1.9$). Since the organic matter was an acidic muck

(histosol) and the pH of the system was approximately 4.0, adsorption probably occurred primarily through hydrogen bonding of molecular species to the acid surfaces. Since there are proportionately more molecular than anionic species in solution at each pH level for the weaker acids as compared with the stronger acids, they would be adsorbed more. It is also reasonable that the less soluble compounds would probably escape the solution phase and adsorb to the acid surfaces more than the more soluble compounds.

The acidic pesticides, except for picloram and the phenols, are considered nonvolatile, and losses of the chemicals from aqueous and soil systems are usually insignificant. Anderson *et al.* (*184*) found no loss of 2,4-D acid and only a small loss of α-naphthaleneacetic acid when the compounds were applied to glass slides. Schliebe *et al.* (*156*) found no loss because of volatizing when chloramben was applied to seven different soils. The vapor pressures of most acid pesticides are low or negligible (Table IV).

Gentner (*185*) found that picloram in the K-salt form was vaporized from soils in amounts which were much more phytotoxic to bean plants than comparable levels of the dimethylamine salt of dicamba or the propylene glycol butyl ether esters of 2,4-D.

Picloram has a vapor pressure of 0.62×10^{-6} mm Hg 35°C. The basic pesticides with vapor pressures between $0.3–0.84 \times 10^{-6}$ mm Hg 20°C were somewhat volatile, and there was much vaporizing of compounds with vapor pressures greater than 1.0×10^{-6} mm Hg 20°C (Tables III and IV).

Ester formulations of the acid pesticides are relatively volatile, and since they do not ionize in solution (as the acid and salt forms do), these compounds behave differently. The esters are discussed under Nonionic Pesticides.

Several investigators have reported that considerable dinoseb is volatilized from soil surfaces (*168, 169, 170, 186, 187, 188*). The vapor pressure of dinoseb is slightly higher than 1.0×10^{-6} mm Hg at room temperature, and thus dinoseb would be somewhat volatile (Table IV). Vaporization depended upon the soil moisture content, soil temperature, and whether or not the soil was limed. Dinoseb was more readily volatilized from wet soils than dry soils and the amount lost increased with an increase in soil temperature. Liming the soil makes the soil solution less acid and drives the reaction shown in Equation 11 to the right, and the resulting predominant phenate ions in the soil solution are not as volatile as the molecular phenol species.

Miscellaneous Ionic Compounds. Also several other ionic pesticides exist which do not readily fall into the categories designated as cationic, basic, or acidic compounds. These compounds have weak acidic or basic

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Table V. Properties of Some

Common Name or Designation	*Trade Name*	*Chemical Name*
Bromacil	Hyvar X	5-bromo-3-*sec*-butyl-6-methyluracil
Isocil	Hyvar	5-bromo-3-isopropyl-6-methyluracil
Terbacil	Sinbar	3-*tert*-butyl-5-chloro-6-methyluracil
Oryzalin	Surflan	3,5-dinitro-*N*,*N*-dipropylsulfanilamide
DSMA	Ansar 184	disodium methanearsonate
MSMA	Ansar 170	monosodium acid, methanearsonate
Cacodylic acid	Phytar 138	hydroxydimethylarsine oxide

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properties and/or possess certain atoms or functional groups which cause them to behave differently from the compounds in the other three categories. Table V contains the chemical properties of several of these compounds; all of the compounds shown are herbicides.

The uracils, bromacil, isocil, and terbacil are mobile and persist in soil systems (*189, 190, 191*). Recent studies by the author (*63*) showed that bromacil moved laterally over the soil surface in surface waters and that it leached vertically into the soil profile. The compound also persisted in the soil for over four years after 2 pounds per acre or higher were applied. The uracils were much less mobile in muck soils than in mineral soils, suggesting that the compounds are partially adsorbed by organic soil colloids (*189, 191*).

The adsorbing of bromacil by soil organic matter relative to several other herbicides is shown in Figure 11. The compound was adsorbed in low amounts, probably as a result of its high solubility. The pH of the system was approximately 5.7, so bromacil was present predominantly in the molecular form and was probably adsorbed through hydrogen bonding or other physical adsorption forces.

In greenhouse experiments McLaughlin (*192*) found that oryzalin (Table V) was inactivated by soil organic matter much less than trifluralin and nitralin (Table VIII). Recent adsorption studies by the author (*63*) showed that oryzalin was adsorbed by soil organic matter much less than the related compounds trifluralin and benefin. This difference is probably because of the ionizability and higher water solubility of oryzalin. Also oryzalin is a more effective herbicide when applied to organic soils than is trifluralin.

The remaining three herbicides shown in Table V are organic arsenicals. These compounds are derivatives of arsonic or arsenic acids and similarly ionize in aqueous systems to form molecular and anionic species as the acid pesticides which were discussed. The anions react similarly

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Miscellaneous Ionic Pesticides

pK_a	*Water Solubility 20–25°C, ppm*	*Vapor Pressure mm Hg 30°C ($\times 10^{-6}$)*
9.1	815	low
9.1	2150	
~9.0	710	0.48
8.6	2.6	1.48
	256,000	
	1,000,000	
6.19	667,000	

with calcium, magnesium, iron, and aluminum in solution to form insoluble salts as did the phosphate anions. Arsenic anions are also thought to be fixed by clay minerals in a manner similar to phosphate fixation. Since the organic arsenic compounds readily react with clay minerals, they do not leach significantly in fine textured soils (*193, 194, 195, 196*). They do, however, leach through coarse textured soils like sands and loamy sands (*193, 197*). Although the organic arsenicals are readily adsorbed in fine textured soils, they are biologically available to microorganisms and plants (*193, 196*).

Adsorption studies showed that DSMA was readily adsorbed by various clay minerals and soil particles in the order: limionite > kaolinite >> vermiculite > montmorillonite > silt = sand (*193*). No specific adsorption mechanism was postulated, but later arsenic was associated with aluminum (*197*).

Nonionic Pesticides

Numerous pesticides exist which do not ionize significantly in aqueous or soil systems. These compounds range in water solubilities from as low as 1 ppb for DDT (Table VI) to as high as 2% for dimethoate (Table VII) and CDAA (Table XI). They range from small molecules —*e.g.*, dichlobenil with a parachor (molecular volume) of 334 (Table XI)—to large complex molecules—*e.g.*, ethion which has a parachor of 815 (Table VII). The compounds differ in their polarities ranging from 0.34–2.84 Debye units for β-BHC and γ-BHC, respectively, (*198*), but with the limited dipole moment values available, polarity is not discussed here. However, water solubilities do reflect their polarities somewhat. The nonionic compounds also vary greatly in their tendencies to volatilize, ranging from a nonvolatile compound—*e.g.*, chloroxuron with a vapor pressure of 2×10^{-8} mm Hg 20°–25°C (Table IX)—to a highly volatile compound—*e.g.*, EPTC which has a vapor pressure of

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3.4×10^{-2} mm Hg 20°–25°C (Table XI). Fumigants have much higher vapor pressures, but they will not be included here since their residues in soils and waters do not usually endure long.

A compound's solubility depends upon the work required to separate the molecules from one another in the crystalline lattice or liquid form and the affinity of the molecules of the compound for water molecules. To dissolve in water, bonds must be disrupted between pesticide molecules and the hydrogen bonded network of the water system. Pesticide molecules must simultaneously become hydrogen bonded to or form dipole–dipole bonds with water molecules to become hydrated. Compounds of extremely low solubility, which do not readily dissolve and thus do not form hydrogen bonds with water molecules, exist as holes in the water structure. Such compounds usually tend to escape the solution phase and adhere to lipophilic substances which may occur in the system, or if their vapor pressures are high enough, they gradually volatilize into the atmosphere.

The vapor pressure shows that the molecules of the compound tend to escape from one another. Since these compounds are nonionic, the

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Table VI. Properties of Some Chlorinated

Common Name or Designation	*Trade Name*	*Chemical Name*
DDT	Gesapon	1,1,1-trichlor-2,2-bis(*p*-chlorophenyl)-ethane
Methoxychlor	Marlate	2,2-bis(*p*-methoxyphenyl)-1,1,1-trichloroethane
Endrin	Endrin	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4-4a,5,6,7,8,8a-octahydro-1,4-*endo-endo*-5,8-dimethanonaphthalene
Dieldrin	Octalox	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4-4a,5,6,7,8,8a-octahydro-1,4-*endo-exo*-5,8-dimethanonaphthalene
Aldrin	Drinox	1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-*endo-exo*-5,8-dimethanonaphthalene
Toxaphene	Phenacide	mixture made by chlorinating camphene to 69% chlorine
Lindane	Gamexane	1,2,3,4,5,6-hexachlorocyclohexane
Chlordane	Octa-Klor	1,2,3,5,6,7,8,8-octachloro-2,3,3a,4,7-7a-hexahydro-4,7-methanoindene
Heptachlor	Drinox H-34	1,4,5,6,7,8,8a-heptachloro-3a,4,7a-tetrahydro-4,7-methanoindene

[a] Calculated according to Mumford and Phillips (*199*).

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forces holding the molecules together are relatively weak intermolecular forces—*e.g.*, dipole–dipole interactions, like hydrogen bonding, and van der Waals forces. Compounds which are relatively volatile have relatively high vapor pressures, and because of the weak forces holding the molecules together, they exist as liquids when pure.

Substituting various moieties onto the primary structure of a particular pesticide family significantly changes the compounds' properties. Thus, it is difficult to predict how the entire pesticide family in a given aquatic or soil system will behave. For example, trifluralin, nitralin, and benefin (Table VIII) are all substituted anilines (or toluidines) and might behave similarly to aniline, but adding nitro and other groups to the aromatic rings weakens the basic character of the aniline molecule. Thus instead of possessing the basic character of aniline, which has a pK_a of 4.6 and a water solubility of 3.5%, the three herbicides are extremely weak bases and have solubilities ranging from 0.05–0.6 ppm. Many other examples could also be cited. Although model adsorbates—*e.g.*, aniline represent the amine herbicides (*181*) and dimethyaminobenzaldehyde represents the uracil, urea, and *s*-triazine herbicides (*200*)—have been

Hydrocarbon Insecticides

Water Solubility 20–25°C, ppm	*Vapor Pressure mm Hg 20–25°C (× 10^{-6})*	*Parachor*[a]
0.001–0.04	0.15	658
0.1–0.25		699
0.23	0.20	494
0.1–0.25	0.18	494
0.01–0.2	6.0	493
0.4	1.0	mixture
7.3–10.0	9.4–45.0	478
very low	10.0	647
very low	300	596

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Table VII. Properties

Common Name or Designation	*Trade Name*	*Chemical Name*
Dimethoate	Cygon	*O,O*-dimethyl-*S*-(*N*-methylcarbamoyl-methyl)-phosphorodithioate
Methyl parathion	Metron	*O,O*-dimethyl-*O*-*p*-nitrophenyl phosphorothioate
Phorate	Thimet	*O,O*-diethyl-*S*-(ethylthio)-methyl phosphorodithioate
Demeton	Systox	*O,O*-diethyl-*O* (and *S*)-[2-(ethylthio)-ethyl] phosphorothioates
Parathion	Phoskil	*O,O*-diethyl-*O*-*p*-nitrophenyl phosphorothioate
Disulfoton	Disyston	*O,O*-diethyl-*S*-[2-(ethylthio)-ethyl] phosphorodithioate
Dursban	Dursban	*O,O*-diethyl-*O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate
Diazinon	Diazol	*O,O*-diethyl-O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate
Malathion	Cythion	*O,O*-dimethyl-*S*-(1,2-dicarbethoxy-ethyl) phosphorodithioate
Carbophe-nothion	Trithion	*O,O*-diethyl-*S*-(*p*-chlorophenylthio-methyl) phosphorodithioate
Ethion	Nialate	*O,O,O′,O′*-tetraethyl-*S,S′*-methylene biophosphorodithioate
Schraden	OMPA	Octamethylpyrophosphoramide

[a] Calculated according to Mumford and Phillips (*199*).

used, these results would probably be limited for predicting the activities of diverse pesticides in soils and waters.

Since the interactions of pesticides in soils and aquatic systems are as different among compounds of the same family as they are among the various families, the behavior of families of nonionic pesticides will be discussed below with exceptions pointed out.

Chlorinated Hydrocarbons. Properties of some chlorinated hydrocarbon insecticides are given in Table VI. All of the compounds, except for lindane, are insoluble in water. DDT is about ten times more insoluble than the other chlorinated hydrocarbons. The vapor pressure of the compounds are classified as follows: low($0.1 - 0.9 \times 10^{-6}$ mm Hg)—DDT, endrin, and dieldrin, moderate ($1.0 - 9.9 \times 10^{-6}$ mm Hg)—toxaphene and aldrin, high ($10 - 99 \times 10^{-6}$ mm Hg)—chlordan and lindane, and very high ($100 - 999 \times 10^{-6}$ mm Hg)—heptachlor.

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of Organophosphates

Water Solubility 20–25°C, ppm	*Vapor Pressure mm Hg 20–25°C ($\times 10^{-6}$)*	*Parachor*[a]
20,000	100	484
50		529
80–85	2300	573
100	1000	553–583
24	37.8	609
60–66	300	613
2	18.7	659
40	140	693
145	40	699
1–2		707
1		815
misible	1000	689

DDT has been studied more than any other pesticide for several reasons. Besides being the first important synthetic organic insecticide and having saved millions of lives by controlling vectors of human disease, the compound along with other chlorinated hydrocarbons has been implicated in the demise of numerable wildlife species (*8, 12, 201, 202, 203, 204, 205, 206, 207*). Several chlorinated hydrocarbons have been detected in various marine and terrestrial life (*205, 208, 209, 210, 211*), food crops (*212, 213, 214, 215, 216, 217, 218*), surface waters (*12, 26, 219, 220, 221, 222, 223, 224*), oil slicks (*225*), rain and snow (*26, 226, 227*), dust (*228*), and soils (*5, 6, 7, 211, 229, 230, 231, 232, 233, 234, 235, 236*). Numerous investigators have confirmed that DDT accumulates in the food chain and is detrimental to wildlife (*211, 237, 238, 239, 240, 241, 242*). Cox (*243*) recently reported that the DDT content of phytoplankton in the sea has been steadily increasing since 1955 even though the amount being used has been declining since about 1965. It is

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probable that this trend will continue for some time since levels of DDT in some orchard soils are over 100 pounds per acre (*5, 7, 232*) and its half-life has been estimated from 10–20 years (*6, 235, 237, 244, 245, 246, 247*). Aldrin oxides to dieldrin (*248, 249, 250*) and endrin and dieldrin have half-lives of 8–10 years (*246, 251*), so they persist in the environment less than DDT.

Toxaphene, lindane, chlordane, and heptachlor (Table VI) have been found in the biosphere, but much less than DDT, aldrin, and dieldrin. Foster *et al.* (*9*) reported that toxaphene was relatively stable in soil, being only slightly less persistent than DDT. It has a half-life of about 11 years (*246*). Although toxaphene is one of the most heavily used chlorinated insecticides, little is known about its exact chemical nature and behavior in soil systems (*252*).

Lindane has a half-life of approximately 2 years (*246*). Chlordan was persistent in soils (*248*) and has a half-life of about 8 years (*246*). Heptachlor was not as persistent (*248*) and has a half-life of from 2–4 years (*246*). It is slowly converted to heptachlor epoxide which is also an effective insecticide. The behavior of pesticides in the environment is discussed further in governmental reports (*15, 19*), books by Gould (*16*), Graham (*17*), Morton and Berg (*253*), and the review of Newsom (*254*).

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Table VIII. Properties of Some Substituted

Common Name or Designation	*Trade Name*	*Chemical Name*
Substituted Anilines		
Nitralin	Planavin	4-(methylsulfonyl)-2,6-dinitro-*N*,*N*-dipropylaniline
Benefin	Balan	*N*-butyl-*N*-ethyl-α,α,α-trifluro-2,6-dinitro-*p*-toluidine
Trifluralin	Treflan	α,α,α-trifluro-2,6-dinitro-*N*,*N*-dipropyl-*p*-toluidine
Phenylcarbamates (and Carbanilates)		
Propham	Chem-hoe	isopropyl carbanilate
Dichlormate	Rowmate	3,4-dichlorobenzyl methylcarbamate
Chlorpropham	Chloro IPC	isopropyl *m*-chlorocarbanilate
Carbaryl	Sevin	1-naphthyl-*N*-methylcarbamate
Barban	Carbyne	4-chloro-2-butynyl-*m*-chlorocarbanilate
Terbutol	Azak	2,6-di-*tert*-butyl-*p*-tolyl methylcarbamate

[a] Calculated according to Mumford and Phillips (*199*).

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Resulting from low solubility of DDT, the compound is immobile in soil systems (*255, 256, 257*). Small amounts of DDT were found in subsoils, particularly in soils containing expanding type clay minerals. Such soils form open cracks under drought conditions and allow the chemical to be washed into the subsoil (*258*). Woodwell (*235, 236*) reported that little DDT was found in the subsoils of forest soils as compared with the surface soils. In reverse leaching studies (capillary movement of water in an upward direction), Harris (*259*) found that DDT showed low movement compared with other pesticides.

Fleming (*6, 260*) found that the inactivating of DDT varied with different soil types and seemed related to the amount of organic matter in the soils. Later investigations confirmed the relationship between DDT inactivation and soil organic matter content (*232, 261, 262, 263, 264, 265*). Shin *et al.* (*265*) found that DDT adsorption in soil increased with the stage of humification of the soil organic matter. Wershaw *et al.* (*266*) found that DDT was more soluble in sodium humate than it was in distilled water, implicating the humic fraction of soil organic matter in the adsorption of DDT.

Adsorption studies with DDT showed that the pesticide was strongly adsorbed on dry soils and muds (*267, 268, 269*), iron oxides, and gels (*269*) and was adsorbed from aqueous solutions by soil particulate mat-

Aniline and Phenylcarbamate Pesticides

Water Solubility 20–25°C, ppm	*Vapor Pressure mm Hg 20–25°C (× 10^{-6})*	*Parachor*[a]
0.6	1.0	768
0.5	38.9	671
0.05	114	671
250–254		426
170		466
88–102	10	466
40–99		453
11–12		522
6–7		706

ter (*263, 269, 270, 271*), and charcoal (*272*). DDT was absorbed from solution in small amounts by a strongly basic anion exchange resin and was not adsorbed by a strongly acid cation exchange resin (*272*). The compound was adsorbed on aquatic vegetation in surface waters (*202*).

Adsorption of DDT by soils and other substances greatly decreased the insecticidal activity of the compound (*267, 268, 273*). Liquid formulations of DDT were inactivated more by dried muds than were wettable powders, probably because DDT in the liquid formulations penetrated the mud surface more than did the powdered formulations (*273, 274*). Adsorption of DDT by soils and other adsorbents depended upon temperature, diffusing faster at high temperature but adsorbing in lesser amounts than at lower temperature (*267, 275*). It also depended upon relative humidity and soil moisture, adsorbing more under dry conditions than under wet conditions (*267, 268, 275, 276, 277, 278, 279*). DDT also has high insecticidal activity for a short time under conditions of high humidity and low activity for a longer period under conditions of low humidity. Several investigators suggested that DDT and water molecules compete for adsorption sites and that adsorption occurred mainly through physical adsorption forces (*255, 268, 272, 278*). Guenzi and Beard (*255*) stated that because of the low solubility of DDT, the compound might precipitate out on the adsorbent surfaces as crystals or be complexed with lipid portions of soil organic matter. They also found that DDT adsorption was related to the surface area of the adsorbents which were used.

Many investigators found that the volatilizing of DDT from soils and various surfaces was small or insignificant (*267, 280, 281, 282, 283*). Methoxychlor was relatively nonvolatile (*284*). Significant amounts of DDT were volatilized from aqueous systems (*264, 285*) and from surfaces when high temperatures (140°F) were used (*286*).

Decomposed DDT adsorbed on clay surfaces has been reported by several investigators. Barlow and Hadaway (*268, 275*) found that DDT decomposed only under anhydrous conditions. Fowkes *et al.* (*287*) found that it decomposed on acid clays but not on neutral clays. López-González and Valenzuela-Calahoro (*288*) found more decomposed DDT on basic clays than on acid clays and that DDT decomposed more on vermiculite than on montmorillonite. Vermiculite decomposed more because it has a higher surface charge density than montmorillonite.

The water solubilities of endrin, dieldrin, and aldrin are considerably higher than that of DDT (Table VI), and the compounds were slightly mobile in soils (*289*). The major portions of the pesticides were retained in the surface soils (*290*) and Harris (*259*), in comparing the compounds' movement through soils, ranked them low along with DDT.

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Adsorption of endrin, dieldrin, and aldrin by soils has directly been related to the organic matter content of the soil (*214, 261, 291*). Higher levels of organic matter in soils also increase the persistence of aldrin in the soil (*216, 249, 261*), decrease the adsorption of dieldrin and endin by crops (*215*) and decrease the volatilizing of the compounds from the soil (*215*). Incorporating aldrin into the soil greatly increased the persistence of the compounds when compared with surface applications (*283*).

Endrin and dieldrin have slightly higher vapor pressures than DDT and were, therefore, slowly volatilized from aqueous solutions (*292*), soils (*282, 292, 294*), mud (*275, 276*), and other surfaces (*268, 280, 295, 296*). The vaporizing rate of the two compounds was much lower than that of aldrin which has a vapor pressure more than 30 times greater than the others (Table VI). The higher volatility of aldrin was also responsible for its much higher fumigant action than dieldrin or endrin (*275, 280, 293, 296*).

Aldrin and dieldrin were adsorbed from aqueous solutions on soil particulate matter (*158*) and volatilized from aqueous systems (*292, 297*), showing that adsorbing and volatilizing are important processes in the disappearing of these compounds from aquatic and soil systems. Greater adsorbing of aldrin in aqueous systems occurred with soils that contained more organic matter and clay minerals (*298*). Charcoal was adsorptive for aldrin and dieldrin (*299*); aldrin and dieldrin were also adsorbed on aquatic vegetation in surface waters (*202*).

Water added to soil systems containing adsorbed aldrin, endrin, and dieldrin released the compounds (*278, 282, 283, 294*). Adsorbing of the compounds by soil was much lower under conditions of high humidity than it was under low humidity (*268, 276, 295, 300*), showing that water molecules displaced the pesticides from soil particulate matter releasing them into solution and/or to the atmosphere. Under conditions of high relative humidity, dieldrin applied to mud exhibited high biological activity for a short time; while under low humidity, the compound exhibited low biological activity for a long time (*276*).

Adsorbing and volatizing of aldrin, endrin, and dieldrin from soil surfaces were greatly influenced by temperature showing that weak physical intermolecular forces were operating in both processes (*282*).

Aldrin and dieldrin in aqueous solutions were chemically oxidized in the presence of ozone or air (*292*). Aldrin, dieldrin, and endrin were catalytically decomposed when mixed with acid clays but not by neutral clays (*287*); aldrin was oxidized to dieldrin in soil systems (*248, 249, 250*). Barlow and Hadaway (*275*) found that dieldrin was not decomposed when it was applied to dried mud blocks.

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Toxaphene, lindane, chlordan, and heptachlor were adsorbed by soil particulate matter (*158, 216, 255, 261, 268, 279, 291, 295, 299, 301, 302, 303, 304, 305*) and volatilized from aqueous (*292, 297*) and soil (*255, 264, 275, 280, 283, 293, 306*) systems in a way analogous to that of aldrin, dieldrin, and endrin. Adsorption of the pesticides was most highly related to the organic matter content of soils and aquatic systems and probably occurred through weak physical intermolecular forces at lipophilic sites. Adsorbing and volatizing processes were involved in the fate of these compounds in aquatic and soil systems. Lindane was much more mobile in soil systems than the others (*246, 255*), probably because of its greater solubility (Table VI), and lindane and heptachlor volatilized much more readily from soils and aquatic systems (*290, 292, 293, 296, 306*).

Lindane in aqueous solutions was degraded by ozonation (*292*), and toxaphene, chlordan, and heptachlor were catalytically decomposed when mixed with acid clays but not with neutral clays (*287*).

Organophosphates. The organophosphates have much greater water solubilities and higher vapor pressures than the chlorinated hydrocarbons (compare Tables VI and VII). With greater solubilities in aqueous and soil solutions and relatively high adsorption by soil particulate matter, the organophosphorus compounds are not readily volatilized into the atmosphere. They do not accumulate in soil fauna like earthworms and concentrate less in birds and fish than the chlorinated hydrocarbons (*307*). Having relatively high toxicity to humans, some organophosphates are more difficult to use than the chlorinated hydrocarbons (*308*). Most are readily degraded in soils and do not accumulate for long periods (*5, 309, 310, 311*). However, a few compounds—*e.g.*, parathion, diazinon, phorate, dimethoate, and demeton—last from 1–3 months in the soil. Some organophosphates translocated to root crops (*218*), and recently parathion which was applied to a sandy loam soil was reported to persist for more than 16 years (*312*). Further investigations of the compounds are needed. Sheets (*313*) has suggested that because of their low persistence the organophosphorus compounds should be substituted for the chlorinated hydrocarbons wherever possible. However because of their greater toxicities, more care must be exercised in using these materials than was used with DDT.

Although the organophosphates are generally more soluble than the chlorinated hydrocarbons, they do not move any more readily in soil systems (*289, 314*). Dimethoate, malathion, phorate, disulfoton, methyl parathion, and parathion move in soils to some degree (*315, 316*). Their movement was related to their water solubilities with the more soluble compounds being the most mobile. The compounds were retained primarily in surface soils and did not leach into subsoils except in small

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amounts (*317, 318, 319*). Harris (*259*) ranks the organophosphorus compounds along with the chlorinated hydrocarbons as having high adsorption and low mobility in soil systems.

The adsorbing of the organophosphates in soil was related to the organic matter and clay contents of the soils (*279, 310, 318, 319, 320, 321, 322, 323*). The compounds were readily adsorbed by charcoal (*324*) and aquatic plant surfaces (*202*). Parathion was strongly adsorbed on soil particles in aqueous systems (*271*). Bowman *et al.* (*325*) recently found that malathion was adsorbed as a double layer in the interlayer spacings of montmorillonite clay. Adsorption occurred by hydrogen bonding between the carbonyl oxygen atoms of malathion molecules and the water of hydration shells surrounding metallic cations on the clay surfaces. Adsorbing in dehydrated systems occurred through a direct ion–dipole interaction between the carbonyl oxygen atoms of malathion and the saturating cations on the clay. Phorate was not significantly adsorbed by kaolinite (*320*). Adsorbing of organophosphates by soil particulate matter greatly reduced their loss by volatilizing (*280, 319, 321*) and their insecticidal activity (*273, 319, 323*). Soil moisture similarly affected the adsorption, volatilization, and biological availability of the organophosphates as it did on the chlorinated hydrocarbons. Adsorbing was lower, and volatilizing and insecticidal activity were higher on moist soils than on dry soils (*278, 282, 300*). It has been suggested that the toxicity of the compounds depends upon their affinity for soil particles and their ability to compete with water molecules for adsorption sites on the particle surfaces (*278*). Temperature affects the degree of volatilizing of phorate from soil, with greater losses occurring at higher temperatures (*282*).

Fumigant action of some organophosphorus compounds was related to their vapor pressures and the water content of the soil. Phorate, disulfoton, and dimethoate were equally effective in soils in wet years, but only phorate and disulfoton were effective in dry years (*326*). Phorate and disulfoton provided much vapor action in dry years because of their high vapor pressures whereas dimethoate did not.

Malathion and parathion were chemically hydrolyzed and biologically degraded by microorganisms in soil systems (*310, 327*). Little parathion is lost from the soil through volatilization; it disappears primarily by hydrolysis or microbial degradation (*327*). Malathion was readily decomposed on acid and alkaline clay surfaces (*328*).

Substituted Anilines. Some properties of three substituted aniline herbicides are given in Table VIII. The compounds are slightly soluble in water only to 0.05–0.5 ppm. Nitralin and benefin have low vapor pressures and are nonvolatile while trifluralin which has a vapor pressure of 1.14×10^{-4} mm of Hg at 25°C and is relatively volatile. Applying

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trifluralin continuously to the same areas greatly shifted the weed population (*121*). Essentially all weeds, except for yellow nutsedge (*Cyperus esculentus*), were controlled and nutsedge reproduced so much that it completely dominated the area. Although trifluralin was toxic to fish (*202, 329*), it was relatively harmless when it was first adsorbed onto dry soil and then exposed to the fish (*330*).

Nitralin, benefin, and trifluralin were relatively immobile in soil systems, remaining essentially where they were applied (*330, 331, 332*). The compounds moved only slightly in soil leaching studies (*137, 151, 333, 334, 335*). Harris (*151*) has classified them among the least mobile of the herbicides. The substituted anilines persisted much longer when the chemicals were incorporated into the soil, probably because less was photodecomposed and volatilized (*331, 332, 336*). Several investigators found that the substituted anilines were readily adsorbed by soil organic matter (*337, 338*). Lambert *et al.* (*339*) related the adsorbing of some substituted anilines by organic matter to the herbicidal activity of the compounds. Compounds which were adsorbed most were least available to growing plants. In later studies, Lambert (*338*) related adsorbing by soil organic matter to the parachor of the compounds; larger molecules were adsorbed more than smaller molecules.

The relative adsorption of trifluralin by soil organic matter as compared with other herbicides is shown in Figure 11. However, the isotherm for trifluralin is not directly compared with the isotherms of other herbicides since only one-tenth as much organic matter was used with trifluralin. Nevertheless, it is apparent that trifluralin readily adheres to the surfaces of organic particulate matter. Field experiments on soils modified by adding montmorillonite clay and an organic muck showed that the phytotoxicity of trifluralin was greatly decreased by the organic matter but was not significantly affected by the clay (*121*).

Adsorption studies with trifluralin showed that the herbicide was adsorbed in small amounts by montmorillonite and kaolinite clays and ion exchange resins (*48, 337*).

Ward and Upchurch (*340*) found an inverse relationship between the solubilities of 18 substituted anilines and their adsorption by nylon ($R^2 = 0.77$) and cellulose triacetate ($R^2 = 0.80$). It was suggested that steric and electronic effects of the molecules were also responsible for the adsorption differences of the compounds. Because of the low solubilities of the substituted anilines, adsorption by organic matter probably occurs at lipophilic sites through dipole–dipole interactions—*e.g.*, hydrogen bonding or charge-transfer complexes. Low adsorption at clay surfaces probably occurs because the hydrophobic molecules do not readily associate with hydrated surfaces. Adsorption of the substituted anilines by dry clays might occur on the soil surface for instance, but in the

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relatively humid atmosphere of the soil the clays are highly hydrated, and adsorption of the compounds is probably not significant.

Increased soil moisture increases volatilizing of trifluralin but not nitralin from soils (*341*). This is attributed to the much higher vapor pressure of trifluralin as compared with nitralin (Table VIII). Stickler *et al.* (*342*) reported that trifluralin activity in soils greatly decreased with increased soil moisture. They attributed the loss in activity to increased degrading by soil organisms. Since trifluralin was relatively volatile, it is also possible that the added moisture may have increased its loss by vaporizing.

Phenylcarbamates and Carbanilates. The phenylcarbamate pesticides are much more water soluble than the substituted anilines (Table VIII), but despite the higher solubilities they are also immobile in soil systems. All are herbicides except for carbaryl which is an insecticide. Chlorpropham and terbutol resisted leaching, and propham leached only slightly (*137, 143, 144, 343, 344, 345, 346*). In herbicide mobility studies in soils, Harris (*151*) ranked chlorpropham with the substituted anilines as having low movement.

Chlorpropham and propham were much less active in fine textured soils than in coarse textured ones, and their inactivation was related to the organic matter content of the soils (*165, 173, 347, 348, 349, 350*). Scott and Weber (*46*) found that organic matter added to soil systems greatly reduced the phytotoxicity of chlorpropham. They postulated that the herbicide was adsorbed to organic colloids through hydrogen bonds between the imino hydrogen and carbonyl oxygen atoms of chlorpropham and carboxyl groups of the organic matter.

Adsorption studies in aqueous systems showed that chlorpropham was greatly adsorbed by muck and that the adsorption process was reversible (*51, 110*). Adsorbing of chlorpropham by various soil types was related to the organic matter content of the soils and depended upon temperature, indicating that the adsorption process was physical (*351*).

The relative adsorption of chlorpropham by soil organic matter is shown in Figure 11. The isotherm was linear in shape and almost the same magnitude as the *s*-triazine compound propazine. Harris and Sheets (*347*) found that chlorpropham was adsorbed by soils more than simazine and that the amounts of adsorption were related to the organic matter contents of the soils.

Chlorpropham and propham were adsorbed in large amounts by charcoal (*48, 180, 182*), in small amounts by exchange resins (*48, 51*), nylon and cellulose triacetate (*340*), and montmorillonite clay (*48, 51, 180*), and in insignificant amounts by illite and kaolinite clays (*180*). Hydrogen bonding was suggested as the adsorption mechanism involved (*180, 340*). Scott and Weber (*46*) found that anion exchange resins

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added to model soil systems decreased herbicidal activity of chlorpropham but that adding montmorillonite and kaolinite clays did not. Recent studies (*63*) carried out under better plant growth conditions showed that montmorillonite clay slightly reduced chlorpropham phytotoxicity and confirmed the lack of herbicide inactivation by kaolinite.

Volatility studies by Anderson *et al.* (*184*) showed that chlorpropham and propham readily evaporated from glass slides; 92% and 80% of the chlorpropham and propham, respectively, were lost in 24 hours. Ennis (*187*) found that chlorpropham vapors escaping from the soil surface damaged growing plants. Incorporating the herbicide into soil greatly increased its effectiveness by decreasing its loss through volatizing (*352*). A small amount of soil incorporation (to a depth of 1/2-inch) resulted in more chlorpropham activity than deeper incorporation (to a depth of 1 1/2 to 3 inches) (*353*). Slight incorporation decreased the volatizing of chlorpropham, but deep incorporation brought the herbicide into contact with much soil, and the resulting adsorption and dilution decreased its herbicidal activity. Vaporizing of chlorpropham and propham from soils was greatly influenced by temperature and soil moisture (*354*). Greater losses occurred at higher temperatures and higher moisture levels.

Unlike chlorpropham and propham, terbutol and carbaryl were not volatilized from soil systems (*282, 344*).

Phenylureas. The phenylureas show extremely weak acidic properties in aqueous systems. Partial ionization occurs in basic (4.2*N* NaOH) solution (*355*). Although the phenylureas are too weak to be titrated in aqueous systems, Cluett (*355*) titrated them in an organic solvent and used the half-neutralization potentials (HNP) as an index of acidity (the larger the HNP, the weaker the acid). The HNP values, along with other properties, for several phenylurea herbicides are given in Table IX. The HNP values decrease as water solubilities decrease and parachors increase.

Phenylurea herbicides are divided into three categories based on their water solubilities. Fenuron at 2900–3850 ppm is much more soluble than the other phenylureas and falls into its own category (Table IX). It is also the smallest molecule having a parachor of 399. Monuron, monolinuron, fluometuron, metobromuron, diuron, linuron, C-6313, norea, and siduron have water solubilities ranging from 18–580 ppm and are in a second category of moderately soluble compounds. Parachors for second category range from 439–569. Neburon, fluorodifen, and chloroxuron have relatively low water solubilities, ranging from 2.0–4.8 ppm, and fall into a third category. Compounds in the third category are much larger molecules than the others, having parachors ranging from 592–634. The majority of the phenylureas except for monolinuron, meto-

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bromuron, and linuron, have relatively low vapor pressures and would not be expected to be too volatile. Volatility problems associated with these exceptions have not been reported.

Fenuron was mobile in soil systems compared with other phenylurea herbicides (*87, 356*). Movement was related to the water solubilities of the compounds (*87*). Fenuron's leachability was also greater in coarse textured soils than in fine textured ones and was related to the organic matter content of the soil. In a recent field experiment fenuron moved substantially in a lateral direction over the soil surface and in a vertical direction into the subsoil (*63*). Fenuron moved into the subsoil much more on coarse textured soils than on fine textured ones, but it moved only when excessive amounts (80–160 pounds per acre) were used (*356*).

Soil mobility of phenylureas in the second category is classified as moderate to high for norea (*151, 357*), monuron (*98, 100, 143, 151, 158, 191, 358, 359, 360, 361, 362, 363, 364, 365, 366, 367, 368, 369*), and fluometuron (*335, 370*), moderate to low for diuron (*87, 101, 148, 151, 191, 335, 360, 362, 363*) and linuron (*189, 335, 371*), and low for neburon (*87*). The relative movement of phenylureas in soil systems generally decreased as the water solubilities of the compounds decreased. Movement of the compounds also decreased as the organic matter content of soils increased (*87, 101, 369*).

Herbicidal activity of the phenylureas in soils decreased as the organic matter content of the soils increased (*165, 347, 350, 372, 373, 374, 375, 376*). Studies showed that adding organic matter to sandy soil greatly reduced the herbicidal activity of fluometuron and fenuron in growth chamber studies with model soil systems (*63*) and in field experiments on modified soils (*121*).

Adsorption of fenuron from aqueous solutions by soil particulate matter was much less than other phenylureas (*377*). The compound was adsorbed less by clay minerals than other phenylureas (*63, 378, 379, 380*).

Adsorption of phenylureas from aqueous solutions by soil particulate matter was related to the organic matter content of the soil (*109, 347, 365, 377, 381*). It generally increased with decreasing water solubilities of the compounds although numerous exceptions occurred. Adsorption isotherms showing the relative adsorption of fluometuron and fenuron by soil organic matter are given in Figure 11. Fenuron was adsorbed in small amounts, similar to the acidic herbicides, 2,4-D and dicamba. Almost twice as much fluometuron was adsorbed by the organic particulate matter, but the amounts were still relatively low compared with many other nonionic herbicides.

The herbicidal activity and adsorption of phenylureas in soil systems was partially related to the clay content of the soils (*365, 378, 382*).

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Other investigators found no relationship between phenylurea adsorption or herbicidal activity and the clay contents of soils (*373*, *375*, *376*, *377*). In small-pot experiments in growth chambers, the author (*63*) found that montmorillonite clay added to model soil systems significantly reduced the phytotoxicity of fluometuron and fenuron but that kaolinite

Table IX. Properties of Some Phenylurea,

Common Name or Designation	*Trade Name*	*Chemical Name*
Phenylureas		
Fenuron	Dybar	1,1-dimethyl-3-phenylurea
Monuron	Telvan	3-(*p*-chlorophenyl)-1,1-dimethylurea
Monolinuron	Aresin	3-(*p*-chlorophenyl)-1-methoxy-1-methylurea
Fluometuron	Cotoran	1,1-dimethyl-3-(α,α,α-trifluro-*m*-tolyl)-urea
Metobromuron	Patoran	3-(*p*-bromophenyl)-1-methoxy-1-methylurea
Diuron	Karmex	3-(3,4-dichlorophenyl)-1,1-dimethylurea
Linuron	Lorox	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea
C-6313	Maloran	3-(4-bromo-3-chlorophenyl)-1-methoxy-1-methylurea
Norea	Herban	3-(hexahydro-4,7-methanoindan-5-yl)-1,1-dimethylurea
Siduron	Tupersan	1-(2-methylcyclohexyl)-3-phenylurea
Neburon	Kloben	1-butyl-3-(3,4-dichlorophenyl)-1-methylurea
Fluorodifen	Preforan	*p*-nitrophenyl-α,α,α-trifluro-2-nitro-*p*-tolyl ether
Chloroxuron	Tenoran	3-[*p*-(*p'*-chlorophenoxy)phenyl]-1,1-dimethylurea
Substituted anilides		
Propachlor	Ramrod	2-chlor-*N*-isopropylacetanilide
Propanil	Rogue	3',4'-dichloropropionanilide
Alachlor	Lasso	2-chlor-2',6'-diethyl-*N*-(methoxymethyl) acetanilide
Dicryl	Dicryl	3',4'-dichloro-2-methylacrylanilide
Solan	Solan	*N*-(3-chloro-4-methylphenyl)-2-methylpentanamide
Phenylamide		
Diphenamide	Enide	*N*,*N*-dimethyl-2,2-diphenylacetamide

[a] Calculated from Mumford and Phillips (*199*).

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clay did not. In field experiments montmorillonite clay significantly reduced the phytotoxicity of soil-applied fluometuron (*121*).

Frissel and Bolt (*103*) found relatively low adsorption (< 1.0 μmole/gram) of monuron and diuron from aqueous solutions by montmorillonite, illite, and kaolinite clay minerals. Bailey *et al.* (*104*) in

Substituted Anilide, and Phenylamide Herbicides

Water Solubility 20–25°C, ppm	*Vapor Pressure mm Hg 20–25°C (× 10^{-6})*	*Parachor*[a]	*HNP*[b]
2900–3850		399	815
230	0.5	439	745
580	150	459	
90	0.5	470	
330	3.0	473	
42		479	655
75	15	499	
50	0.4	513	
150		539	
18		569	
4.8		599	665
<2.0	0.07	592	
2.7–3.7	0.02	634	
700		486	
500		446	
148		626	
8–9		474	
8–9		566	
260		581	

[b] Cluett (*355*); HNP = half-neutralization potential.

similar studies found low adsorption (1.3–1.5 μmole/gram) of monuron and diuron and extremely high adsorption (102 μmole/gram) of fenuron by Na- montmorillonite. Adsorption of monuron on montmorillonite ranged from 1–4 μmole/gram in studies by Harris and Warren (*51*). Geissbühler *et al.* (*382*) found that adsorption of chloroxuron on montmorillonite ranged from 50–400 μmole/gram. Farmer (*379*) found low adsorption of the phenylureas, fenuron, and diuron on external surfaces of montmorillonite but found no adsorption on the internal surfaces of the clay mineral. Adsorption of fenuron, monuron, and norea on interlayer surfaces of montmorillonite was found by Kim (*380*). Ionic bonding did not occur. Adsorption was postulated to occur by hydrogen bonding between the carbonyl groups of the phenylureas and the water of hydration surrounding metal cations on the clay surface or through ion–dipole bonds between the carbonyl groups and the metal cations. The phenylureas were readily desorbed from the clay with deionized water.

Adsorbing of phenylureas by clay minerals was slightly greater under acid conditions than under basic or neutral conditions (*51*, *103*) and was greater by 3–25 times on hydrogen saturated montmorillonite than sodium saturated montmorillonite (*104*).

Numerous investigators found that pH did not significantly affect adsorption (*107*, *383*), mobility (*191*), or herbicidal activity (*374*, *375*, *376*) of the phenylureas, suggesting that these compounds do not ionize appreciably in aqueous systems. Hance (*107*) suggested that the lack of significant pH effect on the adsorption of the phenylureas was evidence that the compounds did not ionize and that adsorption was probably by physical van der Waals forces. The slightly higher adsorption of monuron by montmorillonite at 0°C than at 50°C as found by Harris and Warren (*51*) and the desorption of monuron and diuron from soils with water (*110*, *380*) contribute to Hance's suggestion of physical adsorption.

Coggins and Crafts (*378*) compared the relative mobilities of phenylureas using electrophoresis measurements. They assumed that the compounds had basic properties and became protonated under acid conditions. Migration of the compounds toward one of the electrodes increased with an increase in pH, the greatest movement occurring at pH 10. The investigators attributed low movement at low pH to adsorption of protonated species by the cellulose strips of the electrophoresis apparatus.

Nash (*374*) found slightly greater activity of diuron in soil at pH 7.9 than at pH 4.7 and suggested that two factors were responsible. He suggested that diuron may show anionic character at the higher pH and that it may be more water soluble. Both phenomena would decrease adsorption of the compound by the soil and leave more in solution to be used by the plants.

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The phenylureas were adsorbed in small amounts by anion and cation exchange resins (*51*) and in large amounts by charcoal (*182, 381, 383*). Yuen and Hilton (*383*) found that diuron and monuron adsorbed on charcoal was readily desorbed with water and that a surface active agent (type not specified) decreased adsorption. They suggested that this was evidence that the compounds were physically adsorbed, probably through van der Waals forces.

Recent studies (*63*) showed that fluometuron was not significantly adsorbed by cellulose, kaolinite clay, or a strong acid cation exchange resin (H-form) but that it and several other phenylureas were adsorbed in small amounts by ethylcellulose and in large amounts by a weakly basic anion exchange resin (OH-form). Lack of adsorption by cellulose and kaolinite clay showed that the surfaces of these adsorbents preferred water molecules much more than phenylurea molecules. Lack of adsorption by the strongly acid cation exchange resin (H-form) showed that the phenylureas did not show basic properties. Moderate adsorption by ethylcellulose (0-40 μmole/gram) showed that the phenylureas adhered to relatively hydrophobic surfaces, and the lack of adsorption by cellulose showed that they were not readily retained by hydrophilic surfaces. High adsorption (80–320 μmole/gram) of the phenylureas by the weakly basic anion exchange resin (OH-form) showed that the compounds had some anionic character. Figure 12 contains adsorption isotherms for several phenylureas and one phenylcarbamate compound on ethylcellulose and a weakly basic anion exchange resin (OH-form), respectively.

Isotherms for the adsorption of phenylureas on ethylcellulose are of the C-type (*71*) (top of Figure 12). The constant partition or C-type isotherm is common when new sites become available as the solute is adsorbed from the solution. For every concentration of a particular chemical that is used, the same proportionate amount is partitioned between the adsorbent surface and the solution phase. The difference in adsorption of one compound *vs.* another depends upon the structure and properties of the compounds and the preference by the adsorbent of the compounds over that of water molecules. The phenylureas were readily desorbed from ethylcellulose with water showing that the adsorption mechanism was physical in nature.

Regression analyses showed that several properties of the phenylureas were correlated with their adsorption by ethylcellulose (fenuron excluded) (Table X). Parachor was the parameter most highly correlated with adsorption of the phenylureas.

Lambert (*338*), using data from Hance (*377*), found a similar relationship between the adsorption in soil of a series of phenylureas and

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parachors of the compounds. The larger molecules were adsorbed more than smaller molecules.

When the solubilities of the methoxy methylureas (C-6313, linuron, and metobromuron) and the dimethylureas (diuron, fluometuron, and monuron) were considered separately, the R^2 values increased greatly (Table X). A plot of log aqueous solubilities *vs.* the percent adsorption or desorption showed that the two groups of chemicals fell into two different patterns (Figure 13). Substituting a methoxy group for a methyl

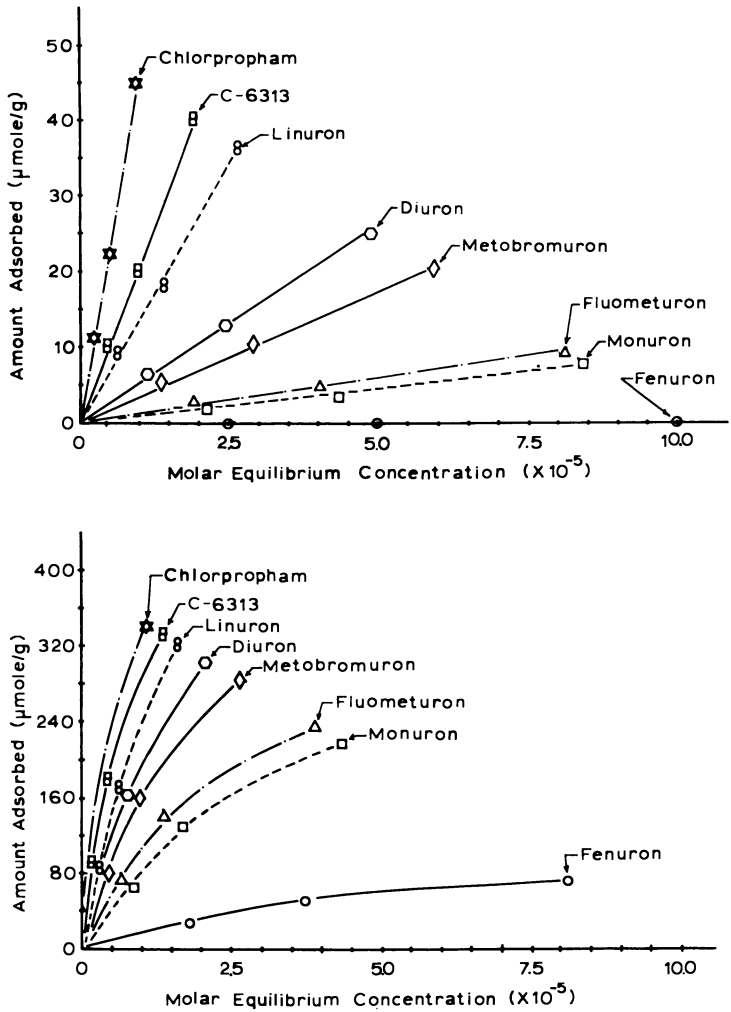

Figure 12. Isotherms for adsorption of seven phenylureas and chlorpropham on (top) ethylcellulose and (bottom) weakly basic anion exchange resin (OH-form) (63)

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Table X. R^2 Values from Regression Analyses of Phenylureas and Adsorption and Desorption by Ethylcellulose and a Weakly Basic Anion Exchange Resin (OH-form) (*63*)

	Adsorbent (R^2 Values)			
	Ethylcellulose		*Exchange Resin*	
Parameters of the Phenylureas	*Ads'n*	*Des'n*	*Ads'n*	*Des'n*
Molecular weight	0.65	0.67	0.75	0.79
Molecular surface area	0.74	0.73	0.79	0.83
Parachor	0.91	0.84	0.86	0.89
Log aqueous solubility	0.32	0.28	0.76	0.69
Log aq. sol. (methoxy-methyl)[a]	0.98	0.97	0.98	0.88
Log aq. sol. (dimethyl)[b]	0.80	0.79	0.93	0.92

[a] methoxy-methyl ureas only.
[b] dimethyl ureas only.

group greatly affects adsorption and may reflect the bonding mechanisms of the two series of compounds.

Similar relationships between the properties of the phenylureas and their adsorption by a weakly basic anion exchange resin were found (Table X). The relationships between the properties of the phenylureas and their adsorption by the two adsorbents will be published elsewhere. In summary, it appears that the phenylureas exhibit weakly acidic properties and are partially adsorbed to particulate matter as anionic species but probably primarily as molecular species. Adsorption is probably primarily through dipole–ion or dipole–dipole bonding mechanisms. Larger molecules are generally adsorbed more than smaller molecules. Compounds of lower water solubility are adsorbed more than those of higher water solubility. Dimethylureas seem to be adsorbed by a slightly different mechanism than methoxy methyl compounds.

Substituted Anilides. The properties of some substituted anilide herbicides are given in Table IX. The compounds are separated into two groups according to their water solubilities. Propachlor, propanil, and alachlor belong to the first group and have moderate solubilities ranging from 148–700 ppm. Dicryl and solan belong to the second group and have lower solubilities on the order of 8–9 ppm.

The movement of the substituted anilide herbicides in soils has not been reported, but weed scientists found that the compounds, alachlor and propachlor, perform better in high organic soils and poorer in coarse textured soils than many other chemicals. This is generally attributed to the relatively high water solubilities and low adsorptivities of the chemicals. Stickler *et al.* (*342*) found that soil incorporation of alachlor and propachlor did not improve their effectiveness over surface applications.

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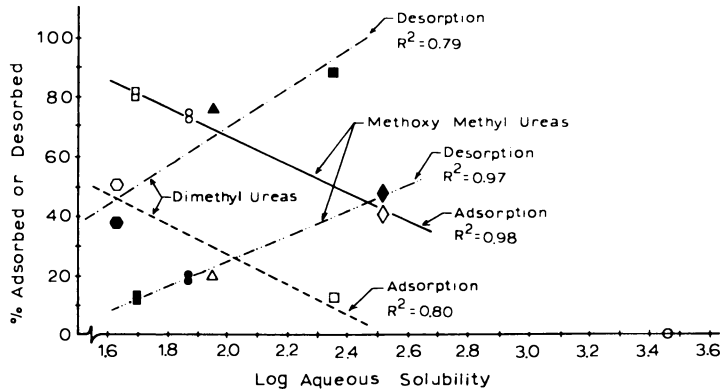

Figure 13. Relationship between the water solubilities of 3 dimethylureas and 3 methoxymethylureas and percents adsorbed by or desorbed from ethylcellulose (63)

They also found that the activity of the herbicides was not significantly affected by soil moisture. Apparently the chemicals were not readily volatilized or photodecomposed on the soil surface and were moved into the soil by normal watering procedures.

Dicryl, solan, and propanil were adsorbed in small amounts (0.05–7.6 μmole/gram) by Na-montmorillonite and a little more (0.84–11.1 μmole/gram) by H-montmorillonite (*104*). There appeared to be no relationship between the amounts adsorbed and the water solubilities of the chemicals.

Ward and Upchurch (*340*) studied the adsorption of 14 acetanilide derivatives from aqueous solutions by various adsorbents. None of the compounds were adsorbed by cellulose. All of the acetanilides were adsorbed to some degree by powdered nylon and cellulose triacetate. Adsorption was somewhat related to the water solubilities and electronic and steric effects of the compounds (R^2 values of 0.63 and 0.60 for nylon and cellulose triacetate, respectively). Adsorption was postulated to occur by hydrogen bonding between the imino H atoms of the acetanilide molecules and the carbonyl oxygen atoms of the adsorbents.

Phenylamides. The phenylamide herbicide diphenamid (Table IX) probably behaves much like the acetanilides in aqueous and soil systems. The compound is moderately soluble, 260 ppm, and leaches much more readily in soils than the phenylurea herbicide linuron (*371*). Deli and Warren (*384*) also found that diphenamid was readily leached through several types of soil. Harris (*151*) found that diphenamid was moderate to high in its mobility in soil, falling between the phenylureas norea and monuron. Diphenamid moved more through course textured soils than

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fine textured ones and moved less as the organic matter content of the soil increased (*371*, *384*).

Adsorption studies with diphenamid showed that the compound was adsorbed in moderate amounts by charcoal and muck and in small amounts by montmorillonite clay (*48*).

Herbicidal activity of diphenamid was greatly reduced by adding soil organic matter to model soil systems (*63*). Montmorillonite clay reduced diphenamid activity slightly, and kaolinite clay did not affect it.

Harris (*150*) found that diphenamid did not move as a vapor through dry soil, so the compound is probably not volatile.

Thiocarbamates, Carbothioates, and Acetamides. One distinguishing characteristic of this group of herbicides is their high vapor pressures (Table XI). All of the compounds are somewhat volatile although dichlobenil and DCPA are much less volatile than the others. The high vapor pressures are indicative of compounds in which the molecules have weak intermolecular forces holding them together. Such compounds also have low melting points, and those with vapor pressures exceeding 2×10^{-3} mm Hg at room temperature are nearly always liquids in the pure state. Thus it is relatively easy to recognize compounds which fit into the categories to be discussed here. In the pure state these compounds are liquids at room temperature and emit a distinct odor when the sample container is opened.

The thiocarbamates, carbothioates, and acetamides behave in similar ways in aqueous and terrestrial systems and will be discussed together.

CDAA, molinate, EPTC, vernolate, pebulate, CDEC, and cycloate are all relatively mobile in soil systems (*123*, *385*, *386*, *387*, *388* *389*, *390*, *391*). The herbicides leached more readily in coarse textured soils than in fine textured ones and did not significantly leach in peat or muck soils (*386*, *387*, *388*, *391*). Leachability of the compounds was related to their water solubilities (compounds of higher solubilities moved more than less soluble ones) and to the organic matter and clay contents of the soils (less movement as the organic matter and clay content increased).

Incorporating the thiocarbamate, carbothioate, and acetamide herbicides into soil increases their effectiveness over applying on the surface (*336*, *352*, *353*, *392*, *393*, *394*). Surface losses were attributed to volatizing because of the herbicides high vapor pressures. Loss by volatizing increased as the temperature and moisture of the soil and air movement over the soil surface increased (*386*, *387*, *391*, *392*, *393*, *395*, *396*, *397*, *398*). Intact EPTC molecules vaporizing from the soil surface were identified by Gray (*392*). Vapor movement of a series of thiocarbamates in soils was related to the compounds vapor pressures (*390*). Vapor moved according to vapor adsorption on soil particulate matter. Move-

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Table XI. Properties of Some Volatile Thiocarbamate, Carbothioate,

Common Name or Designation	*Trade Name*	*Chemical Name*
Thiocarbamates		
EPTC	Eptam	*S*-ethyl dipropylthiocarbamate
CDEC	Vegadex	2-chloroallyl diethyl-dithiocarbamate
Pebulate	Tillam	*S*-propyl butylethylthiocarbamate
Vernolate	Vernam	*S*-propyl dipropylthiocarbamate
Cycloate	Ro-Neet	*S*-ethyl-*N*-ethylthiocyclohexanecarbamate
Butylate	Sutan	*S*-ethyl diisobutylthiocarbamate
Carbothioate		
Molinate	Ordram	*S*-ethyl hexahydro-1-*H*-azepine-1-carbothioate
Acetamide		
CDAA	Randox	2-chloro-*N*,*N*-diallylacetamide
Benzonitrile		
Dichlobenil	Casoron	2,6-dichlorobenzonitrile
Esters		
Methyl ester of chloramben	Amiben methyl-ester	methyl ester of 3-amino-2,5-dichlorobenzoic acid
Isopropyl ester of 2,4-D	2,4-D ester	isopropyl ester of 2,4-dichlorophenoxyacetic acid
DCPA	Dacthal	tetrachloroterephthalic acid, dimethyl ester

ment and vapor loss of the thiocarbamates decreased as the organic matter and clay contents of the soils increased (*358, 386, 390*).

Adsorption studies showed that the thiocarbamates and acetamides were readily adsorbed by various soil types (*358, 389, 390, 397*), by certain clay minerals (*390, 399*), and by charcoal (*390*). Adsorption in soils increased as the organic matter contents increased and as the temperatures and the moisture contents decreased (*358, 389, 390, 397*).

EPTC vapors adsorbed on dry montmorillonite were, by infrared analysis, retained through coordinating carbonyl oxygen atoms of EPTC molecules with metal ions on the clay surfaces (*399*). The adsorbed EPTC was available to germinating seeds growing in agar and was readily desorbed when the clay was suspended in aqueous solutions, showing that the adsorption forces were physically weak.

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Acetamide, Benzonitrile, and Ester Herbicides

Water Solubility 20–25°C, ppm	*Vapor Pressure mm Hg 20–25°C (× 10^{-3})*	*Parachor*[a]
370–375	20–34	482
92	2.2	500
90–92	4.3–4.8	522
90–109	5.4–10.4	522
85–90	2.0–6.2	532
45	13	562
800–912	5.6	455
20,000	9.4–9.6	408
18–25	0.5	334
120		426
	10–15	533
0.5	<10	580

[a] Calculated according to Mumford and Phillips (*199*).

Since the thiocarbamate, carbothioate, and acetamide herbicides are nonionic and their adsorption by and volatilization from soils depends upon the temperature and moisture contents of the systems, adsorption mechanisms involved are probably physical in nature through dipole–dipole or ion–dipole interactions.

Freed *et al.* (*400*) found that the thiocarbamate herbicides had negative heats of solution—*i.e.*, the compounds were more soluble at low temperatures than at higher temperatures. For the thiocarbamates high soil temperatures favor greater losses not only because the compounds are more volatile at higher temperaturs but also because the compounds are less soluble in the soil solution.

Herbicidal activities of thiocarbamate and acetamide herbicides were related to the organic matter (*358, 396, 401*) and clay (*358*) contents of

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the soil. Higher levels of organic matter and clay resulted in lower initial phytotoxicity of the herbicides and lower losses through volatilization. As a result, the compounds were slightly less effective but persisted longer in the finer textured soils.

Correlation studies of soil properties and herbicide phytotoxicity showed that while soil organic matter was highly related to the activity of many herbicides, it was poorly related to the activity of CDEC and CDAA (*350*). This was probably because these compounds were not adsorbed as strongly and were volatilized from the soils in different amounts depending upon the temperature and soil moisture contents. Other herbicides used in the study were not as affected by temperature and moisture as were the volatile compounds.

Benzonitriles. Although there are presently three benzonitrile herbicides used commonly, dichlobenil (Table XI) is the only one which is discussed here. Bromoxynil and ioxynil (Table IV) are hydroxybenzonitriles; their hydroxy groups are ionizable, and they were discussed in Ionic Pesticides because of their acidic properties and low vapor pressures.

Dichlobenil is considerably less soluble in water and has a much lower vapor pressure than the other herbicides given in Table XI, but in aqueous and soils system it behaves similarly. It was relatively immobile in most soils but did leach considerably in sand (*402, 403*). Adsorption was related to the organic matter content of soils (*404*). Much dichlobenil was adsorbed from aqueous solutions by organic soil, lignin, and lanolin wax, but it was not significantly adsorbed by cellulose, sandy soil, sand, or soybean protein (*403*).

Enough dichlobenil vapors were rapidly lost from soil surfaces to damage growing plants (*402, 403*). Soil incorporation reduced the dichlobenil loss and made it much more effective for controlling weeds (*352, 402*). Incorporation also increased the dichlobenil persistence (*402*). Losses of dichlobenil increased with increased temperatures (*402, 405*) and soil moisture contents (*405*). Vaporizing of the herbicide from soils decreased as the CEC (cation exchange capacity) of the soils increased (*405*). The CEC and surface area probably increased as the organic matter and clay contents of the soils increased, and since dichlobenil is nonionic, it was probably adsorbed physically to the organic and inorganic surfaces. Relationships between biological activity and organic matter contents of soils is probably similar to that for CDAA and CDEC.

Esters. The ester forms of acid herbicides are always more volatile and less water soluble than the acid or salt forms (Tables IV and XI). The ester forms are eventually hydrolyzed to acid anions in aqueous and soil systems, but in the ester forms they are nonionic and relatively volatile. Properties of several ester herbicides are given in Table XI.

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Wiese and Davis (*158*) reported that esters of 2,4-D, 2,4,5-T, and silvex move little in soils. Menges and Hubbard (*406*) found that DCPA was not leached into soils in detectable amounts. Talbert *et al.* (*157*) found that chloramben methyl ester leached much less than chloramben salts because of its low water solubility.

Anderson *et al.* (*184*) found that 2,4-D ethyl esters readily volatilized from glass slides. Soil incorporation reduced the loss of ester herbicides from soils, and they became much more effective in controlling weeds (*157, 353, 394, 406*).

Although no information was available about effects of moisture and temperature on adsorption, volatilization, and herbicidal activity of the esters, they probably behave much like the other volatile herbicides given in Table XI. Generally the volatile herbicides are adsorbed to soil particulate matter, and adsorption is greater in fine textured soils than in coarse textured ones. The compounds are not adsorbed by moist soils as readily as they are by dry soils and are displaced from soil surfaces by water molecules through the dissolution process or because water molecules are preferentially adsorbed on hydrophilic sites. Furthermore, the volatile herbicides vaporize more readily at high temperatures than they do at low temperatures. Therefore, the moisture content of the soil and the temperature of the system greatly affects adsorbing and volatizing of herbicides from aqueous and soil systems.

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Summary

Various organic pesticides react with particulate matter in aquatic and soil systems in many different ways. Cationic compounds are adsorbed on clay minerals and organic soil colloids by ion exchange reactions. They are immobile in soil systems, and their biological activity is greatly reduced or nonexistent in the adsorbed state. As a result of their geometrical orientation in the interlayer spacings of expanding type clay minerals, some cationic pesticides are not biologically degradable. Acidic pesticides are only weakly adsorbed by particulate matter and are mobile in soil and aquatic systems. Basic pesticides are physically adsorbed to particulate matter in neutral solutions, but they become protonated and ionically adsorbed in acid systems or on acid surfaces. The biological activity of adsorbed basic pesticides depends greatly upon the pH of the system and is greater under alkaline or neutral conditions than under acid conditions.

Adsorption by particulate matter, movement in soils, and biological activity of adsorbed nonionic pesticides depends greatly upon the chemical properties of the compounds and the types of particulate matter involved. Highly water soluble compounds which are only weakly ad-

sorbed by particulate matter are relatively mobile in soil and aquatic systems. Compounds which have low water solubility are adsorbed to organic lipophillic particulate materials and are relatively immobile. The biological activity of most organic pesticides depends greatly upon the amount of organic matter and sometimes upon the clay minerals present. Pesticides with vapor pressures greater than 1×10^{-6} mm Hg at 20°C may have losses resulting from volatilization from aquatic and soil systems. Their evaporation rate depends upon the type of particulate matter with which they are associated, the soil's moisture content, and the system's temperature.

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Sorption from Aqueous Solutions by Organic Clays: I. 2, 4-D By Bentone 24

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Bentone 24 (Wyoming bentonite coated by sorbed dimethylbenzyl octadecyl ammonium chloride, DMBOA) sorbed equivalent to 13 mg of 2,4-D per gram of adsorbent (65% of the total available), reaching equilibrium within 30 minutes. Sorption of 2,4-D by Wyoming bentonite clay uncoated was less than detectable limits. Sorption (weak) is dependent on the clay:water ratio and 2,4-D concentration. Sorption increased almost linearly with increased percentage clay coverage by the DMBOA in fresh preparations. Specific surface (ethylene glycol) was 73 m²/gram. The Xm *value was 15.0 mg of 2,4-D per gram of clay. Higher sorption in more concentrated solution or at more acid pH increased sorption* (Xm) *from 13 mg to 20.6 mg/gram (100% of surface) at pH 3.4, a maximum.*

The extensive use of 2,4-dichlorophenoxyacetic acid (2-4-D) has caused interest in its sorption by solids. Sorption by soil can reduce the effectiveness of the herbicide which accumulates from application (*1*, *2*). If sorption onto soil particles occurs, seeping of the 2,4-D through the soil to ground water will be reduced (*3*). Scientists concerned with water quality recognize that 2,4-D sorbed into eroded soil can be carried into streams and reservoirs. There it might eventually desorb and pass into municipal water systems. Degradation of the 2,4-D may produce phenols as products. The various phenols in minute concentrations—*e.g.*, 2,4-dichlorophenol at 2–8 μg/liter (*4*)—impart odors and tastes to water. Also, concentration of 2,4-D in reservoir muds are possible, but the effects of such concentrations are not elucidated.

Sorption of 2,4-D by relatively pure clays is weak (*5*, *6*). The term weak indicates that sorption depends upon solute concentration and on

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the nonspecificity of the sorption process (physical sorption). Sorption by soils is greater than by pure clays alone (*1*, *7*, *8*). The sorption increases with higher contents of organic matter in the soil. However, the heterogeneity of the soil organic matter completely hides any simple understanding of this sorption mechanism when studied on bulk soils.

Although it is not believed that clays in soils are completely coated by organic materials, many organic matter–clay reactions do exist (*9*, *10*, *11*). The organic molecules sorbed (or bonded) to clays probably have an orderly orientation because of the clays' crystalline nature. Such orderly orientations of many simple organic molecules on clays are known (*12*, *13*, *14*, *15*, *16*, *17*).

Clays probably indirectly sorb the negatively charged molecules such as 2,4-D. The clay sorbs organic molecules in a specific orientation; the resulting organic surface then sorbs the 2,4-D. The physical and chemical nature of this initial organo-clay surface partly determines the extent of sorption of other organics to it (*18*).

Organo-clay, as used here, follows the concept given by Nahin (*19*)—*i.e.*, a product of specific clay minerals with specific organic molecules involving the formation of chemical bonds. These bonds are primarily between the positively charged amine groups of the organic molecules and the negatively charged (cation exchange) sites of the clay.

The above implications of the reactions are extensive. The agriculturalist is interested in sorption of herbicides by soils (its mobility, strength, and active period). Also, many industrial wastes contain organic substances which strongly bond to clays to produce organic-clay substances. For example, numerous cationic detergents, disinfectants, cationic dyes, flotation chemicals, and various amines in chemical plant wastes migrate into surface waters. When these substances contact clays, they bond to them by relatively strong cationic exchange (coulombic forces), thereby exposing an organic surface on which other organic molecules in the water can sorb. Many organo-clays, as the one discussed here, are used in diverse products such as paints, lipstick, and greases and find their way into surface waters.

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Methods and Materials

All equilibration studies, except those studying dilution effects, were done at constant temperature with 50 ml of aqueous solution containing 5 mg of 2,4-D and 0.250 gram of clay. The solution was buffered with air-equilibrated $Mg(HCO_3)_2$ solution with pH adjusted by HCl. The buffer was $5 \times 10^{-3}M$ with respect to Mg^{2+}. Samples were shaken continuously and gently during sorption for about 45 hours. Desorption

studies were done by shaking the clay filtered from 2,4-D solutions or previous water solutions in fresh distilled water volumes.

The surface was measured using the glycol equilibration method modified by Bower and Gschwend (*20*). All quantitative measurements of 2,4-D were done with a Beckman DK-2A Ratio Recording DU Spectrophotometer using the procedure given by Aly and Faust (*21*) for aqueous solutions. Filtration of the clay using a vacuum and No. 2 Whatman filter paper gave adequate separation for analyzing the solution. X-ray diffraction was done with a Siemans diffractometer equipped with scintillation detector, pulse height analyzer, copper X-ray tube, and Ni filter. It was scanned at 0.5 degrees per minute with a time constant of 3 seconds.

Bentone 24 is a partially fractionated Wyoming bentonite treated with dimethylbenzyl octadecyl ammonium chloride (DMBOA) equal to the cation exchange capacity of the clay (almost exactly 100 meq per 100 grams). The octadecyl (C-18) is replaced by a C-16 chain in about 25% of the material.

Wyoming bentonite, a partially fractionated montmorillonite with less than 1% non-clay impurities, was used as the non-treated clay and to prepare Bentone 24. Both materials were obtained from the National Lead Company, Houston, Tex., through the courtesy of J. W. Jordan.

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Results and Discussion

Sorption of 2,4-dichlorophenoxyacetic acid (2,4-D) by Bentone 24 was rapid and occurred in considerable quantities, as shown in Figure 1. Although uncoated Wyoming bentonite had no sorption of 2,4-D within the detectable limits (less than about 0.3 mg/liter) of the analysis, the Bentone 24 sorbed about 13 mg of 2,4-D per gram of organo-clay when the equivalent of 20 mg of 2,4-D per 200 ml of aqueous solution was available. This sorption was nearly complete within 30 minutes and remained constant after 3 hours. Longer periods were used for equilibration because they were convenient. These longer periods also assured equilibrium at other temperatures used.

Water–Clay Ratio Affects. The strength of sorption is indicated by the ease or difficulty of desorption, the equilibrium concentration left in solution, and the effect of dilution (Figure 2). After sorption of the 2,4-D, resuspension of the filtered clay with its sorbed 2,4-D did not result in desorption of as much 2,4-D as predicted from the sorption curve. If the sorption was non-specific and only physical, the desorption curve should follow the sorption curve. The 2,4-D, once sorbed, is removed with difficulty, resulting in a hysteresis sorption–desorption curve. This desorption curve is above the sorption curve on a X/m *vs.* Ce plot.

The 2,4-D sorbed or desorbed is sensitive to the equilibrium concentration in the solution. Higher 2,4-D concentrations in solution result in

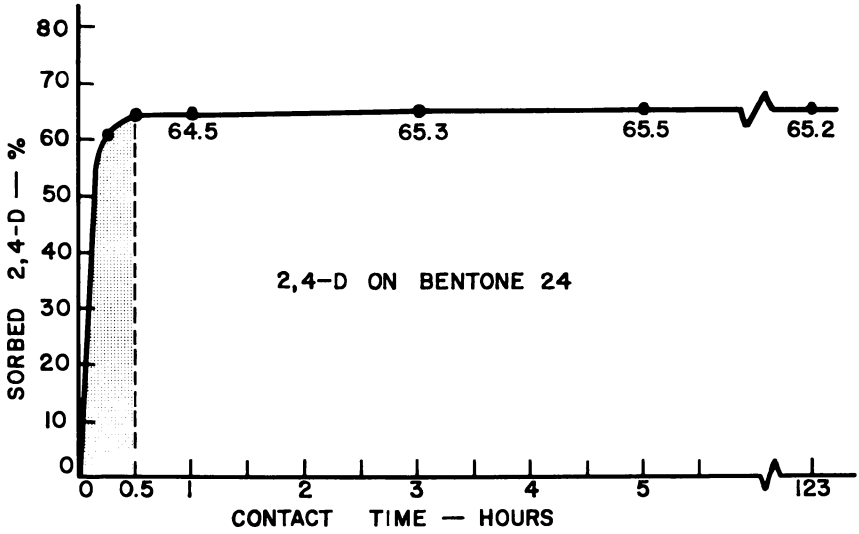

Figure 1. Sorption of 2,4-D by Bentone 24 from aqueous solution containing about 5 × 10^{-3} molar $Mg(HCO_3)_2$, 50 ml volume, 0.25 gram of clay, and 5 mg 2,4-D at 20.5°C (each point an average of 4 replications)

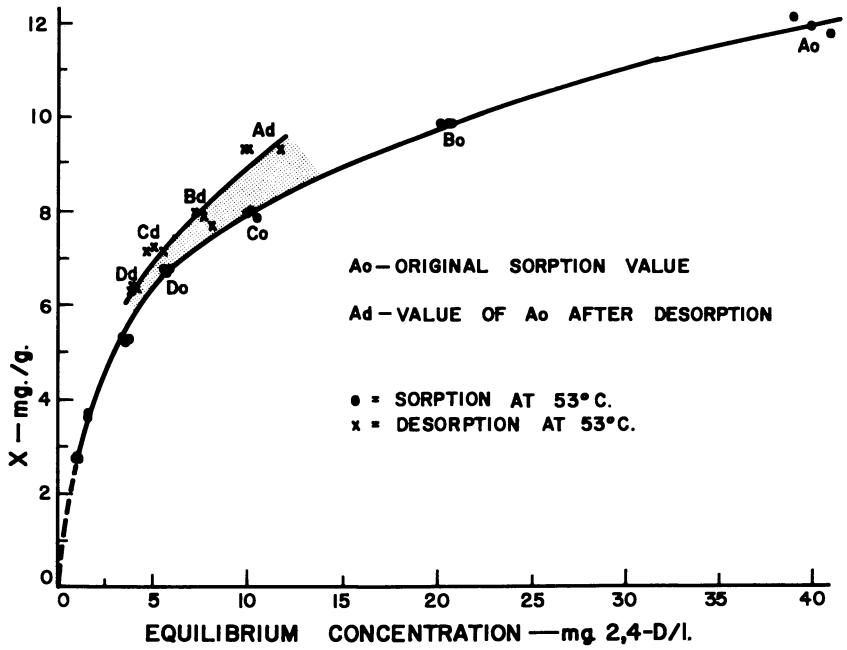

Figure 2. Sorption curve for 2,4-D by Bentone 24 at 53°C and desorption values for selected samples resuspended in fresh water–buffer solution

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larger quantities sorbed. This relationship seems different quantitatively for sorption and for desorption. Although the equilibrium time is possibly longer in desorption, this factor is not believed to affect this experiment.

Keeping the solution volume constant and altering the clay content shows a pattern like that obtained by altering the water volume with a constant weight of clay (Table I). From the data the value of X (mg of 2,4-D sorbed per gram of clay) is reduced by larger water volumes and by larger clay weights per weight of 2,4-D added. For both it results from limited 2,4-D concentration which determines the X value. As the water volume increases, the 2,4-D concentration decreases, and a lower X value results. When the treatment using 1 gram of Bentone 24 was used, calculations verify that the 2,4-D present was insufficient for an X value higher than about 9.7 when the equilibrium concentration in the study was obtained.

Table I. The Effect of Water:Clay Ratios on Sorption of 2,4-D by Bentone 24 at 20.5°C[a]

Water Volume,[b] ml	*pH*	*Equil. Conc. of 2,4-D, mg/liter*	*Amount Sorbed, %*	X, *mg/gram*
50	7.5	61	59	17.8
100	7.6	36	52	15.7
200	7.4	21	44	13.1
400	7.2	11	41	12.4
600	7.2	7.9	37	11.0
1200	7.1	4.6	26	7.7
1800	7.1	3.2	23	6.8

Clay Weight[c] Used, grams	*pH*	*Equil. Conc. of 2,4-D, mg/liter*	*Amount Sorbed, %*	X, *mg/gram*
0.100	8.0	77	23	11.7
0.250	8.0	35	65	13.1
0.36	7.9	18.2	82	11.4
1.00	8.1	2.8	97	4.8

[a] Each value is an average of four replications.
[b] Clay is 0.250 gram, 2,4-D is 7.5 mg.
[c] Volume of 50 ml; 2,4-D is 5.0 mg.

Solution Variables. Increased sorption occurred at increasingly more acid pH values below 7 (Figure 3). Minor changes occurred in adsorption between pH 7 and 9 (variation of 2% of the amount added at adsorption values of 65%). However, as the pH was altered to values near 4.2, sorption increased to 84%. This might result from several effects. Increased H_3O^+ ion concentrations could increase protonation of any exposed min-

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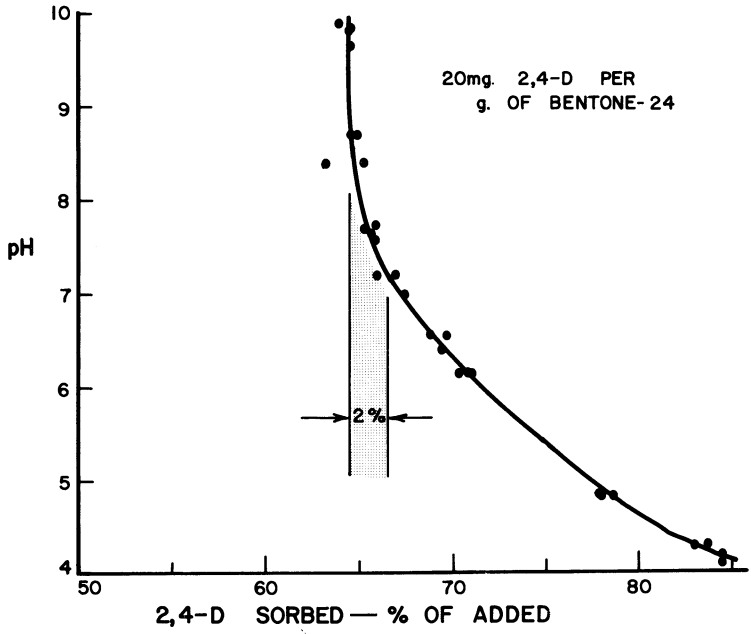

Figure 3. Relation of pH to percentage 2,4-D sorbed by Bentone 24 in 50 ml volume, 5 mg 2,4-D, and 0.25 gram of clay at 20.5°C

eral surfaces, and these might affect bonding to 2,4-D oxygen through H-bonding. However, the major effect of increased acidity is believed to be the reduction of the ionization of the carboxyl-H of the 2,4-D acetic acid group. Such action implies that H-bonding through the carboxyl and, perhaps, altering the species to an uncharged ion are important to sorption. Numerous scientists have suggested that negatively charged ions (or molecules) are repelled somewhat by the negatively charged clays.

Table II. The Sorption of 2,4-D by Bentone 24 as Affected by Varing Concentration of $MgCl_2$[a]

$MgCl_2$ Concentration, gram/liter	*pH*	*Portion of 2,4-D Sorbed, %*
0.02	8.0	66
0.12	8.1	67
0.42	8.1	65
2.02	8.0	61
10.02	7.8	49

[a] The regular buffer contained approximately 0.02 gram/liter $MgCl_2$ equivalent. 2,4-D concentration is 100 mg/liter.

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Table III. Effect of Kind of Mineral Salt Buffer on Sorption of 2,4-D by Bentone 24[a]

Buffer Used[b]	*pH*	*Portion of 2,4-D Sorbed, %*
$Mg(HCO_3)_2$	7.5	66
$CaCO_3$ suspension	7.7	66
$KHCO_3$	7.5	68
$NaHCO_3$	7.6	64

[a] Each value an average of four replications; 2,4-D = 100 mg/liter.
[b] 5×10^{-3} molar in the final test solution.

The competitive effect of soluble metallic cations is shown by the results with Mg^{2+} ion listed in Table II. Increasing concentrations of $MgCl_2$ decreases adsorption of 2,4-D; however, the cause is not apparent. It is possible that a residual + charge results from the ionic double layer before adding $MgCl_2$. An increased salt concentration compresses and reduces double layer charge. Mg may also precipitate insoluble Mg–2,4-D, but if this occurred here, it is unknown. The salt concentrations shown are high, and the results illustrate some influence of simple inorganic cations on sorption of 2,4-D. Precipitation of insoluble magnesium or calcium salts of 2,4-D in this study should not occur. The highest magnesium concentration studied was 10,200 mg/liter. According to Faust and Aly (*22*), the magnesium salt is soluble at 25°C at about 11,000 per liter. If the solubility at the 20°C temperature used is less, some solubility effect could occur at the highest magnesium concentration used. Also, the concentration of 2,4-D used is less than 100 mg/liter.

Apparently, the effect of kind of salt is unimportant at low concentrations. The similarity of adsorption data in various buffers, all at concentrations of 5×10^{-3} molar (Table III), shows this. Since clay was dispersed by $NaHCO_3$ and the lattice possibly collapsed with $KHCO_3$ in some of the work with untreated clay, the $Mg(HCO_3)$ buffer was selected for preliminary work. When the original clay does not disperse, either sodium or potassium buffers are suitable and are more easily prepared than the Mg buffer. Work reported later also indicates that acetates may be suitable. Suspensions of slightly soluble $CaCO_3$ are not believed to be suitable as buffers for altering pH to various values. Adjusting pH with HCl or NaOH and eliminating buffers is also used satisfactorily in some situations.

Percentage Coverage by Organic Amine. Some researchers believe that the sorption of phenols by organo-clay is at a maximum when organic coatings on the clay and adjacent uncoated mineral surfaces occur (*23*, *24*). If this is true and if the sorption of 2,4-D is similar to that of phenols, a maximum sorption should be reached when part of the clay

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(30 or 40%) has no organic coating. Figure 4 shows a roughly linear increase in sorption with increased organic coating used. The steepest increase in sorption is between about 60–80% saturation of cation exchange sites. Possibly at this coverage, islands or clumps of molecules and isolated molecules of the chemisorbed organic material (DMBOA) at lower percentage coverage now join into more extensive units and are more effective or efficient as sorbents. However, the proportionally equal adsorption of 2,4-D even at low coverage seems to be some evidence of a molecule-to-molecule sorption or some other relative sorption.

The lack of internal sorption of 2,4-D makes it difficult to visualize the nearly linear increase in 2,4-D sorbed as the percentage of amine sorbed is increased. At lower percentage covered by the amine, much of the amine should be used to cover interlattice surfaces of the clay. X-ray evidence indicates that in saturated clays, these interlattice surfaces do not likely sorb any 2,4-D. Calculations of the milliequivalents of added DMBOA and of the 2,4-D sorbed indicate that there are ten-fold or more of the DMBOA molecules compared with the number of sorbed 2,4-D molecules. Thus, sorption of 2,4-D by DMBOA can easily be on the external surface alone.

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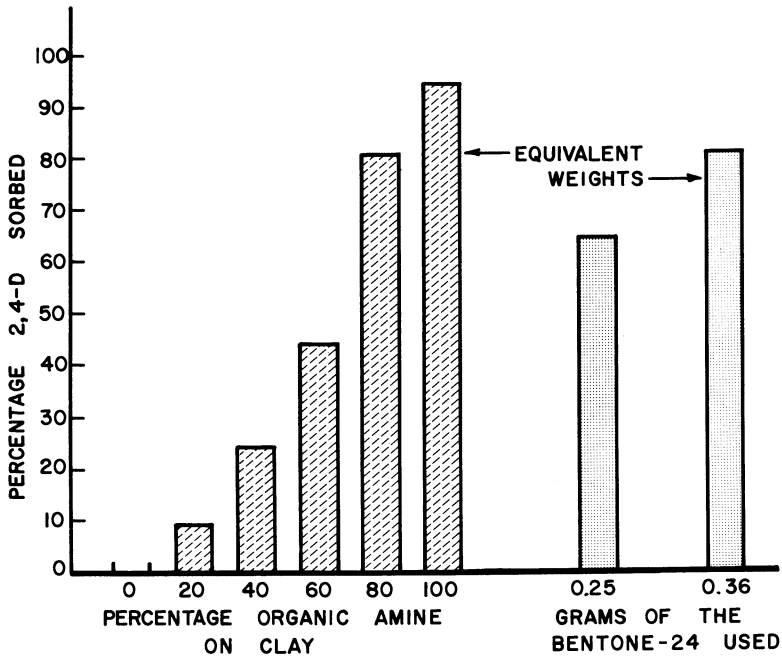

Figure 4. Effect on the sorption of 2,4-D of percentage of cation exchange capacity saturated by dimethylbenzyl octadecyl ammonium chloride; freshly prepared clays used (each value an average of 4 replications at 20.5°C)

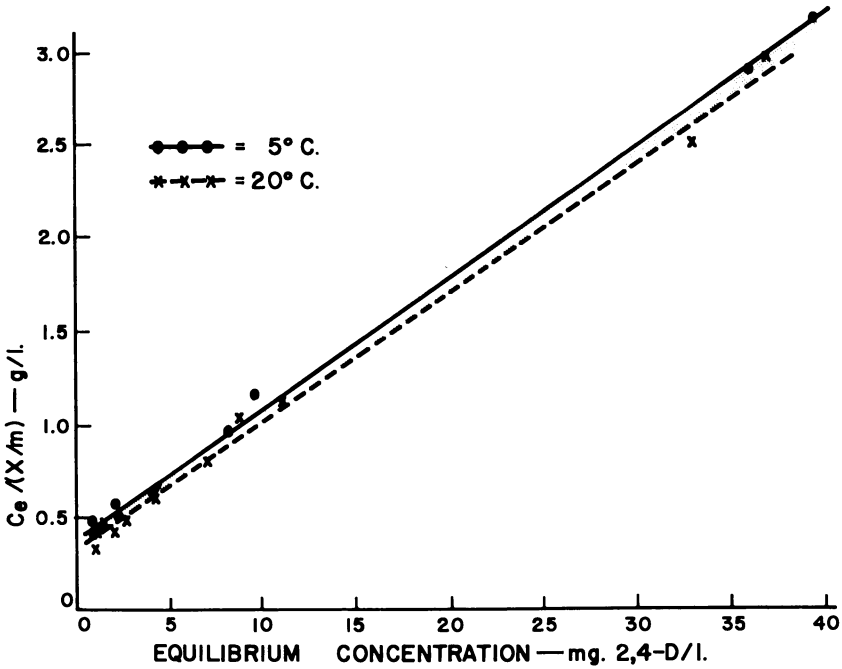

Figure 5. Langmuir isotherms at 5°C and 20.5°C for sorption of 2,4-D by Bentone 24 from aqueous solution (each point an average of 4 replications)

Affect of Temperature. Temperature slightly affects sorption (Figure 5). Sorption is generally an exothermic reaction, and increased temperature lowers sorption. The reverse of this expected reaction occurs with 2,4-D sorption onto Bentone 24 at the two temperatures studied. At 5°C the sorption is slightly less than at 20.5°C. This might indicate a low activation energy in the sorption which is aided at higher temperature, resulting in higher sorption at higher temperature. Values at higher temperatures generally show reduced sorption at higher temperatures.

X-ray Data. There is no evidence of lattice expansion (probably no penetration into the lattice) by either ethylene glycol or sorbed 2,4-D when the sorption is done at low temperatures. The X-ray data (Table IV) illustrate that variable swelling is lacking in interlayer spaces with different treatments imposed on the organo-clay. Appreciable penetration by 2,4-D probably does not occur without lattice expansion because the voids are too small. Expansion to accommodate 2,4-D likely requires much activation energy.

The Δ-values, measurements of the thickness of layers of organic molecules in the internal clay lattices (*6*), are thicker than the approximately 7.8–8.0 A value for a double layer of benzyl molecules lying flat.

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However, the dimethylbenzyl amine with a long carbon chain attached (octadecyl) requires more thickness than a benzyl ring alone. The octadecyl carbon chain and benzyl and methyl groups attached to the nitrogen result in a thickness approaching 5 A (9.5–10 A for a double layer) for the molecule in a position where either the chain or the aromatic ring lies parallel to the clay surface. This value is obtained from measuring a LaPine–Leybold atom model of the molecule.

The DMBOA molecules, sorbed to exchange sites on both siloxane surfaces of an interlamellar space of the clay forming two layers of DMBOA molecules, can be visualized. These could have a thickness of 9–10 A, depending upon their positions relative to each other and to the amount of keying into the oxygen net of the clay surface. The extent of reduction in the *d* spacing, resulting from keying of the sorbed molecule (amine) into the oxygen net surface of the clay, is not considered here. Generally, 0.5–1.5 A are the maximum reducing or shortening of the *d* distance. An aromatic ring lying keyed into the clay lattice oxygen ring shortens the calculated *d* distance 0.2–0.3 A (*6*).

When the organo-clay is freshly formed in water and has sorbed 2,4-D or glycol at warm temperatures, the Δ-values are increased a little; the reasons for these increases are not clear. The forming of organo-clay from a water solution of the amine could result in less flat orientation of some molecules and thus wider *d*-spacing. Upon warming with excess glycol, the ethylene glycol might enter some parts of interlattice channels. Such entry channels should be limited and be a close fit. However, the heat-activated penetration might result in slight prying and propping open of the lattice. This concept is supported by ethylene glycol surface measurements discussed below. At room temperature the glycol appar-

Table IV. Measured d-Spacings for Bentone 24 after Various Treatments

Treatment	d-*Spacing*[a]	Δ-*Value*[b]
Wet by water, air-dried, 20°C	19.0	9.5
Clay + sorbed 2,4-D in water at 20°C, air-dried	19.0	9.5
Freshly prepared Bentone 24 solution at 83°C for 45 hours	19.6	10.1
Freshly prepared Bentone 24 + sorbed 2,4-D from solution at 83°C for 45 hours	20.5 *m* 22.1 *s*	11.0 12.6
Commercial Bentone 24 + excess ethylene glycol, warmed 35 hours at 70°C, desorbed to monolayer	19.6	10.1

[a] The symbols *s* means small peak; *m* means major peak.
[b] The difference between *d*-spacing and the lattice thickness (9.5 A) for the Wyoming bentonite (interlattice spacing).

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ently does not appreciably enter into interlattice areas. However, heating at 70°C greatly increases the specific surface (measured by glycol) which is an added portion of the interlattice surface.

Since no other evidence indicates 2,4-D penetration of the interlayer area, the increased Δ-value when the freshly prepared Bentone 24 had 2,4-D sorbed at 83°C is unexplained. The increased spacing is too small for a layer of 2,4-D. However, since a 19.0 A peak is absent, the increased spacing is considered random layer sorption, but absence of a higher order peak diminishes this possibility. No explanation is presently available to describe the slightly increased Δ value.

Surface Measurements. If only external surface is presumed to be the area available for sorption of 2,4-D, it is estimated that the clay retains about 20.6 mg 2,4-D/gram of clay. Surface measurements using ethylene glycol (specific surface) gave a value near 73 square meters per gram for Bentone 24. This is a reasonable value for external surface of a montmorillonite (*19*) although values in the literature are variable. The *Xm* value from the experimental sorption data is determined as 15 mg/gram and is based upon a 2,4-D dimension of 8.7 by 12 A and the concept that orientation of 2,4-D is not always the same. Thus, any particular molecule must have sufficient space to orient in any direction (12 A diameter circle). Thus the actual *Xm* (monolayer) coverage by 15.0 mg 2,4-D/gram clay is calculated from the slope of a plot of $Ce/(X/m)$ *vs.* Ce. This partial monolayer coverage would cover an area of

$$(113\ A^2/\text{mole})\ \frac{15 \times 10^{-3}\ \text{gram}}{221\ \text{gram/Mole}}\ (6.02 \times 10^{23}\ \text{molecules/Mole}) =$$
$$46.2 \times 10^{20}\ A^2 = 46.2\ m^2$$

The total available area is 73 m^2. The 15 mg of 2,4-D sorption would be covering about 63% of the available area. However, if the area sorbed (interspace area between close-fit circular 2,4-D sorption areas) is not included, about 13% of the surface area is not usable. Thus 15 mg of sorbed 2,4-D would cover about 73% of the usable surface. A coverage of 100% of such areas requires about 20.7 grams of 2,4-D/gram of clay.

Sorption to freshly prepared DMBOA–Clay resulted in a sorption of 18 mg of 2,4-D per gram of organic clay (*see* Figure 4). Later work shows strong pH–sorption dependence with a maximum at about pH 3.4 and sorption of about 20.6 mg 2,4-D/gram clay (equal to 100% of area).

The validity of the previous assumptions is questioned. Although there is no evidence of crowding of sorbed 2,4-D, is there a preferred orientation which permits closer packing of the 2,4-D molecule? The numerous studies on sorption of non-ionic molecules on minerals and of

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sorption of cationic molecules illustrate that the orientation of these organic molecules depends upon their concentration and upon the molecule structure. The less specific and strong the connecting bond, the more the orientation is altered by various conditions. The ease with which sorbed 2,4-D is removed by increasing the water volume suggests that the bond of attachment to the organo-clay is not strong enough to force only one orientation of the 2,4-D. Thus it seems feasible that 2,4-D orients in many directions at different sites. Even the sorbed amine forming the organo-clay coating likely has varying orientations. Such random orientation tends to support the concept of using circular sorption sites for each molecule. Yet, concentration pressures could possibly force some orientation and result in a sorption greater than the 100% value (20.6 mg/gram).

A second possible explanation of the sorption phenomenon is the forced orientation or maximum permitted adsorption that results from sorption of 2,4-D only to certain groups of the DMBOA molecules on the clay. If sorption only occurred at the amine group of DMBOA, the surface area of each DMBOA molecule would limit the amount of 2,4-D that could be sorbed.

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Conclusions

Sorption of 2,4-D by the organo-clay Bentone 24 was at a stable state within 30 minutes. Sorption by the mineral clay (no organic coating) was not detected by the procedure used. Sorption of 2,4-D by Bentone 24 was increased by increased 2,4-D concentration, increased clay–water ratio, and increased acidity from 7.0–3.4 pH. Sorption of 2,4-D was decreased by less DMBOA on the mineral clay, at pH more acidic or less acidic than 3.4, by more dilute 2,4-D concentrations, and by a high Mg^{2+} concentration. Sorption of 2,4-D to Bentone 24 occurs only on external surfaces of the organo-clay. X-ray data verify a double layer of DMBOA between clay lattice layers, but these layers do not permit entry of 2,4-D (nor of ethylene glycol used for surface measurements). Assuming 2,4-D sorbed at random orientation with the ability to rotate, circular sorption areas of 12 A diameters were used to calculate the amount of surface coverage obtained. These are summarized as follows:

1. Bentone 24 surface by ethylene glycol—73 m^2
2. Determined *Xm* value at pH 7.0—15 mg 2,4-D/gram clay coverage = 73% (= 46.2 m^2)
3. Sorption (*Xm*) at pH 3.4—20.6 mg/gram coverage = 100%

These data include the lost areas between circular sorption areas when these circular areas are in close-fit orientation.

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6

Herbicidal Residues in Aquatic Environments

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The conclusion drawn from pesticide monitoring studies carried out in various areas of the United States is that nonpurposeful herbicide contamination of natural waters occurs infrequently and at low levels. Residues in water from purposeful use of herbicides for control of weeds in aquatic sites are relatively high initially; however, the levels are reduced rapidly, and residues are often not detectable after a few days or weeks. Herbicide residue levels found in aquatic organisms commonly reflect the concentrations of herbicides present. With few exceptions aquatic herbicides do not accumulate and persist in fish or shellfish. Most aquatic organisms cleanse themselves of herbicide residues soon after these disappear from the water. Herbicide use, while controversial, continues until more effective and acceptable control measures evolve.

Various groups are pointing to pesticides as major pollutants of the environment. It is difficult to deny that serious consequences have followed extended use of several pesticides. Fortunately and despite contradictory indictments, few herbicides, when used properly, have had long lasting or unexpected effects on the environment. We all are advocates of pure water, and few of us would argue that herbicides in our water do not constitute a degree of pollution. Nevertheless, a 1967 paper convincingly argued that aquatic herbicides are antipollutants (*1*). Without attempting to justify the use or the presence of herbicides in water, it is readily apparent that water pollution from this source is inconsequential when compared with the disastrous results observed from the presence of municipal, industrial, and agricultural wastes in our waters. Actually, the over-abundance of aquatic weeds that necessitates

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the use of herbicides in water has often followed water pollution from these other sources.

Origins of Herbicidal Residues in Water

The sources of most herbicidal residues are not difficult to determine. Residues occur directly from the use of herbicides to control aquatic or marginal weeds or indirectly from and incidental to the control of other types of vegetation. The origins of residues are:

1. In runoff water from agricultural and nonagricultural land
2. Drift from aerial or ground applications of herbicides
3. From applications of herbicides to control floating, submersed, and marginal aquatic vegetation
4. From control of ditchbank vegetation

Residues occur in the aquatic environment from emptying and washing herbicide application equipment or from discharge of industrial waste water. These occur infrequently and do not arise from normal herbicide usage.

Magnitude of Herbicidal Residues

Runoff or Drainage Water. Contrary to expectations, measurable levels of herbicides are not found frequently in natural sources of water. Residues that could be attributed to runoff water have been found. However, in the monitoring studies carried on during the past 10 years, herbicide residues were found in water only rarely and usually in concentrations of a few ppb (*2*). On several occasions small quantities of esters of 2,4-dichlorophenoxyacetic acid (2,4-D) were found in irrigation supply waters (*3*). Esters of 2,4-D were found more frequently in waste drains; however, the highest residue level was only 18 ppb which was much higher than the average of all levels found. Less than 1 ppb of 2,4-D was occasionally found during extensive monitoring of streams in the Western United States (*4*). Even more rarely found were small residues of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and 2-2,4,5-trichlorophenoxypropionic acid (silvex). Treatments of entire watersheds, or sizable fractions of watersheds, were usually followed by low levels of residues in the drainage water (*5*, *6*, *7*, *8*).

Drifts from Aerial or Ground Applications. From studies reported on problems of herbicide drift, we can assume that residues from drift sources are found occasionally in aquatic environments. Residues from drift during ground applications have not been reported. When residues were reported in drainage water during and following aerial applications of herbicides, no attempts were made to distinguish residues attributable to drift from those that appeared in the water through other means. In

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one instance water samples were taken from a stream directly adjacent to a forested area during the application by helicopter of the amine salt of 2,4-D. Residues of 2,4-D were present in the water at levels ranging from traces to 7 ppb (*9*).

Residues from Control of Floating Aquatic Weeds. The concentrations of herbicides found in aquatic environments following the use of herbicides to control floating vegetation are determined by the treatment rate, water depth, type of floating weeds, and the amount of exposed water surface. In one series of experiments, growths of alligatorweed (*Alternanthera philoxeroides* [Mart.] Griseb.) were sprayed with the propylene glycol butyl ether (PGBE) ester of silvex at 8 pounds per acre (*10*). Based on the water depth, the highest concentrations possible ranged from 2.7–3.04 ppm. The highest level of silvex detected in the water at any time was approximately 1.6 ppm. In similar studies involving applications of the dimethylamine salts of 2,4-D and silvex at 4 pounds per acre on alligatorweed and waterhyacinth (*Eichornia crassipes* [Mart.] Solms), almost all of the highest residue levels were between 0.65–1.0 ppm (*11*). Because the maximum concentrations did not appear in the water until one to two weeks after the treatment, it was concluded that the herbicides were absorbed by the floating plants and released later into the water.

Residues from Control of Submersed Weeds. Recommendations for use of herbicides to control submersed aquatic weeds usually specify treatment concentrations in terms of ppm. Granular formulations of herbicides such as 2,4-D, 2,6-dichlorobenzonitrile (dichlobenil), and 2,3,6-trichlorophenylacetic acid (fenac) are applied at pound-per-acre rates. The herbicides most commonly used to control submersed aquatic weeds are listed in Table I with normal rates of application. The initial residue levels represent the concentrations effective on submersed vegetation. For comparison, treatment rates given in pounds per acre are also shown as ppm in an arbitrarily selected water depth of 4 feet.

The concentrations given in Table I occur only if the herbicides are dispersed completely in the water and in most instances are of short duration. Acrolein and aromatic solvents are lost rapidly by volatilization. The residue levels of all the herbicides are reduced through absorption by plant growth, and also copper sulfate and 6,7-dihydrodipyrido-[1,2-a:2′,1′-c]pyrazinediium ion (diquat) are rapidly absorbed and precipitated by organic matter, soil, or sediments (*12*, *13*). Granular formulations reduce the concentrations of residues in water by confining portions of the herbicides at the soil surface. Examples of residue levels lower than expected resulting from the use of granules are shown in Table II. The highest level of residues of dichlobenil and 2,4-D observed in water following treatments of 0.40 and 1.33 ppm were 0.23 and 0.067 ppm, respec-

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Table I. Herbicides and Application Rates Used for Control of Submersed Aquatic Weeds

Herbicide	*Form*	*Application Rates*[a]
Acrolein	Liquid	0.1–0.6 ppm[b] 4–7 ppm[c]
Aromatic solvents	Emulsified	600–740 ppm
Copper sulfate	Pentahydrate	0.1–2.0 ppm
Dichlobenil	Granular	10–15 lb/acre 0.9–1.4 ppm[d]
Diquat	Cation	0.25–1.5 ppm
Endothall	Disodium salt	0.5–4 ppm
	Amine salt	0.05–2.5 ppm
Fenac	Granular	15–20 lb/acre 1.4–1.8 ppm[d]
Silvex	Potassium salt	1.5–2 ppm
2,4-D ester	Granular	20–40 lb/acre 1.8–3.6 ppm[d]

[a] USDA Suggested Guide for Weed Control, Agr. Handbook 332 (1969). Application rates are in terms of acid equivalent or active ingredient.
[b] For extended application time in flowing water.
[c] For treatment of weeds in quiescent water.
[d] Ppm concentration arbitrarily expressed in terms of 4 feet of water.

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tively. Simultaneously much higher concentrations of the herbicides were found on and in the surface 1 inch of soil. The granules behave as reservoirs of the herbicides which are released into the water for some time. Studies made by the Tennessee Valley Authority confirm the low levels of 2,4-D found in water following the use of granules (*14*).

Residues from Control of Marginal and Ditchbank Vegetation. Little attention has been given to residues in the aquatic environment following the use of herbicides on marginal and emersed weeds. Significant data have been developed in the past several years on herbicide residues that occur in water because of ditchbank vegetation control (*15, 16*). Workers with the U. S. Bureau of Reclamation at Denver, Colo. and Ephrata, Wash. monitored the 2,4-D content of water during and following herbicide applications on the banks of 20 irrigation canals (*17*). Residues of 2,4-D ranged from a few ppb to levels of approximately 100 ppb. Usually the residues were well below 100 ppb. Residue data obtained in other studies are shown in Table III.

Disappearance of Herbicidal Residues

Dilution. Herbicidel residues disappear from the quatic environment in several ways. Perhaps the simplest mechanism is dilution. In water impoundments, particularly the smaller ponds and lakes, the effects

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of dilution are often reduced to simple mathematics; however, the effects of dilution in flowing water are unpredictable because of the complex hydrodynamics of water flow in irregular channels.

Degradation of Herbicidal Residues. Herbicidal residues disappear through various processes of degradation. Most studies do not distinguish between losses resulting from degradation and losses from other causes. The pathways of herbicide degradation (photo, chemical, and biological) in the aquatic environment presumably are similar to the pathways involved in the terrestrial environment. The specific modes of degradation may be significantly different. Whereas, terrestrial degradation occurs predominantly in an aerobic medium, the aquatic environment by comparison is largely deficient in oxygen. Biological degradation mediated by anaerobic organisms is particularly expected to differ widely from that caused by aerobic forms with respect to metabolic rates, processes, and end products.

Photodegradation of 2,4-D and its derivatives by ultraviolet light progresses at a relatively rapid rate in water (*18*). It is reasonable to assume that other phenoxy compounds undergo similar degradation. The rate of photodegradation is influenced strongly by pH, becoming more rapid as the pH of solutions increases. Fortunately, the phenol produced as an intermediate in the degradation is destroyed by light even more rapidly.

Most organic herbicides used to control aquatic weeds are resistant to chemical degradation. While herbicides such as the phenoxyalkanoic acids are readily converted to salts, and the ester derivatives are easily hydrolyzed to acids, the basic herbicide molecules are stable. Dichlobenil is practically immune to degradation by refluxing in concentrated acid and base. Similarly, diquat and 1,1′-dimethyl-4,4′-bipyridinium ion (para-

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Table II. Residues in ppm in Soil and Water from Ponds Treated with 0.40 ppm Granular Dichlobenil and 1.33 ppm Granular 2,4-D[a]

Days after Treatment	*Dichlobenil*		*2,4-D*	
	Water	*Soil*	*Water*	*Soil*
1	0.16	6.41	0.024	4.96
4	0.18	4.88	0.034	1.02
8	0.23	5.63	0.048	2.67
12	0.17	5.76	0.053	0.60
18	0.12	1.90	0.067	0.45
36	0.04	1.06	0.001	0.06
56	0.02	0.50	—	0.10
85	0.006	0.18	—	0.005
160	0.001	0.12	—	—

[a] Frank and Comes (*26*).

Table III. Highest Concentrations of Residues Found in Irrigation Water Following Ditchbank Treatment with Several Herbicides[a,b]

Herbicide and Irrigation Waterway	*Treatment Rate, lb/acre*	*Volume of Water Flow, cfs*	*Highest Concentration of Residue, ppb*
Amitrole			
Farmer's ditch	4	4	24
Manard lateral	4	40	31
Yolo lateral	3	23	43
Dalapon			
Five mile lateral	20.0	15	399
Lateral no. 4	6.7	290	23
Manard lateral	9.6	37	39
Yolo lateral	10.5	26	162
TCA			
Lateral no. 4	3.8	290	12
Manard lateral	5.4	37	20
Yolo lateral	5.9	26	69
2,4-D Amine			
Lateral no. 4	1.9	290	5
Manard lateral	2.7	37	13
Yolo lateral	3.0	26	36

[a] In almost all instances the highest concentrations were found in the water a short distance downstream from the sites of application.
[b] Frank *et al.* (*16*) and Demint *et al.* (*15*).

quat) are freed, unaltered from organic matter and mineral soils by refluxing in 18*N* H_2SO_4 (*19*).

Silvex is not degraded by HCl or NaOH (*20*), and neither chlorine nor $KMnO_4$ are effective in removing 2,4-D or its ester derivatives from surface waters (*21*).

Among the agents of biological degradation are the various forms of aquatic fauna, flora, and the microbial population. All major groups of fauna present in water containing a herbicide have some residue of the chemical (*14, 22, 23*). Whether the eventual loss of herbicide from these organisms is resulting from metabolism or from excretion into the surrounding medium has not been determined. The large volume of water, compared with the total mass of animal life, makes it unlikely that degradation by aquatic fauna plays a significant role in the degradation of herbicides.

The masses of vegetation produced by weed species such as elodea (*Elodea canadensis* Michx.), coontail (*Ceratophyllum demersum* L.), and Eurasian watermilfoil (*Myriophyllum spicatum* L.) remove herbicide residues from water (*14*). *Najas* sp. and *Potamogeton* sp. in plastic pools

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treated with 0.5 ppm of diquat or paraquat contained 20 to 40 ppm of these herbicides (*24*). Weed samples taken from drainage ditches treated with 1 ppm of paraquat had residues of 18 ppm (*13*). Residue levels ranging from 0.046 to 1.6 ppm were measured in composite samples of algae and vascular weeds treated with the PGBE ester of silvex at 8 lb/acre (*10*). Except for the work of Thomas (*25*), who showed that endothall-resistant elodea rapidly metabolized this herbicide to a nontoxic form, there have been few studies demonstrating the role of aquatic plants in detoxification or degradation of herbicides in the aquatic environment. Diquat and paraquat were unaltered after essentially complete uptake from water by submersed weeds. The dead vegetation slumped to the surface of the soil, and as it decomposed, the herbicides were incorporated into the organic detritus of the hydrosoil (*26, 27*).

Future studies will probably show that microbial activity is responsible for most of the degradation of herbicide residues in aquatic situations. In lake water alone 2,4-D was not degraded during a period of 120 days (*18*). However, by seeding the solutions of 2,4-D with lake mud, total degradation occurred in 65 days, and successive additions of 2,4-D to the same media were totally degraded in shorter periods. Adapted populations of microorganisms were capable of metabolizing 81–85% of the 2,4-D in 24 hours, and they persisted in lake mud for an extended period. Microbes adapted to metabolism of [(4-chloro-*o*-tolyl)oxy]acetic acid (MCPA) also readily degraded 2,4-D (*28*). There is evidence that herbicides that persist in the terrestrial environment also persist in the aquatic environment (*29*).

Dissipation of Herbicidal Residues

Dissipation is a term used when residues disappear, and no distinction is made as to the various avenues by which they are lost. Most of the work done is of this nature. Experimentation under natural conditions is difficult and provides reliable data only when the influent and effluent water can be controlled. Pilot studies in large bodies of water do not lend themselves to dissipation studies because the water is not confined. The behavior of herbicides in streams and canals is even more difficult to establish. Consequently, many of the dissipation data available were derived from artificial ponds or pools, or from irrigation canals where herbicidal residues frequently appear during normal weed-control operations on these systems. Almost all of the herbicides registered for use in the aquatic environment have water-use restrictions which permit partial or complete dissipation of the residues before normal water use is resumed.

Dissipation in Static Water. The pathways which lead to dissipation of herbicidal residues in static water depend largely upon the nature of

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the herbicides. Sorption processes predominate in the disappearance from water of herbicides such as diquat, paraquat, and possibly endothall. Biological degradation accounts for much of the loss of 2,4-D, silvex, dichlobenil, and other herbicides. Some of the most effective herbicides also are among the most persistent. The excellent and often complete control of weeds by herbicides such as dichlobenil and fenac is attributed to their persistence. Diquat, paraquat, 2,4-D, and endothall disappear from ponded water at rapid to moderate rates. While rapid dissipation of herbicides from water is desirable from the standpoint of residues, it may result in total ineffectiveness of diquat and paraquat in waters containing organic matter or suspended sediments. At concentrations normally used for weed control, residues of diquat are frequently not found after 5–8 days and rarely longer than 10–14 days (Table IV). Water treated with endothall is used for irrigation after 7 days, and fish are used for food after 3 days. Residues of fenac were observed in soil and water 160 days after treatment (*26*), and residues of dichlobenil were observed in water (*30*) and soil (*31*) after 100 and 312 days, respectively. The dissipation rates of 2,4-D and silvex are similar (*11*, *20*) and usually follow the pattern shown in Table II.

Dissipation of Herbicidal Residues in Flowing Water. Acrolein and emulsified xylene are used extensively to control submersed weeds in irrigation canals. The three principal routes by which residues of these herbicides are dissipated are volatilization, dilution, and absorption by plants. Volatility accounts for the greatest loss. Typical reductions of xylene residue levels range from 50–60% during a distance of water flow of 5 miles. No precise data are available for the dissipation of acrolein.

The dissipation of water-soluble herbicides such as the salts of 2,4-D, 2,2-dichloropropionic acid (dalapon), and trichloroacetic acid (TCA) was caused largely by dilution resulting from the longitudinal dispersion of the herbicides in flowing water (*16*). Residues of these herbicides which enter the water during ditchbank treatment are low initially and are reduced to lower concentrations as they are carried downstream. Insignificant residue levels would remain after a water flow of 20–25 miles.

Effects of Herbicidal Residues in Water

Desirable Effects. Following the purposeful introduction of herbicides into the aquatic environment we expect favorable or positive effects. These are measured in many ways. A favorable effect of the residues is the opening and maintenance of navigable waterways. The saving of irrigation water (*32*) and the restoration of normal flow volumes in irrigation canals are also favorable effects. Often the esthetic and monetary values of waterfront property are increased greatly because of herbicide use.

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Table IV. Residue Dissipation in Ponded Water Following Application of Herbicides

Herbicide	*Application, ppm*	*Concentration Detected*			
		Highest		*Final*	
		(ppm)	*(days)*	*(ppm)*	*(days)*
Liquid					
2,4-D dimethylamine salt[a]	1.5	0.139	1.0	0.004	41
Silvex, PGBE ester[b]	2.9	1.6	7.0	0.02	182
Diquat[c]	0.62	0.49	1.0	0.001	8
Paraquat[c]	1.14	0.55	1.0	0.001	12
Endothall[c]	1.0	0.18	2.0	0.001	36
Copper[d]	0.50	0.42	0.1	0.19	3
Endothall[e]	1.2	0.79	4.0	0.54	12
Granular					
Dichlobenil[c]	0.58	0.32	36	0.004	160
Dichlobenil[c]	0.40	0.23	8	0.001	160
Fenac[c]	1.0	0.71	8	0.07	160
2,4-D butoxyethanol ester[c]	1.33	0.067	18	0.001	36

[a] Averitt (*11*).
[b] Cochrane *et al.* (*10*).
[c] Frank and Comes (*26*).
[d] Toth and Riemer (*68*).
[e] Yeo (*69*).

Among the most effective means of controlling anopheline mosquitoes and snail hosts of *Schistosoma* trematodes is the removal of aquatic weeds. Recreational waters may be restored to their normal uses of swimming, fishing, boating, or skiing. The magnitude of the positive effects of herbicide use may often be established in terms of the consequences of nonuse.

Fisheries management is primarily concerned with the control of nuisance weeds (*33*). Herbicides as tools in fish and wildlife management become more important each year. Weed control is reported to be a major phase of fish management in more than a million acres of ponds in southern United States (*34*). Florida alone has seen the construction in recent years of more than 4000 farm ponds. From 1945–1965, over 1.25 million ponds, plus numerous other water retaining structures, were built by the Soil Conservation Districts throughout the United States (*35*). Fishing and other recreational activities in many of these waters, especially those in the southern states, would be impossible without some form of weed control.

In some regions of the United States, notably the eastern and southeastern states, large areas of weed growth have eliminated almost entirely the harvest of fish and waterfowl. The harvest of oysters (*Crassotrea virginica*), clams (*Mya arenaria*), and crabs (*Callinectes sapidus*) is being

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restricted in certain estuarine waters by weed species such as watermilfoil and eelgrass (*Zostera marina*). The use of diquat and 2,4-D for control of weeds in tidal areas opens the water to commercial and sport fishing, and releases from competition the native plants that attract waterfowl (*36, 37*). Excellent results from the use of herbicides for developing and maintaining shallow impoundments for wildfowl habitat have been reported (*38*).

Potable water supplies frequently become infested with algal blooms, some of which produce objectionable flavors and odors. These may become offensive enough to make the water unfit for consumption. Copper sulfate has been used for many years to prevent occurrence of such growths and currently is the only herbicide used to any extent in potable water.

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Undesirable Effects. The first concern of managers of potable water systems when considering the use of herbicides is the possible deleterious effect on water quality. Their product must be wholesome in appearance and palatability. For many years the permissible level of copper sulfate in drinking water was 12 ppm. This was reduced recently to 4 ppm. The reduction was caused not by the toxicity of copper, but by the undesirable flavor. There are relatively few reports of herbicidal residues in drinking water even though herbicides are used occasionally in potable water sources. During 1966 the Tennessee Valley Authority used large-scale applications of granular butoxyethanol ester of 2,4-D at rates of 40–100 pounds per acre for control of Eurasian watermilfoil. The highest concentration of 2,4-D recorded at any of the water-treatment plants downstream where the water was monitored was 2 ppb (*14*). Phenols are notorious for imparting objectionable flavors to water, and their permissible level in water is 0.001 ppm (*39*). Threshold odor and taste levels for 2,4-dichlorophenol are reported to be 2 and 8 ppb, respectively. There was considerable apprehension that phenoxy herbicides might be degraded to chlorinated phenols in the aquatic environment with consequent fouling of water supplies. Although 2,4-D was broken down to 2,4-dichlorophenol, the degradation rate of the phenol exceeded that of 2,4-D, and only under extreme conditions might 2,4-dichlorophenol be detected in water (*18*).

Except for sodium arsenite, the hazards of acute or chronic toxicity to humans, livestock, and wildlife of herbicide residues in water are probably overemphasized. Organic herbicides are plant toxicants that have little or no effect on animals except in large or unusual dosages. Acute poisonings of livestock have been accidental, often resulting from animals drinking left-over herbicide solutions. Livestock have higher tolerance levels than fish; consequently, the presence of live fish is good evidence that the water is safe for livestock (*40*). Unlike many insecti-

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cides, herbicides are rapidly excreted in body wastes with little or no accumulation in tissues. When residues are found in body tissues or milk of livestock, they do not persist for longer than several days.

Herbicide residues in the aquatic environment usually evoke concerns of toxicity to fish. Acute toxicity data are extensive. In general, the herbicide levels required for weed control are much lower than those which cause acute toxicity in fish. Numerous LC_{50} values for various fish have been reported (*41, 42, 43, 44, 45, 46*). Ester derivatives of aquatic-weed herbicides are more toxic than acids, amines, or salts (except for the cocoamine salts of endothall). Different formulations of the same herbicide may vary widely in toxic effects on fish (*42*). The toxicity of two formulations of diquat containing the same concentration of herbicide was reported to vary from 64–430 ppm. Water quality, temperature (*47, 48*), and length of exposure are important factors in assessing acute toxicities.

Toxic effects, usually from high experimental applications of herbicides, often improve the quality of fishing. Young and small fish are usually least tolerant of herbicide residues. In overpopulated waters the removal of small fish resulted in large growth increases of the survivors (*31, 49, 50*). Chronic toxicity of herbicide residues to fish has not been studied extensively. The chronic effects of 2,4-D and diuron on bluegills (*Lepomis macrochirus*) (*33, 50, 51*), cocoamine salts of endothall on redear sunfish (*Lepomis microlophus*) (*52*), and dichlobenil on several fish species have been published recently. Chronic toxicity is difficult to assess in fish (*33*), whereas death is a definite and significant criterion of acute toxicity. The most frequent and serious losses of fish and other aquatic fauna following the use of herbicides occur from the development of anaerobic conditions brought about by the decay of dead vegetation.

The effects of herbicide residues on phytoplankton and invertebrate fauna have been described in considerable detail (*43, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62*). The usual pattern observed has been:

1) death of macrophytes and reduction of phytoplankton numbers
2) decrease in insect number associated with rooted plants
3) decrease in microfauna population
4) increase in density of phytoplankton
5) increase in population of various forms of aqutic fauna.

The time required for the series of events was 2 to 3 weeks. Only in rare instances were the overall effects detrimental to fish-food organisms or fish production. Where fish-food organisms were adversely affected, the problem was linked to anerobiosis in the aquatic sites.

The accumulation of herbicides in fish and other seafood does not seem to be an overwhelming problem. With the possible exception of diuron (*51*), the residue levels in fish are closely related to the levels

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of residues in the water (*62*, *63*). Samples of whole fish taken from water treated with silvex at 5 and 10 ppm did not contain detectable residues three days after the treatment (*62*). At no time were detectable residues found in fish taken from water treated with less than 5 ppm of silvex. Similar data were obtained with 2,4-D (*14*), except that mussels (*Elliptio crassidens*) often retained residues of less than 1 ppm for longer periods. Neither diquat nor dichlobenil accumulated in fish against a concentration gradient (*27*, *62*), and while trout held for 11 days in a solution of 1 ppm diquat contained wholebody residues of 0.36 ppm, no measurable residue was found in the muscle tissue. Other studies of herbicide residue levels in fish produced similar results (*60*, *64*, *65*).

Attempts are being made to reclaim large areas of natural oyster beds in the Chesapeake Bay area with 2,4-D. The ability of oysters and clams to concentrate and retain certain pesticides is well known. Shellfish and shrimp are tolerant of many herbicides when exposed to concentrations of 1 ppm (*66*). The adverse effects noted in a few instances disappeared rapidly. Analyses of oysters and clams taken from experimental areas showed the highest levels of 2,4-D occurred during the first few days and were lost at a fairly rapid rate thereafter. In several tests made by Thomas and Duffy (*59*), residues of 2,4-D in oysters ranged from 1.45 to 3.0 ppm. No residues were found after 21 days at one location; however, in another location the residues persisted for 59 days. In other studies, oysters and clams accumulated maximum 2,4-D residues of 3.8 and 3.6 ppm, respectively (*23*). Although oysters and clams do accumulate residues of 2,4-D, the rates of elimination are such that they would cleanse themselves of the herbicide before the normal harvest season.

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Summary

There is presently much concern regarding the hazards of herbicide residues in the aquatic environment, and as was recently stated, "The positive side of pesticides seems somehow to be drowned out by the negative aspects" (*67*). While herbicides do constitute pollution in the sense that foreign substances are added to water, in most instances herbicides are used to return the aquatic environment to an earlier ecological state destroyed by other, and in most instances, greater pollution problems. No one postulates the existence of good pollution. However, few would sacrifice the use of our water resources for navigation, recreation, agriculture, or potable water simply to deny the reasonable and safe use of aquatic herbicides.

Perhaps there are better methods than chemicals for controlling aquatic weeds. So far few have been identified or developed. Although biological and other nonchemical methods are receiving greater emphasis in current research, the gravity of the weed problem and the lack of other

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suitable methods of control mean that there is a definite role for herbicides now and in the foreseeable future. The benefits derived from the proper use of aquatic herbicides outweigh the unfavorable effects of their presence in the aquatic environment. Used with proper care, there are no serious threats to man, animals, or desirable plants. Herbicides are the most readily available means of containing or reversing the detrimental effects of widespread weed infestations.

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Interaction of Organic Pesticides with Natural Organic Polyelectrolytes

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Natural organic polyelectrolytes are some of the most active components of natural soil-water systems entering into physical and chemical reactions with practically all other components of the systems. Most pesticides are strongly sorbed by insoluble natural organic polyelectrolytes, such as humic acid. The soluble humic salts, however, may solubilize insoluble pesticides. Pesticides also enter into chemical reactions with natural organic polyelectrolytes. The mechanisms of most of these interactions have not yet been elucidated. Elucidation will require isolation of well-defined, chemically and physically homogeneous natural polyelectrolyte fractions.

The behavior of an organic pesticide in a natural water system is regulated to a large extent by the interactions of the pesticide with the natural organic polyelectrolytes. The types of interactions that take place can be conveniently classified into the categories outlined in Table I. This classification is based on the mechanisms of the interactions at the molecular level. It is not always easy to obtain enough definitive experimental information to assign a particular interaction to one of these categories. However, to predict the behavior of a pesticide or any other compound after it is introduced into a soil-water system, a detailed understanding of the mechanisms of the interactions that are operative in the system is necessary.

Organic Polyelectrolytes

Soil-water systems contain most if not all of the polyelectrolytes that are found in living systems and some that are not found in living systems. Two groups of compounds, however, are normally in much

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Table I. Mechanisms of Interaction

Physical Interactions
- A. Adsorption
  - (1) Hydrogen bonding
  - (2) van der Waals bonding
- B. Solubilization

Chemical Interactions
- A. Chemisorption
- B. Ion exchange
- C. Other chemical reactions

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higher concentrations than any of the other organic polyelectrolytes. These are the highly active polyelectrolytes, humic and fulvic acids, which interact with practically all the other components of the systems. We shall, therefore, limit the discussion to the interactions of pesticides with these two groups of polyelectrolytes.

Humic and fulvic acids are defined on the basis of the procedures used in their isolation. Humic acid is the colored organic material which is extracted from soils by a strong alkaline solution and which is insoluble in aqueous solutions of pH values less than about two. Fulvic acid, however, is the colored organic material which is soluble in basic and acidic solutions.

Humic and fulvic acids result from the polymerization of degradation products of plant and animal matter (*1*, *2*). Martin, Richards, and Haider (*3*) and Martin and Haider (*2*) have shown that humic acid-like substances are produced by soil microorganisms from relatively simple organic molecules—*e.g.*, dextrose and glucose—and from more complex substrates—*e.g.*, bean straw and corn stalks. Their evidence indicates that microorganisms convert nonaromatic hydrocarbons into aromatic acids, such as orsellinic acid and *p*-hydroxycinnamic acid. Methyl groups or side chains on these aromatic acids are oxidized, and decarboxylation and hydroxylation take place, yielding phenolic and quinonic compounds which undergo autooxidation and polymerization to humic and fulvic acids. Phenolic compounds derived from bacterial and plant cells, peptides, amino acids, and partially decomposed lignin residues apparently are also incorporated into the humic acid polymers.

The chemical structures of humic and fulvic acids are still largely a matter of conjecture. However, a number of the functional groups in the molecules have been identified. Those functional groups which have commonly been found in humic and fulvic acids are listed in Table II (*1*, *4*, *5*). These functional groups can interact with pesticides and with organic compounds in many ways.

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Pesticides

The pesticides that are commonly used in rural and urban applications fall into a few well defined chemical groups (*6*, *7*); the compounds within each of the chemical groups will generally have more or less similar chemical and physical properties which will govern their interactions with natural organic polyelectrolytes. However in assessing the effect of herbicides and insecticides on natural soil-water systems, one must consider not only the chemical and physical properties of the pesticides themselves but also the chemical and physical properties of their degradation products, which often may also pose a pollution problem. The situation is further complicated by the fact that the side functional groups of the pesticides are often modified during formulation to obtain the desired properties. This is particularly true with herbicides which are commonly applied as esters, acids, or salts of weak bases.

Adsorption

Adsorption from solution is normally divided into two categories, physical adsorption and chemical adsorption. Physical adsorption which arises from weak interactions such as van der Waals bonding or hydrogen bonding is generally reversible. Chemisorption which, however, is a result of the formation of chemical bonds in many cases is not reversible.

The mathematical models that have been applied to the physical adsorption from liquid solutions are generally extensions of the theories that have been developed to describe the sorption of gases on solid surfaces with modifications to account for the competition between the solute and solvent for the adsorption sites. Two of these models have been applied to the adsorption isotherms of nonelectrolytes from solution; they are the Langmuir model and the Brunauer, Emmett, and Teller (BET) model; in addition the Freundlich empirical equation has also been used. In the Langmuir model it is assumed that the adsorbed species forms a monolayer on the surface of the adsorbent, that the adsorbed molecules

Table II. Functional Groups in Humic and Fulvic Acids

Fused ring aromatic groups
Carboxylic acid groups
Phenolic OH groups
Alcoholic OH groups
Quinone moieties
Carbonyl groups
Ester linkages
Ether linkages
Fused ring aromatic groups
Amino and amide groups

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do not interact one with another, and that the adsorption sites are all similar. Most adsorption surfaces however are not homogenous, and the Freundlich equation is an attempt to deal with this heterogeneity. The BET adsorption model in contrast to the Langmuir model assumes multilayered adsorption.

Soil organic polyelectrolytes appear to be the major sorbents of organic pesticides in most soils (*8, 9*). Organic pesticides are strongly sorbed by the organic fraction in soils; this strong sorption influences the phytotoxicity, insecticidal activity, movement, and degradation of pesticides in natural water systems (*6, 10, 11*). The sorption or chemical interaction of a pesticide by the organic components of a soil will also most likely effect the extraction recoveries obtained in analysis for the pesticide, especially if any chemical bonds (chemisorbtion) are formed between the pesticide and the sorbent.

Several mathematical models have been proposed for representing the overall adsorption of pesticides by soils. The most comprehensive one appears to be that of Lambert *et al.* (*9*), in which the partition of pesticides between soil water and soil is represented by a linear adsorption equation similar to the Langmuir equation. In this model they have assumed that the active adsorbent for pesticides in soils is the soil organic matter. This approach has been successful in modeling the adsorption of nonionic pesticides on soils (*12*). Lambert (*13*) has introduced an index of soil adsorption of pesticides which is intended to indicate the amount of active organic matter in a soil and therefore may be used to compare the adsorption capacity of one soil with that of another. Lambert states that the index is independent of the pesticide being adsorbed.

Shin *et al.* (*14*) have found in their studies of adsorption of DDT on soils that there is no simple correlation between soil organic matter content and adsorptive capacity of the soil for nonionic pesticides. They attributed this lack of correlation to three sources:

(1) lipid deposits limiting the accessibility of sorption sites

(2) differences in the surface properties of the organic materials caused by different minerals complexed by the organics

(3) differences in the relative amounts of humidified and nonhumidified organic matter in different soils

In some of the studies attempts have been made to elucidate the details of the adsorption mechanisms for particular pesticides. Two different approaches have been used in these studies; some workers have used whole organic soils as the sorbents in their experiments, whereas others have used humic acids extracted from soils. The whole soils are certainly heterogeneous, and it has been shown that the humic acids extracted from them consist of fractions of different molecular weight and different chemical structure (*15*). In systems in which heterogeneous

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sorbents are present, it is likely that more than one mechanism is responsible for adsorption; therefore, the results obtained will not be definitive.

Hayes *et al.* (*16*) carefully reviewed the literature up to 1969 on the adsorption of *s*-triazine herbicides by soil organic materials and found that some authors favor an ionic bonding mechanism for the adsorption, whereas others interpret their data to indicate that hydrogen bonding is taking place. We shall outline some of this work to illustrate the differences in interpretation. Hayes *et al.* (*17*) studied the adsorption of *s*-triazine herbicides on muck soils, humic acids, humins, and fulvic acids. They pointed out that their data on muck soils are open to a number of different interpretations of the mechanism of adsorption, including hydrogen bonding, ion exchange, ligand exchange, and charge transfer. Generally their data on the adsorption of *s*-triazines on calcium- and hydrogen-saturated humic and humin preparations may also be interpreted in several ways. However, Hayes *et al.* (*17*) apparently prefer a hydrogen bonding mechanism for the adsorption on the hydrogen-saturated materials. The adsorption of *s*-triazines on fulvic acid appears to be caused by van der Waals or hydrogen bonding.

Sullivan and Felbeck (*18*) in one of the most definitive studies to date found evidence by infrared spectrometry which suggests that the *s*-triazine herbicides form with humic acid hydrogen-bonded complexes at lower temperatures and ionic complexes at higher temperatures. They proposed that hydrogen bonding takes place between the amino groups of the herbicides and the carboxyl groups of humic acid. Weber *et al.* (*19*) found that the amount of adsorption of *s*-triazine herbicides from solution by an organic soil in which the water-soluble fraction has been removed is a function of pH; the maximum adsorption of any particular compound taking place at pH values close to the pK_a (negative logarithm of the ionization constant) value of the compound. These authors proposed two possible mechanisms for the sorption:

(1) exchange of protonated *s*-triazine species with acidic functional groups of the organic polyelectrolytes

(2) complexing of the *s*-triazine molecules with unassociated hydrogen atoms

Nearpass (*20*) studied the adsorption of triazole and *s*-triazine herbicides in different organic soils, some of which were hydrogen saturated and some of which were calcium saturated. He concluded that the adsorption is the result of the formation of monovalent cations by protonation of the herbicides on the soil surfaces and subsequent ionic bonding of these cations to the surface.

Wershaw *et al.* (*21*) found that the sorption of 2,4,5-T by humic acid fitted a Langmuir isotherm when the sorbate was dissolved in 0.1*N* NaCl solution but that sorption from a water solution did not fit a Langmuir

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isotherm. As Kipling (*22*) pointed out, adsorption of a weakly ionized organic compound in which there is a small charge associated with a large ion will be caused by van der Waals forces acting on the uncharged groups of the ion and by electrical forces acting on the charged groups. Apparently, therefore, the data of Wershaw *et al.* (*21*) indicated that in the NaCl solution of 2,4,5-T the abundance of counter ions effectively surpresses the electrical interactions and adsorption is caused by van der Waals forces only.

Several authors have attempted to interpret the differences in adsorption behavior of different compounds within the same group of pesticides. Briggs (*23*) has studied the effect of changes in substituent groups in substituted phenylurea compounds and alkyl-*N*-phenyl carbamates on the partition of these compounds between solutions and soils in contact with solutions. He found a linear relationship between the logarithms of the partition coefficients and the Hammett constants and the Taft constants of the substituted phenylurea compounds. However, in alkyl-*N*-phenylcarbamates, linear relationships between the logarithms of the partition coefficients and the Hansch constants of the compounds are obtained. The Hansch constant (π) is defined in the following way by Fujita *et al.* (*24*):

$$\Pi = \log Px - \log Ph$$

where Ph is the partition coefficient of a parent compound between two solvents and P*x* is that for a derivative. Briggs (*23*) states that:

For the phenylureas without long alkyl side-chains, ring deactivation by substituents in the ring or by replacement of a methyl group on the side-chain nitrogen by hydrogen or methoxyl seems to be the factor controlling sorption, possibly through charge-transfer bonding to activated sites on organic matter. Similar bonding by activated rings to deactivated sites on organic matter could occur. The Hammett and Taft constants are a measure of the deactivating effect of the substituents. The electron distribution in the ring is about the same in the various alkyl-*N*-phenylcarbamates, and changes in sorption are caused by increasing lipophilicity with increasing length of the alkyl chain. Their sorption is probably an accumulation at hydrophobic sites at the organic matter/water interface in a way similar to surface-active agents. π is a measure of lipophilicity or hydrophilic–hydrophobic balance and seems to express these properties better than parachor or water-solubility.

Lambert (*12*) correlated the relative amount of adsorption of different analogs of an aniline herbicide by soils with the parachors of these compounds. He has also been able to make similar correlations for substituted phenylurea herbicides. Briggs (*23*), however, stated that except

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for the phenylureas Lambert's parachor relationships "were poor predictors of sorption."

The observed differences in the data obtained by different workers on the adsorption of the same pesticides by soil organic materials are probably a result of differences in the chemical and physical properties of the organic and inorganic components of the soils used in their studies. A much more fruitful approach would be one in which the adsorption of pesticides was studied on carefully characterized soil organic fractions. With these materials it would then be possible to use techniques such as infrared spectroscopy, surface area measurement, and selective chemical blocking of adsorption sites, all of which have been used successfully in elucidating the mechanisms of adsorption in clay–mineral systems, biological systems, and natural- and synthetic-fiber systems. For example, much work has been done on the bonding of dyes to cellulose whose molecular structure is well understood. This work has shown that aromatic cellulose dyes assume a linear configuration parallel to the cellulose polymer strands with all the aromatic nuclei in coplanar configuration; the dye molecules are bonded by hydrogen bonding (25). With adsorption data obtained on homogeneous absorbents, it should be possible to use one of the more comprehensive adsorption models such as that of Everett (26). A comparison of the data obtained from adsorption studies of all the components of soils with data from whole soils should yield a more complete understanding of the mechanisms of sorption and of the interactions between the components of soils.

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Solubilization of Pesticides

Several authors have noted that the soluble salts of humic acid are surface active; however, Wershaw *et al.* (21) were the first to demonstrate that soluble humic acid salts solubilize insoluble pesticides, such as DDT. Soluble humic salts are present in many soils, and they form in any organic soil on which alkaline fertilizers such as urea or anhydrous ammonia has been applied. Ballard (27) has shown in experiments with agricultural soils that DDT is solubilized by humic acid salts when the soils are fertilized with urea.

Chemical Reactions

Several types of chemical reactions can take place between pesticides and natural organic polyelectrolytes:

(1) pesticides can be incorporated into the natural organic polymers during their polymerization

(2) pesticides can be partially or completely decomposed by contact with active surfaces

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(3) pesticides can enter into ion-exchange and chemisorption reactions with the sorbent

At the present time not all these reactions have been demonstrated to occur between pesticides and soil organic polymers; nevertheless, as shown below, it is probable that they all are operative.

Ogner and Schnitzer (*28*) found that alkanes, fatty acids, and dialkylphthalates were released from fulvic acids after methylation of the fulvic acids. These compounds however were not released by less drastic techniques such as solvent extraction. Therefore, the molecules apparently are chemically bonded to the fulvic polymer. It is not clear, though, whether the compounds occupy only surface positions and have become part of the polymer by chemisorption or whether they have been incorporated into the entire polymer while it formed. If these compounds were incorporated into the fulvic acid polymer during its formation, it seems reasonable that other similar compounds might also be incorporated into the humic and fulvic polymers during polymerization. Thus a pesticide, which is chemically bound to a constituent of plant tissue, might be incorporated into the humic and fulvic acids which polymerize from the degradation products of the tissue if the bonding of the pesticide to the plant tissue survives the degradation reactions. Swanson (*29*) has shown that benzoic acid herbicides do form complexes with the constituents of plant tissue and that this complexing does inhibit the degradation of the herbicides. Caro (*30*) found that chlorinated hydrocarbon insecticides accumulate in the leaves of corn plants, and it is not unreasonable to attribute some of this accumulation to complexing.

Pesticides may also form complexes with metals that are bound to the humic and fulvic acid molecules. Ashton (*31*) and Russell *et al.* (*32*) have shown that the triazole herbicide, amitrol, forms coordinate complexes with copper, nickel, and cobalt. Farmer and Mortland (*33*) found that pyridine can coordinate with copper ions that are in the exchange sites of montmorillonite. Amitrol would probably act in the same way. Similarly soil organic polyelectrolytes form stable complexes with polyvalent cations (*34*). Edward and Bremner (*35*) demonstrated that polyvalent metals act as bridges binding clays and organic polyelectrolytes in soils. Since some pesticides also form metal complexes, it is reasonable to assume that the metal cations also form bridges between pesticides and soil organic polyelectrolytes. This hypothesis could be tested by the infrared techniques used by Farmer and Mortland (*33*) for montmorillonite complexes. To obtain definitive results, however, homogeneous, well-characterized organic polyelectrolyte fractions should be used.

In addition to forming complexes with metal ions, some pestcides also form complexes with organic functional groups—*e.g.*, Geissbuhler (*36*) found that the substituted urea herbicides apparently form com-

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plexes with peptides and proteins; therefore, we would also expect them to form complexes with the protein and peptide groups in humic and fulvic acid molecules.

Active groups on the surfaces of humic and fulvic acids may also take part in the degradation of pesticides. It has been known for many years that pesticides decompose in the solid formulations of pesticides and clay or talc carriers in which they are often applied. The decomposition of the chlorinated hydrocarbon insecticides has been attributed to acid sites on the carrier particles. Lopez-Gonzalez and Valenzuela-Calahorro (*38*) have shown that the dehydrohalogenation of DDT also takes place on active surfaces such as those of hydrogen- or sodium-saturated bentonite; thus, if pesticides come in contact with active sites of soil organic polyelectrolytes, similar decomposition reactions could take place. Probst and Tepe (*39*) found some evidence for this; their data suggest that soil organic matter may provide the protons for the reduction of dinitroaniline herbicides.

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Conclusions

Humic and fulvic acids are highly active soil organic polyelectrolytes which interact chemically and physically with pesticides and with other organic pollutants that are in natural water systems. In practically all instances the chemical and physical mechanisms of these interactions have not been elucidated. The elucidation of these interactions will require the use of well defined, homogeneous soil polyelectrolyte fractions. A better understanding of the chemical structure of humic and fulvic acids will also be necessary. With a more detailed understanding of interactions of pesticides with all of the components of natural water systems, it should then be possible to tailor their properties so that a minimum of undesirable alteration of environment will result from their use.

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The Rates of Photodecomposition of Picloram in Aqueous Systems

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The rates for sunlight-caused photodecomposition of picloram in aqueous solutions were determined by five experiments. The photolysis follows pseudo first-order kinetics for concentrations up to 4.14 × 10^{-4}M and in circulating solutions as deep as 3.65 m. Hazy sunlight and water impurities had only a small effect on rate in the systems in which they were studied. A linear relationship relates the photochemical half-life of picloram to solution depth for solutions from 0.292–3.65 m deep.

Picloram (4-amino-3,5,6-trichloropicolinic acid) is a herbicide used mainly to control woody plants and herbaceous weeds. This chemical is used to improve grassland or to maintain watershed and could contaminate surface water. Upon entering surface water, photochemical or microbiological processes are the most likely routes for picloram degradation.

Studies of the toxicity of picloram to microorganisms in soil (*1*, *2*) and pure cultures (*1*, *3*) reveal that it significantly affects some specific soil processes at picloram concentrations of 0.01–0.1 weight % but does not affect population counts in soil or pure cultures with picloram concentrations up to 0.1%. While picloram is relatively nontoxic to microorganisms, it is a poor energy source for microorganisms and is not degraded in pure cultures when a continuing supply of energy substrate for the growth of the organisms is absent. Less than 2% loss in 2 months for 19 test organisms inoculated into dilute broth cultures containing picloram are reported (*4*). This implies that the degrading of picloram in surface water will not proceed rapidly *via* microbiological processes and that photodecomposition is the most probable method of achieving speedy losses.

Hall *et al.* (*5*) have shown that picloram in solution is decomposed by sunlight. Their data indicated an apparent zero-order reaction for a

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starting concentration of $2.0 \times 10^{-2}M$. Watershed (*6*) and grassland (*7*) runoff studies, however, have shown maximum picloram concentrations in surface waters after normal soil applications of less than $2 \times 10^{-6}M$.

The extent of a photochemical reaction is proportional to the amount of light absorbed (the quantum yield), and the absorbance is proportional to the concentration by Beer–Lambert's law. Thus, the rate of degradation with a constant light flux is proportional to the rate of change of absorbance, the concentration, if the photoproducts do not absorb the photochemically active wavelengths. This results in a pseudo first-order reaction. If the concentration of the chemical or its absorbance is so great that essentially all the photochemically important light is absorbed even after extensive degradation, the total absorbance remains approximately constant, and the reaction seems to be zero order. Considering the weak absorption of picloram in the near ultraviolet (*see* absorption spectrum (*5*)), it is reasonable to assume the photolysis of dilute solutions near concentrations expected in the environment is pseudo first-order.

Several investigators at this laboratory over the last few years have studied the photodecomposition of picloram in aqueous solutions exposed to sunlight. Picloram concentrations were reduced to approach the maximum expected in the environment, yet kept high enough to measure accurately. Our analysis of the photolysis kinetics for these experiments and the resulting pseudo first-order rates found are presented below.

General Procedures

The time values reported in days represent continuous 24 hour exposure. The actual light flux was not measured during these experiments, but these time intervals are considered to be proportional to the light dosage. For each experiment weather and season are assumed to be sufficiently constant so that dose comparisons can be made within the experiment. Results from different experiments are not compared because they were conducted at different times during different years.

Table I. Concentration/Time Data—Case 1: Hazy Sunshine Exposure

Exposure Time, Days		*Picloram Concentration*
Actual	*Estimated*	M $\times$ 10^6
0	0	37.3
5	4	26.5
7	6	22.0
9.2	8	21.6
15	11.5	13.1
30	26	4.1

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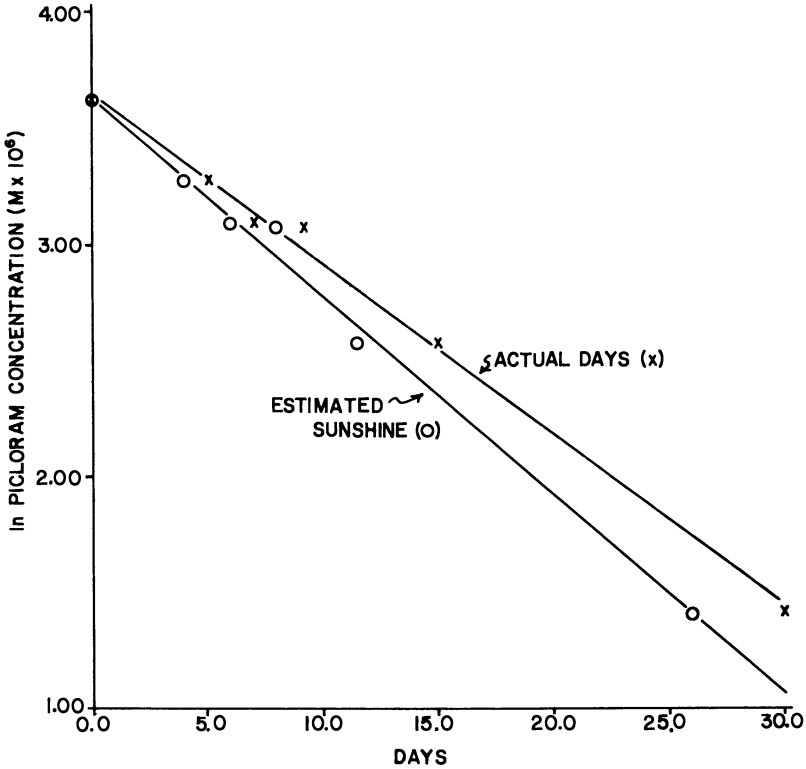

Figure 1. Rate of photodecomposition of picloram, Case 1. Comparison of actual days of exposure and estimated days of effective sunlight.

ln *picloram concentration* (M × 10^6) = 3.655–0.0738 × *days (actual)*
ln *picloram concentration* (M × 10^6) = 3.632–0.0855 × *days (estimated)*

Check samples were prepared for Cases 1–4. These samples were duplicates of the exposed samples except that they were shielded from the light. Bioassay analyses of these check samples detected no loss of picloram. This result eliminates microbiological or adsorptive processes as significant factors contributing to the loss of picloram in these experiments.

The data from the following experiments were analyzed by least squares linear regression (*8*) to determine the best straight line for a first-order kinetic equation and the significance of the correlation (*9*). All except three of the calculated regressions had correlation coefficients significant at the 99% level of confidence. Exceptions were the two rate calculations in the experimental comparison of distilled *vs.* canal water (Case 3) and the correlation of half-life with solution depth (Case 5).

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Only three points were available for these calculations, but the correlations were still significant at the 95% level of confidence.

The regression line for each rate determination was also calculated by forcing the intercept of the line (*8*) to be equal to the natural logarithm of the initial concentration. The forced intercept for the bioassay data in Case 4 was significantly different from the intercept of the original least squares line. In all other experiments the two intercepts were not significantly different from each other at the 95% confidence level. Never was the new slope for the forced intercept line significantly different from the original slope. Only the initial least squares regressions are presented here.

Case 1: A Hazy Sunshine Study. An experiment was conducted at Seal Beach, Calif. in March sunlight to study how hazy sunshine affected picloram photodecomposition. The solution used was 8 cm deep, $3.73 \times 10^{-5}M$ in picloram, and adjusted to pH 7.

During the exposure period, the Seal Beach area was subjected to fog and haze because of its location near the ocean. The estimated days of effective sunlight at each sampling date are shown in Table I along with the actual exposure time. The concentration data were calculated from the ultraviolet absorption spectra of samples taken at the indicated times, and the final point was confirmed by bioassay.

Figure 1 shows the standard, first-order kinetics plots of the data: natural logarithm of concentration *vs.* time. The rate of loss based on estimated sunlight is faster than that for actual time, but the difference loses significance at the 95% confidence level.

The increased ratio of scattered to direct sunlight, resulting from prevailing weather conditions, and high starting concentration did not

Table II. Concentration/Time Data—Case 2: Photodecomposition in a Deep Container

Exposure Time (Days)	*Picloram Concentration* (M $\times$ 10^6)
0	4.14
7	3.70
14	3.31
21	2.94
28	2.61
35	2.30
42	2.05
49	1.82
56	1.635

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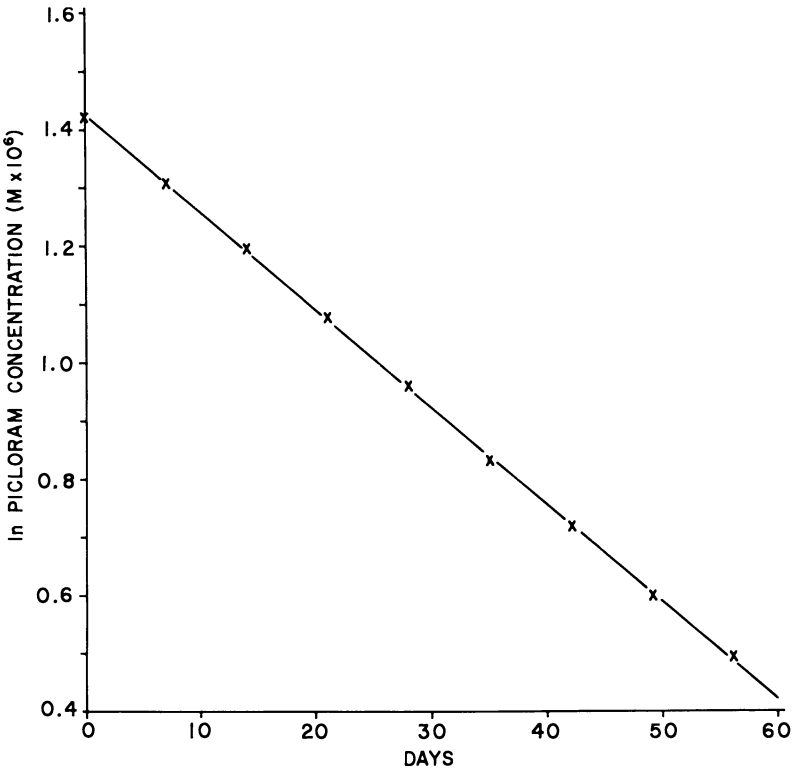

Figure 2. Rate of photodecomposition of picloram, Case 2. Loss from 3.65 m deep circulating solution.

ln *picloram concentration* (M × 10^6) = 1.426–0.0168 × *days*

adversely affect the photodecomposition. The reaction is still pseudo first-order, and the half-life for picloram is calculated to be less than 10 days.

Two check samples were used in this study. One was the usual unexposed sample, and the other was exposed inside a greenhouse where the window glass absorbed the short wavelength ultraviolet light. Neither check showed picloram losses.

Case 2: Photodegradation in Deep Containers. An experiment was conducted at Walnut Creek, Calif. to determine how a deep solution affected picloram photodegradation. Two identical columns, 30.5 cm in diameter and 3.65 m deep, were filled with a 4.14 × $10^{-6}M$ picloram solution at pH 7. The solution in one column was circulated at approximately 4.5 liters per minute, and the other solution was not circulated.

Exposure of the solutions began in May. The first sampling at 94 days showed that picloram completely decomposed in the solution which

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Table III. Concentration/Time Data—Case 3: Distilled *vs.* Canal Water

Exposure Time (Days)	*Picloram Concentration (M × 10^6)*	
	Distilled Water	*Canal Water*
0	20.7	20.7
7	1.97	3.23
15	0.207	0.311

was circulated. The still solution showed 78% loss at 94 days and 89% loss when sampled again at 154 days.

While the exposure of the still solution continued after the first sampling, the second column was refilled with a fresh solution and exposed for 8 weeks (September and October). Weekly samples were

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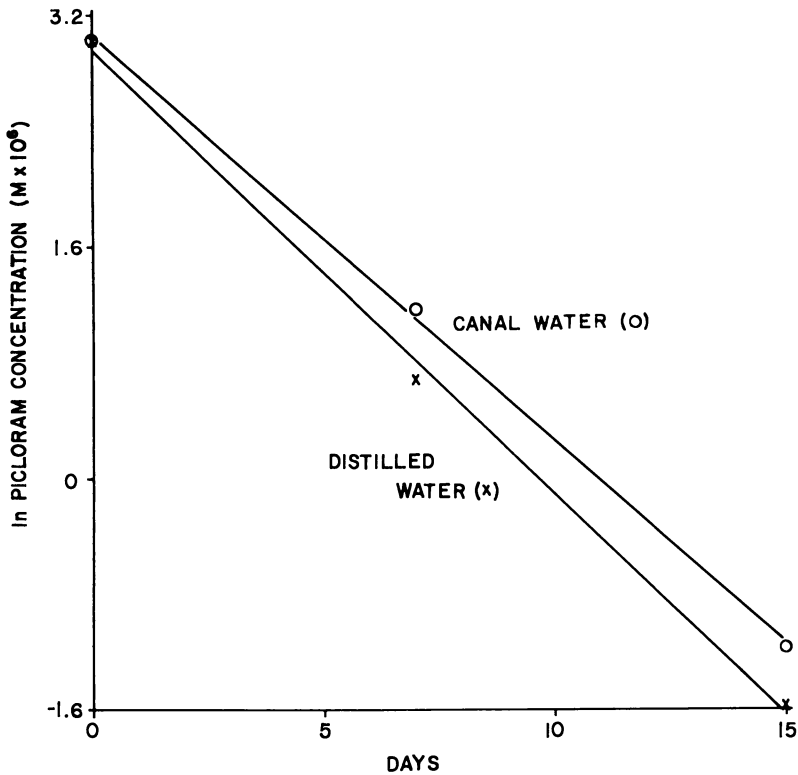

Figure 3. Rate of photodecomposition of picloram, Case 3. Comparison of distilled and canal water.

ln *picloram concentration* (M × 10^6) = 2.958–0.306 × *days (distilled)*
ln *picloram concentration* (M × 10^6) = 3.066–0.280 × *days (canal)*

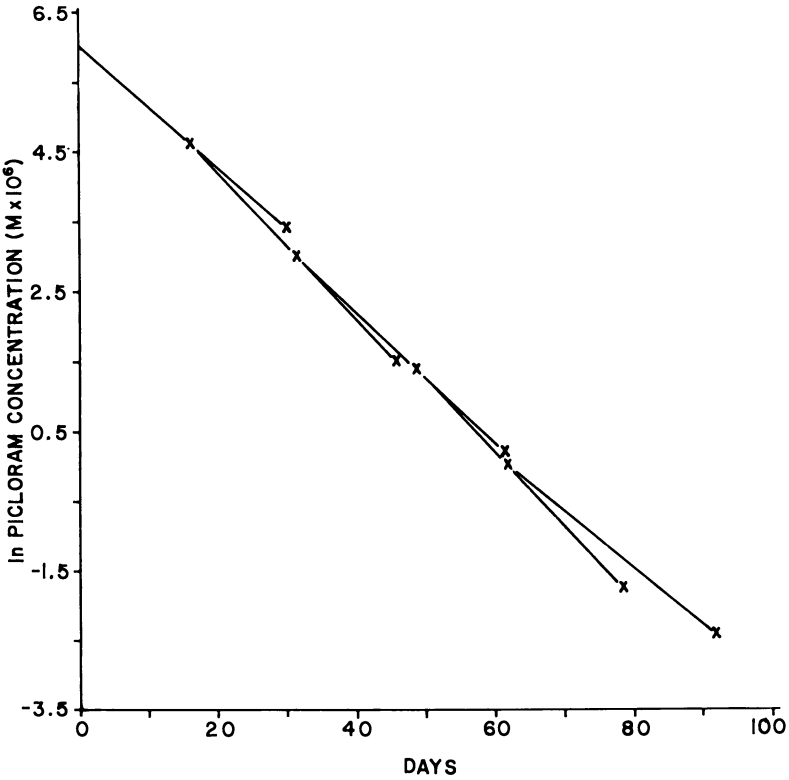

Figure 4. Construction formed by combination of concentration/time bioassay data from Case 4

taken and analyzed by drenching the solution onto soil followed by bioassay with safflowers (*10*).

Table II presents the data for the 8-week exposure of the circulated solution; these data are plotted in Figure 2. These data display the best pseudo first-order kinetics of any of the experiments. The correlation coefficient is 0.9998 (99.96% of the sample variation accounted for by the regression equation).

During the summer all picloram in the circulated solution was decomposed in 94 days, indicating a half-life no greater than 10 days. The fall exposure suffered from shadowing of the solution by the column wall, caused by the lower sun angle, and fewer hours of light per day, resulting in less available light. The calculated half-life of 41 days for the fall exposure demonstrates these effects.

This experiment also shows the effects of slow convection mixing *vs.* circulating the solution rapidly. Light of 290 nm wavelength, the lower limit of the sunlight spectrum (*11*), can penetrate a $4.14 \times 10^{-6}M$ picloram

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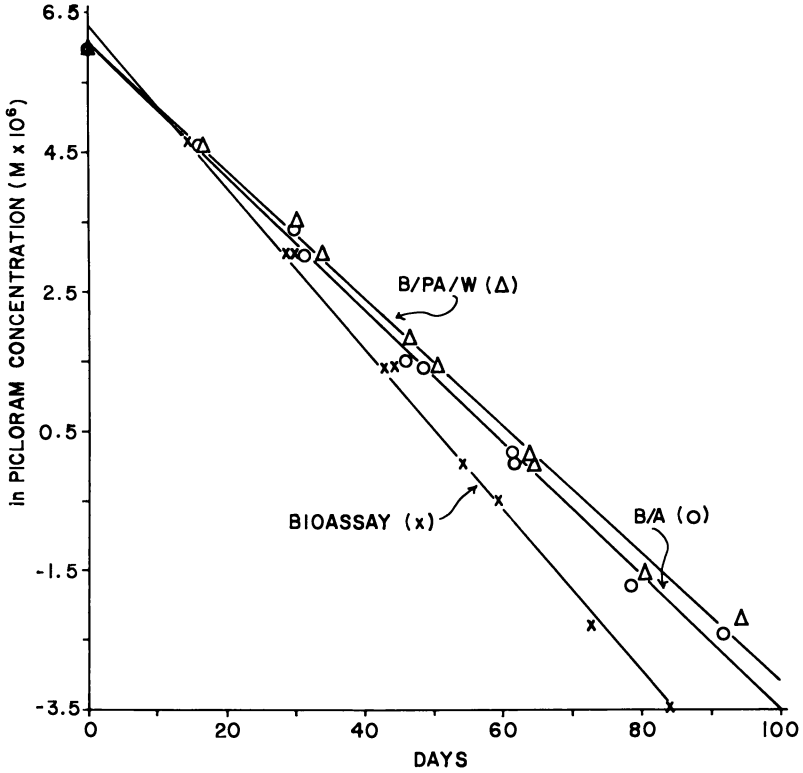

Figure 5. Simulation of extensive photodecomposition of picloram in most concentrated solution from Case 4 (see Figure 4 for method)

ln *picloram concentration* (M × 10^6) = 6.296–0.115 × *days (bioassay)*
ln *picloram concentration* (M × 10^6) = 6.068–0.0956 × *days (B/A)*
ln *picloram concentration* (M × 10^6) = 6.075–0.0915 × *days (B/PA/W)*

Table IV. Concentration/Loss Data[a]—

	Bioassay		
Initial Concentration	*Final Concentration*	*% Loss*	*Half-Life*
414.1	21.11	95	6.99
103.5	4.221	96	6.50
20.7	0.603	97	5.88
4.141	0.1005	97	5.59
1.035	0.03115	97	5.94

[a] All concentration values expressed as $M \times 10^6$, half-lives in days.

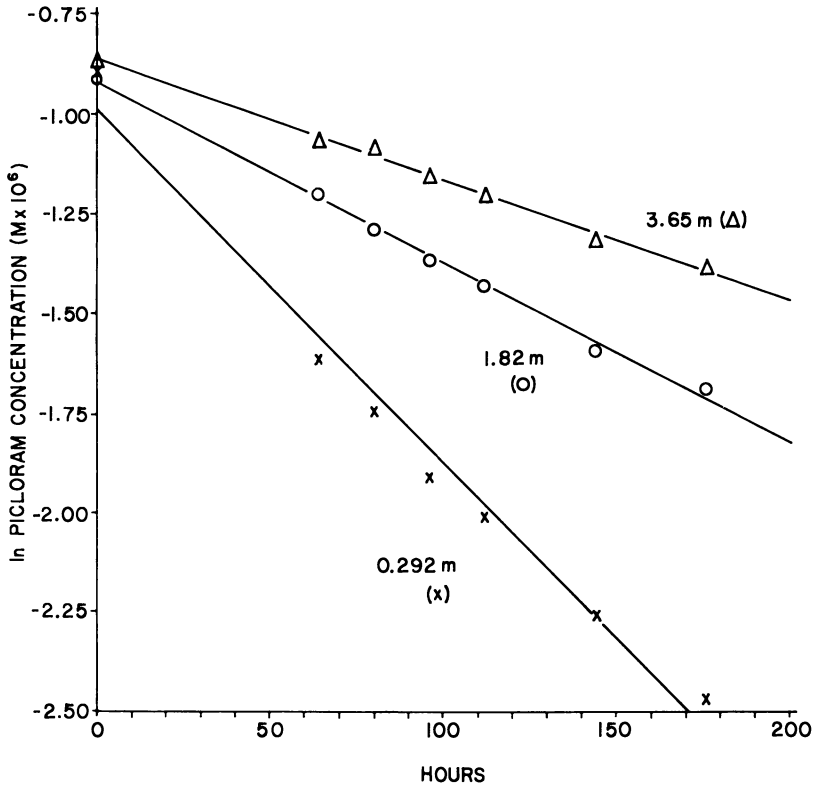

Figure 6. Rate of photodecomposition of picloram, Case 5. Variation of rate with solution depths of 0.292 m, 1.816 m, and 3.64 m.

ln *picloram concentration* (M × 10^6) = −0.9902–0.00883 × *hrs (0.292 m)*
ln *picloram concentration* (M × 10^6) = −0.9215–0.00449 × *hrs (1.816 m)*
ln *picloram concentration* (M × 10^6) = −0.8627–0.00301 × *hrs (3.64 m)*

Case 4: Variation of Initial Concentration

Butanol–Ammonia Chromatography			*Benzene–Propionic Acid–Water Chromatography*		
Final Concentration	*% Loss*	*Half-Life*	*Final Concentration*	*% Loss*	*Half-Life*
30.35	93	7.96	32.86	92	8.21
4.573	96	6.67	6.241	94	7.40
1.246	94	7.40	1.166	94	7.23
0.1789	96	6.62	0.2121	95	7.00
0.09145	91	8.58	0.1085	90	9.22

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solution about 1.5 m before being 50% absorbed. The low light flux in this region of the sunlight spectrum (*11*), coupled with its absorption by water and picloram, prevent significant photodecomposition in the bottom portion of the still solution. As the picloram concentration decreases, light transmission increases so that 290 nm light reaches 50% absorbance at 1.9 m in a $1.04 \times 10^{-6}M$ picloram solution. Forcing the solution to circulate makes all the picloram available for reaction; thus, the solution behaves as if it were less deep than it actually is, and the photodecomposition rate is faster than in the still solution.

Case 3: Distilled *vs.* Canal Water. The effect of impure water was studied by following the picloram loss from $2.07 \times 10^{-5}M$ solutions in 2.5 cm deep aluminum trays. Distilled water (pH 7) and water from the Contra Costa Canal (pH 8), Walnut Creek, Calif. were used to make the solutions. Exposure was during the month of August at Walnut Creek.

Table III shows the data obtained from bioassay with safflowers; the semi-logarithmic plots of the data are shown in Figure 3. The effect of the suspended solids (0.04% by weight) seems insignificant at this shallow depth. Substances in the solution which absorb or scatter the light are expected to diminish the photodecomposition rate by reducing the amounts of light available. Here the fraction of light absorbed and/or scattered is insufficient to reduce the amount available for photodegrading picloram.

Case 4: Varied Initial Concentrations. An experiment conducted during July at Walnut Creek studied how varying the initial concentration affected photodecomposition rate. A series of five concentrations from 1.035×10^{-6} to $4.14 \times 10^{-4}M$ in distilled water adjusted to pH 8 were exposed to sunlight in 4-ounce ointment jars, 4.6 cm deep. The series was duplicated with a second series containing totally labeled picloram-^{14}C (*12*).

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Table V. Concentration/Time Data—Case 5: Variation in Solution Depth

Exposure Time, Hours	*Picloram Concentration (M × 10⁶)*		
	0.292 m Deep	*1.82 m Deep*	*3.65 m Deep*
0	0.409	0.401	0.421
64	0.199	0.301	0.345
80	0.176	0.276	0.339
96	0.149	0.256	0.316
112	0.135	0.240	0.301
144	0.105	0.204	0.268
176	0.0853	0.185	0.251

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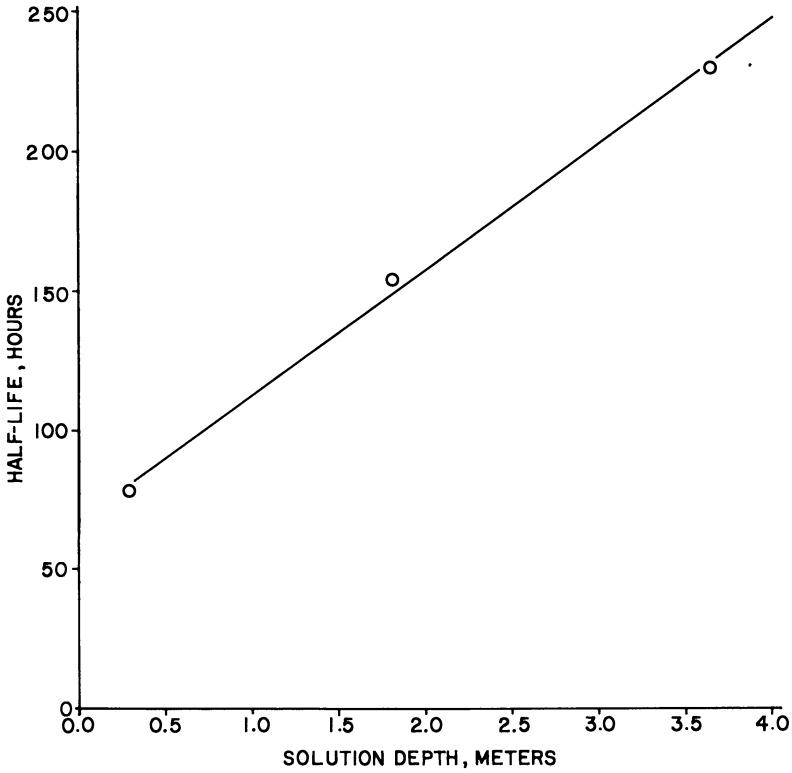

Figure 7. Variation of half-life for photodecomposition of picloram with solution depth

Half-life (hours) = 67.82 + 45.15 × depth in meters

The samples were exposed to sunlight for 30 days and then analyzed. One series was analyzed by bioassay with safflowers, and the radioactive series was analyzed by liquid scintillation counting and paper chromatography. The chromatography solvents were 1-butanol saturated with 1.5*N* ammonia and the supernatant organic phase of a benzene/propionic acid/water mixture (2/2/1 by volume). The calculated pseudo first-order half-lives (Table IV) show good consistency, indicating the assumed reaction order is valid. The average half-lives and standard errors determined by the three methods are: 6.2 ± 0.3 days, bioassay; 7.4 ± 0.4 days, butanol/ammonia chromatography; 7.8 ± 0.4 days, benzene/propionic acid/water chromatography. This experiment demonstrates the pseudo first-order reaction kinetics of the picloram photodecomposition over a 400-fold concentration range. Also, the biological and radiochemical assays agreed which indicates that the photolysis products are not phytotoxic or in too low concentration to be detected.

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Table VI. Summary of Experimental

Case	*Initial Conc.*[a] *(M × 10⁶)*	*Solution Depth*	*Time of Year*
1	37.3	8 cm	March
2	4.14	3.65 m	September–October
3	20.7	2.54 cm	August
4[b]	414.1	4.6 cm	July
5[c]	0.409	0.292 m	August–September
	0.401	1.82 m	
	0.421	3.65 m	

[a] For conversion to other units, $4.14 \times 10^{-6}M$ piclogram is about equal to 1 ppm or 2.72 pounds per acre-foot of water.

The data were also examined by generating the construction shown in Figure 4. The first-order rate equation was calculated for loss of picloram from the most concentrated sample. The time at which the concentration would decrease to the initial value of the next lower concentrated solution was determined, and the equation was found for decomposition in this solution beginning at the calculated time. The process was repeated sequentially using all five concentrations. This technique yielded a series of concentration/time values which could be used to simulate picloram photodegradation in the most concentrated solution. By using the data from each of the analytical methods, three regression lines (shown in Figure 5) and half-lives were calculated. Half-lives obtained by this method range from 6 days (bioassay) to 7.6 days (benzene/propionic acid/water chromatography).

Case 5: Variation of Rate with Depth. Three columns were erected to study how solution depth affects the photodegradation rate of picloram. Each column was 0.305 m in diameter, 0.292, 1.82, or 3.65 m deep, and filled with a $4 \times 10^{-7}M$ aqueous solution (pH 7) of the ammonium salt of carboxy-^{14}C labeled picloram.

The exposure period was from August 10 to September 25. The columns were exposed 4 hours per day when the sun was most directly overhead (11:00 a.m.–3:00 p.m., Pacific Daylight Time) while a centrifugal pump on each column circulated the solutions. Water lost by evaporation was replaced as needed.

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Variables and Kinetics

Other Variables	*Rate Constant*	*Half-Life*
Actual days	0.0738 day^{-1}	9.4 days
Esti. sunshine	0.0855 day^{-1}	8.1 days
—	0.0168 day^{-1}	41.3 days
Distilled water	0.306 day^{-1}	2.3 days
Canal water	0.280 day^{-1}	2.5 days
Bioassay	0.116 day^{-1}	6.0 days
$BuOH/NH_3$ Chromatography	0.0956 day^{-1}	7.3 days
$C_6H_6/C_2H_5COOH/H_2O$ Chromatography	0.0915 day^{-1}	7.6 days
—	8.83×10^{-3} hr^{-1}	78.5 hr
—	4.49×10^{-3} hr^{-1}	154 hr
—	3.01×10^{-3} hr^{-1}	230 hr

[b] Calculations based on construction method shown in Figure 4.
[c] Time values based on noncontinuous exposure, 4 hours per day at midday.

The solutions were analyzed periodically by extracting an acidified aliquot with ethyl acetate and counting the radioactivity in the extract by liquid scintillation techniques. Paper chromatography of the extract with the benzene/propionic acid/water solvent system used in Case 4 confirmed the purity and identity of the picloram in the extract. The results of the analyses are shown in Table V.

The calculated regression lines from the data in Table V are shown in Figure 6. The half-lives calculated for picloram photodegradation from the pseudo first-order rate constants are 78.5, 154, and 230 hours for the 0.292, 1.82, and 3.65-m depths, respectively. Figure 7 is a graph of the regression of half-life on solution depth. The regression equation shown on the figure indicates that from a base of 67.8 hours each meter of depth adds 45.1 hours to the half-life of the picloram in the solution. However, this equation should be considered valid only over the depth range studied until further work is done to extend the range.

The conditions, pseudo first-order rate constants, and half-lives for all the experiments are summarized in Table VI.

Conclusions

Several experiments have shown that picloram will photochemically decompose in aqueous solutions. The loss follows pseudo first-order kinetics over a wide range of concentrations and depths. The half-lives of picloram in water are affected by depth, amounts of sunlight, and the presence of interferring substances.

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9

The Photodecomposition of Pesticides in Water

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Sunlight decomposes many pesticides in water. Water provides a transparent and sometimes reactive medium in which air oxidations, for example, are effectively energized by ultraviolet light. In the presence of hydroxide ions or other nucleophiles, photonucleophilic displacement reactions result in hydrolysis and the conversion of aromatic halides to phenols and eventually to insoluble polymers. Photoreduction also may often be interpreted as a hydride ion transfer. Extensive degradation to small fragments and the combination of reactive intermediates with natural substrates may help explain the difficulties encountered in extending laboratory observations to field situations.

More than 70% of the earth's surface is covered with water. Raindrop, brook, crystal lake, and surging sea are familiar examples of the liquid whose stability, solvent properties, heat capacity, and transparency to light have shaped and sustained life on our planet.

The physical and chemical properties of pure water substance have achieved considerable definition (*1*, *2*) (Table I), including extensive knowledge of the changes produced by ultraviolet light and other radiation (*3*). In solid water (ice) each oxygen atom is tetrahedrally coordinated with four hydrogens; the structure is sufficiently rigid and open so that it remains in part even after melting, which explains why water is more dense at 4°C than at 0°C. Much internal cohesion is retained in liquid water and results in its unusually high boiling point, viscosity, and surface tension compared with similar substances such as ether (Table I). The high polarity reflected in its dielectric constant and dipole moment causes it to associate strongly with other polar substances and makes it a good solvent for them. Water appears to be stable to radiation almost

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Table I. The Physical Properties of Water and Ether

	H_2O	$(C_2H_5)_2O$
Melting point, °C	0.0	−117.6
Maximum density, gram/cc	$1.00^{4.08°}$	$0.92^{-118°}$
Boiling point, °C	100.0	34.5
Viscosity, cp, 25°C	0.89	0.22
Surface tension, dynes/cm, 20°C	72.8	17.0
Dielectric constant, 20°C	80.10	4.34
Dipole moment, *D* (gas, 25°C)	1.85	1.15
Dipole moment, *D* (benzene, 25°C)	1.77	1.23

into the x-ray region although mercury-sensitized dissociation into radicals is measurable at 254 nm (*4*).

Anyone who has looked carefully into the depths of a pond, tasted the ocean, or only observed the bubbles forming on the inner wall of a glass of cold water knows that hydrogen oxide, as we encounter it in nature, is far from chemically pure. The variety and concentration range of the impurities are too extensive to be catalogued; Table II provides typical values for a few concurrent chemical species most characteristic of fresh- and sea-water.

Natural waters contain variable amounts of dissolved gases, principally from the atmosphere. Oxygen is perhaps the most important to our present discussion; depending (inversely) upon temperature and salinity, its saturation concentration is normally about 0.3 millimolar (*5*). Carbon dioxide, minute amounts of hydrogen, and locally significant levels of ammonia and hydrogen sulfide also are present.

Pure hydrogen oxide dissociates slightly into hydronium and hydroxide ions (Equation 1). The equilibrium constant K_w varies from 0.113 ×

$$2H_2O \rightarrow H_3O^+ + OH^- \quad (1)$$

10^{-14} at 0°C to 5.47 × 10^{-14} at 50°C; $[H_3O^+]$ is 1.00 × 10^{-7} at 25°C (*6*). However, the concentrations of hydronium and hydroxide ions are highly variable in natural water. Lakes and rivers have a wider range of pH values than sea water, although the relatively high alkalinity at the surface of the ocean decreases rapidly to about pH 7.6 with increasing depth (*2*). In fresh water a pH of 10 (representing 0.1 millimolar OH^-) is not uncommon (*7*). Other nucleophilic species such as Cl^-, Br^-, and HCO_3^- also are ubiquitous, and cations of the metallic elements including Cu^{2+}, Fe^{2+}, Mn^{2+}, and others known for their catalytic effect on organic reactions occur widely, especially in the ocean (*2*).

Organic Matter

In recent years, the small amounts of discrete organic compounds found throughout natural waters have begun to be recognized and investigated. (Water also contains microscopic plant and animal particu-

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lates, living and dead.) Fresh water often carries dissolved or suspended organic compounds—*e.g.*, quinoid polymers (humic acids) derived from decaying woody vegetation are common (*8*), and Weiss (*9*) has isolated natural alcohols. Rain contains 2 to 12 mg/liter of dissolved organics (*10*), and the dissolved and colloidal organic constituents of sea water include carbohydrates (up to 1 mg/liter) (*11*), common amino acids such as glutamic acid, glycine, and lysine at levels exceeding 1 mg/cubic meter (*12, 13, 14*) and, especially, the lower fatty acids in mg/liter amounts (*15, 16*).

The insoluble surface "slicks" and thicker films of organic matter are interesting. On the open sea, these thin layers probably are primarily of natural origin and consist of C_8–C_{22} fatty acids (both saturated and unsaturated), esters, alcohols, olefins, and alkanes (*17, 18, 19, 20, 16*). Natural petroleum seeps, fats from decaying plants and animals, rainout from air, and coagulation of soluble organics by rising bubbles represent potential sources (*21*).

Of course, dissolved organics and films also can result from pollution by man, especially in shallow water close to shore. An amazing variety of inorganic and organic chemicals and waste products are regularly introduced into waterways and the sea. Detergents, petroleum, phenols, metals, agricultural manure, and raw or treated sewage represent only a few examples. Most of these unintentional (or intentional) pollutants have remained poorly defined in chemical terms although Hunter and Heukelekian (*22*) identified 40 specific chemical constituents of domestic sewage.

Of the more-or-less pure organic constituents detectable in water as analytical methods improve, the insecticides, fungicides, and weedkillers probably have received the most attention. Although inland surface waters have been monitored for about a decade, essentially nothing is known about pesticide levels in the ocean, and existing information comes from indicator organisms. Even current quantitative data from water analyses stretch the limits of accuracy and confirmation of identity (*23*).

Table II. Impurities in Fresh and Ocean Water

	Lake	*Ocean*
Typical surface temperature, °C	20	12 (San Francisco) 18 (Los Angeles)
pH	5.0–9.0	7.6–8.4
% T_{300}, 1 ft depth[a]	85	85
$[O_2]^{15°}$, m*M*	0.30	0.26
$[Cl^-]$, m*M*	0.16	550
$[Br^-]$, m*M*	0.002	0.8
$[Cu^{++}]$, m*M*	Variable	0.0002
Organic C, ppm	10	2–7

[a] Ultraviolet transmission at 300 nm.

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Table III. The Occurrence of

Concentration,

Source	*DDT*	*DDD*	*DDE*	*Dieldrin*
Rainfall: Ohio (*60*)	20–1300			D[a]
Surface waters: U.S. (*59*)	316	840	650	407
Estuary: California (*61*)	200[c]		100	D
Cod liver oil: Arctic (*62*)	1650[d]			160

[a] D = detected.
[b] Total organophosphates and carbamates.

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Table III lists some common pesticides which have been widely reported to be extracted from water. The aqueous solubilities of pesticides vary within wide limits; many, including chlorinated hydrocarbon insecticides, probably do not even occur as such in water but are always adsorbed to silt or other particles or dissolved in surface films (*24*). Overall concentrations, nevertheless, generally do not exceed the parts per trillion range—*i.e.*, nanomolar ($10^{-9}M$). Reagents such as oxygen, hydroxide ion, and even metal ions normally are present in from perhaps 100- to 100,000-fold molar excess over the amounts of pesticides which are to be found in water (Table II).

Light

Most of the energy required to drive the environmental transformations of organic compounds comes directly or indirectly from solar radiation. Pesticides, dissolved or suspended in a transmitting medium, could be expected to absorb light and be subjected to reaction either internally or with external reagents. Water—fresh or salt—efficiently transmits ultraviolet light of wavelengths longer than 30 nm (*25*); however, the intensity falls off with increasing water-depth and radiation frequency, and photolysis probably proceeds at infinitestimal rates at depths beyond a few meters.

For practical purposes, the energy derived from sunlight does not exceed about 95 kcal/einstein (corresponding to 300 nm) because of absorption by atmospheric ozone (*25*). Few pesticides absorb appreciable light above about 400 nm, and also the quantum energy available at the longer wavelengths (less than 60 kcal/einstein) is insufficient to break most kinds of chemical bonds commonly found in these compounds

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Pesticides in Natural Waters

ng/liter (ppt)

Aldrin	*BHC/ Lindane*	*Heptachlor Epoxide*	*Phosphates*	*Other*
D	10–70	D		Atrazine 100 2,4-D 100
85	112	67	380[b]	Chlordan 169 2,4-D D Endrin 133
	40	150	Parathion 260 Others D	
		20		Endrin 30

[c] Includes DDT and DDD.
[d] Includes DDT, DDD, and DDE.

(Figure 1). Therefore, the effective wavelength range within which most environmental transformations of pesticides take place would be distinctly limited except where some form of photosensitization is operating.

Although exact values depend upon the specific compound under consideration, approximate values for the homolytic dissociation energies of common bonds have been tabulated (*26*, *27*). For example, homolytic cleavage of the C–H bonds in benzene requires 104 kcal/mole; H–CH_2OH, 92; phenyl C–Cl, about 80; H–OH, 118; and HO–OH, 48 kcal/mole. Figure 1 shows that while the sunlight spectrum (B) is ex-

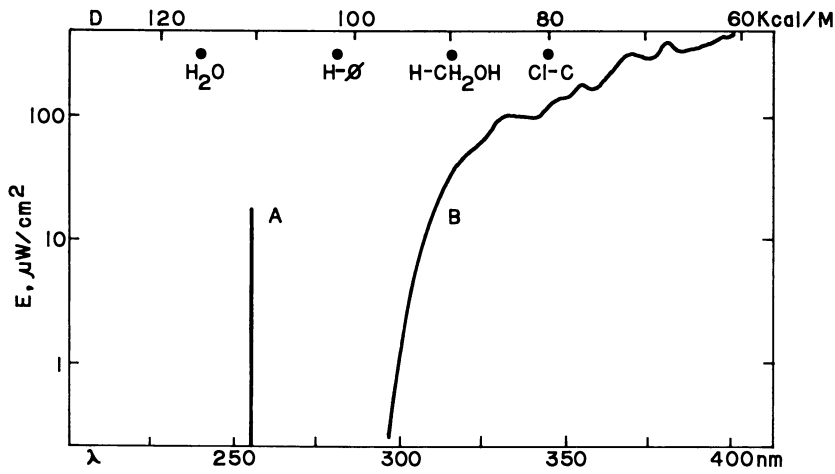

Figure 1. Spectral energy of sunlight

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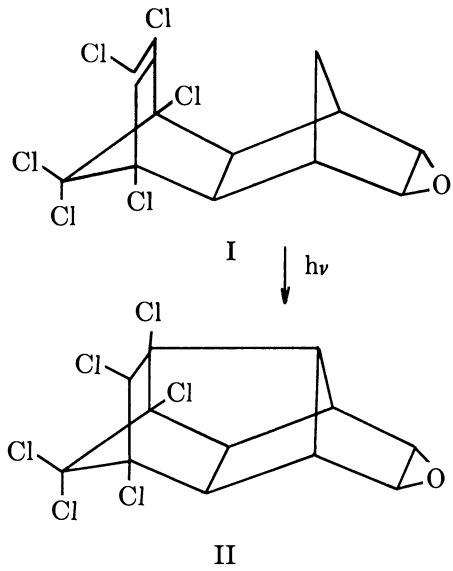
pected to deliver enough energy to allow homolytic cleavage of the phenyl C–Cl bond or the C–H bond in an aliphatic alcohol, the aromatic C–C bond and the H–OH bond would be expected to be stable in the absence of sensitization. However, most photochemical investigations have used mercury-arc light which appears primarily at 253.7 nm (A) with an energy of 112 kcal/einstein. Consequently, this distinction between energy sources can become most important when considering the possible pathways of environmental photodecomposition of pesticides. Virtually all experiments reviewed below were conducted at wavelengths longer than 290 nm.

Photodecomposition Reactions

With a low concentration of photon-absorbing pesticide present in a warm, transparent medium, a large excess of reactive oxidants, reducing agents, and nucleophiles, and with the entire system bathed in plenty of energy, let us examine what probably occurs.

Water as Reaction Medium. Being transparent to the near-ultraviolet spectrum of sunlight, pure water can serve as an inert medium in which pesticide transformations take place. For example, Henderson and Crosby (*28*) have shown that suspensions of the chlorinated hydrocarbon insecticide dieldrin (I), although essentially insoluble in water, undergo a photocondensation reaction to give photodieldrin (II) (Equation 2).



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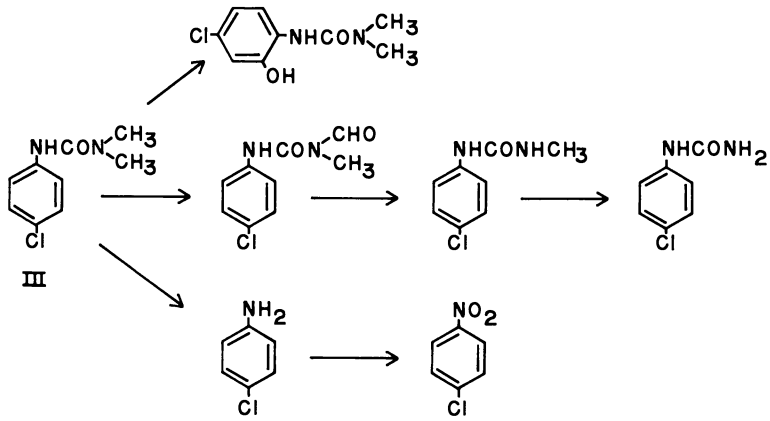

Figure 2. Photolysis of monuron

The same substance was formed upon irradiation of dieldrin dissolved in organic solvents (*29*) or deposited as thin films (*30*); apparently neither water nor its contained solutes reacted.

Water also can serve as a reaction medium—*e.g.*, in photooxidations. The herbicide monuron (III), suspended or dissolved in water, participates in at least three types of reaction with oxygen under the influence of light (Figure 2) (*31*). The *N*-methyl groups are successively oxidized, and the resulting *N*-formyl derivatives decompose to give formic acid. A more remarkable oxidation is the direct hydroxylation of the aromatic ring of monuron at the position ortho to the urea sidechain. An unusual photooxidation converts 4-chloroaniline, produced by hydrolysis of the urea, into 4-chloronitrobenzene (*32*); this type of reaction previously has been associated only with the powerful peracid oxidants. The fact that the dealkylation of monuron, tenoran (*33*), and similar compounds occurs also in essentially anhydrous thin films on glass plates indicates the passive role of water in this type of oxidation.

Participation of Water. Water may participate subtly in photolytic reactions. Many instances now have been identified in which the generation of hydrated electrons provides a driving force (*34*). In some cases, they are generated optically from organic anions such as salts of phenylacetic and phenoxyacetic acids (*35*).

This reaction could explain the products observed after the irradiation of aqueous solutions of salts of the chlorinated phenylacetic acid herbicide fenac (*36*) or 1-naphthaleneacetic acid (NAA, IV) (*37*) (Figure 3). Removal of the electron in its solvent cage could generate a radical (V) which reacts rapidly with oxygen; the resulting peroxy radical could disproportionate by well-known routes to provide the transiently

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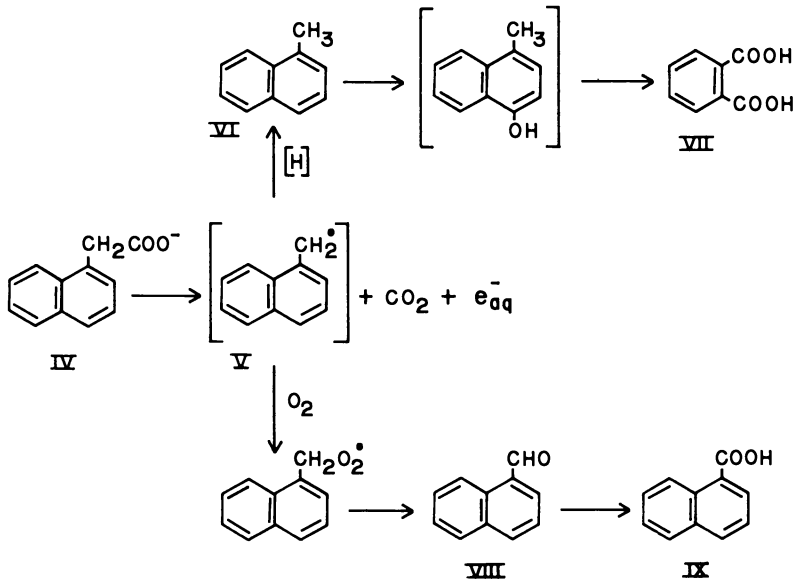

Figure 3. Photolysis of 1-naphthaleneacetic acid

observed 1-naphthylcarbinol and 1-naphthaldehyde (VIII). The stable end products from the sunlight photolysis of napthaleneacetic acid in aqueous solution were shown to be the 1-naphthoic (IX) and phthalic (VII) acids resulting from further oxidation of the sidechain and ring.

Sunlight irradiation of an aqueous solution or suspension of the anilide herbicide, propanil (3′,4′-dichloropropionanilide), provided propionic acid and 3,4-dichloroaniline (and other anilines) as major intermediate products (*38*). Propanil, otherwise quite stable in neutral aqueous solution in the dark, apparently underwent a light-energized hydrolysis.

4-CPA (4-chlorophenoxyacetic acid, X) and other phenoxy herbicides were photolyzed to produce the corresponding chlorinated phenol as a major product (*39, 40*) (Figure 4). Isolation of the formate ester of the phenol—*e.g.*, 4-chlorophenyl formate, XI—indicated the operation of an oxidative mechanism analogous to that proposed for naphthaleneacetic acid. The ester was converted to the phenol by either photohydrolysis or elimination of carbon monoxide. Here water could serve simultaneously as cage for the solvated electron, as reaction medium, and as a reagent.

Hydroxide Ions. The photolysis of propanil, 4-CPA, and other chlorinated aromatic pesticides in water also can generate phenols through the replacement of halogen by hydroxyl groups (*39, 41*). Oxygen does not seem to have an important part in this reaction, if it is involved at all, and observation that the replacement proceeds upon irradiation

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with sunlight suggests that energy sufficient to permit the abstraction of hydroxyl radicals from water by phenyl radicals is not expected. The nucleophilic displacement of chloride by hydroxide ion presents an alternative.

Photonucleophilic reactions have been investigated by a number of previous workers (*42*, *43*, *44*), but irradiations generally were accomplished with high-energy, mercury-arc light. However, 4-chlorophenol, a close relative and photolysis product of 4-CPA, was reported by Omura and Matsuura (*45*) to react with aqueous cyanide solutions in light of wavelengths greater than 300 nm to form 4-cyanophenol, in direct analogy to the hydroxylation of the herbicides. 2,4-Dichlorophenoxyacetic acid (2,4-D; XII) has been shown to undergo stepwise replacement of its chlorines (*39*) as well as photooxidation to form 1,2,4-benzenetriol which is rapidly converted in air to a polyquinoid humic acid (XIII) (Figure 5).

Pentachlorophenol (PCP, XIV) also could be considered to enter into the same photonucleophilic reaction in aqueous solution to give, among other products, tetrachlororesorcinol and chlorinated quinones (*46*). Further oxidation and condensation reactions then result in several unusual diphenyl ethers and aryloxyquinones (Figure 6). In alkaline solution, photonucleophilic attack of pentachlorophenoxide ion on an ortho chlorine of PCP could produce a chlorinated diphenyl ether which then goes on to form 1,2,3,4,6,7,8,9-octachlorodibenzo-*p*-dioxin (XV) (*40*).

The hydroxide ions of water also contribute to more common reactions whose rates are increased by exposure to light. The hydrolysis of esters and amides to the corresponding acids is an example (*38*, *47*, *48*).

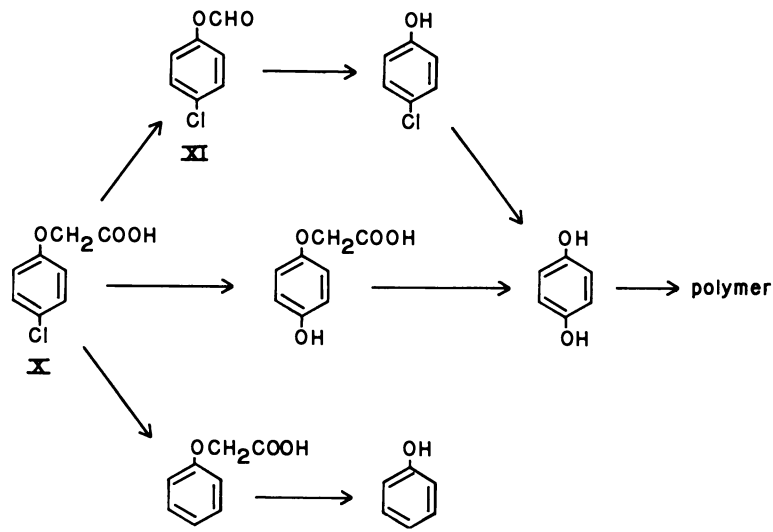

Figure 4. Photolysis of 4-chlorophenoxyacetic acid

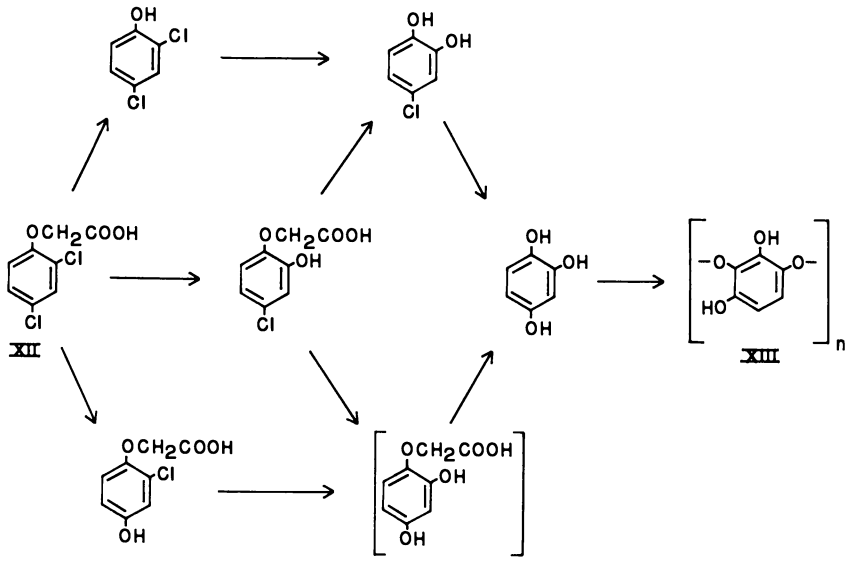

Figure 5. Photolysis of 2,4-D

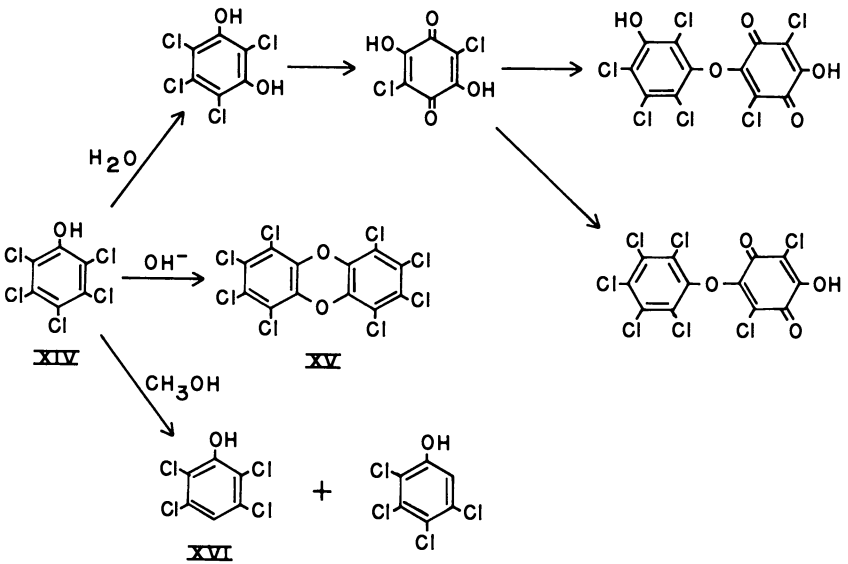

Figure 6. Photolysis of pentachlorophenol in water

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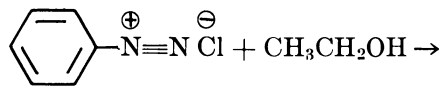
Reduction. In many instances the photooxidation or photonucleophilic substitution reactions of pesticides are accompanied by photoreduction—*i.e.*, the replacement of a substituent by a hydrogen atom. For example, gas chromatographic analysis of the products formed early in the photolysis of NAA in water (*37*) revealed significant amounts of 1-methylnaphthalene (VI); this compound which bears a reduced side chain was nearly the exclusive photolysis product when NAA was irradiated in the absence of oxygen (Figure 3).

The replacement of the ring halogen in 4-CPA with hydroxyl also was accompanied by photoreduction (replacement with hydrogen) when the growth regulator was irradiated in aqueous solution (*41*) (Figure 4), and in model experiments the ring chlorines of chlorophenylacetic acids related to fenac also were replaced by hydrogen (*36*). The isomeric chlorobenzoic acids were converted to the corresponding hydroxybenzoic acids upon irradiation as sodium salts in aqueous solution (*49*, *50*), but benzoic acid was always a persistent by-product. The source of hydrogen for these reactions became more apparent when the irradiations were conducted in methanol rather than in water. In the organic solvent it was demonstrated that benzoic acid formed exclusively and that polychlorinated benzoic acids were reduced stepwise with initial replacement predominantly at the position ortho to the carboxyl (*50*).



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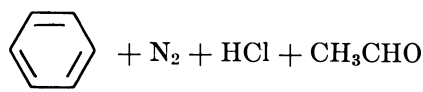

Plimmer (*50*) suggested that the observed reductions occur in solvents such as methanol as a result of an abstraction of hydrogen atoms from solvent by the phenyl radicals generated in homolytic cleavage of the phenyl–chlorine bond. While the energetics of this reaction seem feasible (Figure 1), another mechanism also is possible. An examination of known methods for the replacement of aromatic ring substituents by hydrogen recalled the classical use of alcohol to reduce benzenediazonium salts to the corresponding hydrocarbons (*51*) (Equation 3). This reaction, which takes place readily under mild conditions, has been shown to involve transfer of a hydride (H^-) ion from the α-carbon of the alcohol —*i.e.*, a nucleophilic displacement of the diazonium group by hydride.

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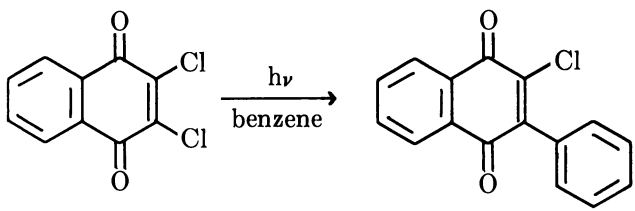
Consequently, the substitution of H for Cl in substances such as the herbicidal benzoic acids could be construed as another example of a photonucleophilic reaction.

Possible additional support for a photonucleophilic hydride transfer mechanism comes from further observations on the photolysis of PCP. When this compound was irradiated in methanol rather than in water, no oxidation or displacement of chlorine by hydroxyl was detected; instead, photoreduction produced primarily 2,3,5,6-tetrachlorophenol (XVI) together with a small proportion of what seemed to be the 2,3,4,5-tetrachloro isomer (Figure 6) (*52*). Hydrogen abstraction from solvent by polychlorophenyl radicals is expected to produce some of each of the three isomers representing replacement of an *o*-, *m*-, and *p*-chlorine, with the first two predominating because of doubled probability.

The operation of an ionic reduction mechanism certainly would not exclude pesticides from also taking part in the well-known free-radical abstraction of hydrogen atoms. Indeed, it seems inevitable that certain reactions such as the light-energized phenylation of the fungicide Phygon (XVI) (*53*) must take place exclusively *via* the free-radical route (Equation 4), and sensitized photooxidations and photoreductions in the presence of natural water constituents such as chlorophyll and riboflavin undoubtedly will be shown to be important in pesticide transformations in the environment.



(4)

While the availability of hydrogen atoms and/or hydride ions for photoreductions in organic solvents is apparent, the usual presence of reduced products from the photolysis of pesticides in aqueous media remains anomalous. Energy for the homolytic cleavage of water (about 118 kcal/mole) probably would not be derived from the sunlight spectrum, and the unlikely "backward" ionic dissociation of water to form hydride and hydroxonium (HO^+) ions never has been demonstrated.

One possible source of reducing power could be the normal organic component of water. Wangersky (*54*) reported that even triple-distilled, permanganate-treated water in the laboratory contains significant amounts of unidentified volatile organic constituents, and aliphatic hydrocarbons are generated photochemically in cell-free water (*55*). Another source could be the photolyzed pesticides themselves; the conversions which are

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accompanied by reduction have never been proved completely quantitative, and the extent of reduction always is small.

Still another possibility involves the solvated electrons mentioned previously. Most, if not all, of the demonstrated photoreduction reactions of pesticides in water take place with substances likely to form hydrated electrons—*e.g.*, NAA, fenac, the phenoxyacetic acids, and the chlorinated benzoic acids. Although they have measurable independent lifetimes, hydrated electrons eventually undergo reactions such as those shown in Equations 5, 6, 7, and 8 (*34*, *56*).

$$e^-_{aq} + H_3O^+_{aq} \rightarrow H\cdot + H_2O \quad (5)$$

$$e^-_{aq} + H_2O \rightarrow H\cdot + HO^-_{aq} \quad (6)$$

$$e^-_{aq} + H\cdot \rightarrow H^- \xrightarrow{H_2O} H_2 + HO^-_{aq} \quad (7)$$

$$e^-_{aq} + O_2 \rightarrow \cdot O\text{–}O^- \xrightarrow{H\cdot} HO_2^- \quad (8)$$

If such reactions were to be coupled with the photochemical generation of organic free radicals or excited molecular states before the H-atoms combined or hydride ions reacted with H_3O^+, the presence of photoreduced products would be explained. The generation of the powerfully nucleophilic peroxy radical-ions and hydroperoxide ions (Equation 8) also could be involved in instances of the oxidative displacement of halide from aromatic rings.

Conclusions

This discussion has reviewed a variety of photolytic reactions of pesticides as observed in laboratory irradiations conducted in distilled water (or other solvents) in the presence of suitable reagents—*e.g.*, oxygen, nucleophilic ions, reducing agents, etc. Although certainly no substitute for the real aquatic world, such conditions can represent natural waters far better than might have been expected. From Table I, it is apparent that both fresh and salt water contain adequate concentrations of oxygen, hydroxide ion, and organic sources of hydrogen to ensure reaction; these concentrations are virtually constant and represent a practically inexhaustible supply.

Even the potential reducing power of hydrated electrons is available. Swallow (*57*) has calculated that sunlight wavelengths below 325 nm could generate them in the oceans at a rate of as much as 3×10^{12} e^-_{aq}/gram/sec, equivalent to 10^{19} e/liter/hour or 0.1 mmole of reducing power per gallon for every daylight hour. For that matter, the hydrophobic surface films of both seawater and inland waters also would be expected to provide highly favorable conditions for photoreduction—relatively high

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concentrations of pesticides spread in a thin film of organic reductant under irradiation by unobstructed sunlight.

But does the photodecomposition of pesticides really take place in the aquatic world? Are light-energized transformations of pesticides environmentally important? Unfortunately, almost no incontrovertible evidence has been reported. The complex photolysis products of PCP found in rice-paddy water (*46*) (Figure 6) are sufficiently unusual to make a case, and the sunlight photolysis of diquat (6,7-dihydrodipyrido[1,2-a; 2′,1′-c]pyrazindiium chloride) on plants and in water is so rapid that again the presence of its photolysis products in field samples is to be expected (*58*). Few other examples are known.

Perhaps the lack of evidence should not be surprising. Unlike the controlled irradiations of the laboratory, environmental photodecomposition can be almost a continuous process in which low concentrations of pesticides are exposed to vast and renewable excesses of reagents. Except in unusual instances, we could expect to observe only terminal products—*i.e.*, polymers equivalent to natural humic acids, inorganic fragments such as phosphate and chloride ions, or simple organic substances such as benzoic acid which have long been recognized as normal environmental constituents. Furthermore, the photochemical intermediates leading to these products are highly reactive and could combine readily with environmental substrates. Such pesticide photodecomposition products would be indistinguishable from natural compounds by present techniques.

Photodecomposition, especially photooxidation, destabilizes pesticides in terms of further metabolic degradation by microorganisms. Many photolysis products are identical to the metabolites produced by living organisms. Does the DDD [1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane] detected in surface waters (*59*) represent the photoreduction of DDT or metabolism?

Still, all of the required conditions are present to make the photolysis of pesticides in natural waters inevitable. It seems that final proof of its extent and significance must await either more sophisticated methods for detecting and measuring transient chemical species or the actual application of photochemical principles to the practical-scale removal of pesticides from water.

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Chemical Hydrolysis and Oxidation of Parathion and Paraoxon in Aquatic Environments

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The kinetics of oxidation of parathion by Cl_2, ClO_2, and $KMnO_4$ was evaluated. Several products were detected: paraoxon, p-*nitrophenol, 2,4-dinitrophenol, 2-hydroxy-5-nitrobenzoic acid, and 2,2′-dihydroxy-5,5′-dinitrodiphenyl. Paraoxon and 2,4-dinitrophenol are significant because of their toxic properties. $KMnO_4$ was the oxidant for parathion. Preadjustment of the pH to alkaline values was essential to increase the rate of the reaction and to prevent accumulation of paraoxon.* p-*Nitrophenol is the major product of parathion–$KMnO_4$ reaction at pH 9.0. Oxidation of parathion by $KMnO_4$ under neutral or acidic conditions produces paraoxon and not* p-*nitrophenol. Large dosages of Cl_2 or ClO_2 are required for the oxidation of parathion at a pH value of 7.4 with accumulation of paraoxon. The efficiencies of Cl_2 and ClO_2 was increased by raising the pH from 7.4 to 9.0 and was decreased by lowering the pH from 7.4 to 3.1.*

Organic pesticides have been found in drinking, recreational, irrigational, fish, and shellfish waters and in the attendant sediments and bottom muds since 1945. The early evidence for this overall distribution was mainly obtained from physiological responses of aquatic organisms. From 1961 to date, however, direct analyses by gas–liquid chromatography and other techniques indicate that most natural waters and their equilibrium solid phases contain trace amounts of organic pesticides (*1, 2, 3, 4, 5, 6, 7, 8, 9*). Since pesticides enter water resources regardless of

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precautions in their use, public health and water treatment officials must have the knowledge and the plant facilities to remove them. Concentrations of these chemicals in public water supplies should conform to the appropriate quality criteria (*10*).

Technology for removing organic pesticides from water has not paced the problems that have resulted from the increased quantities used, new products and formulations placed on the markets, and new sources for their entry into the environment. Some organic pesticides are resistant or unaffected by conventional water and wastewater treatment practices (*11*). Also, many organic pesticides resist biological degradation in aquatic environments, hence they may persist for some time (*7, 12, 13, 14*).

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Methods to remove trace organic compounds of all types from aqueous solution (*15, 16, 17*) have been studied extensively. One was to deal with pesticide pollution of water supplies by using an oxidant for chemical degradation. Among the many chemical oxidants available, certain ones have shown that they reduce the concentration of organic contaminants—*e.g.*, ozone, chlorine dioxide, chlorine, the peroxides, and potassium permanganate (*18, 19, 20, 21*).

Under certain environmental conditions, different organic compounds will react differently to any particular chemical oxidant. No general statement is made concerning the oxidation of organic materials by a given oxidant. The interaction of environmental conditions, types and concentrations of organic compounds, and reaction time drastically affects the efficiency of chemical oxidation processes.

Kinetic studies may be used to evaluate the factors affecting the efficiency of removing trace organic pesticides from water by chemical oxidants. The rates of oxidative reactions and the optimum conditions under which the reactions occur are determined in the laboratory before applying them to pilot plant or field studies. Kinetic data also compares the efficiencies of different oxidants with the economy of different treatment processes.

Kinetic studies are also required to define more clearly the mechanisms inherent in the chemical reactions and the end products inherent in utilizing a specific chemical oxidant under different environmental conditions with various types of organic pesticides. The rates of accumulating and degrading any toxic intermediate oxidation product(s), formed during oxidation of the parent compound, are evaluated to determine the optimum conditions of removal.

Organophosphorus Insecticides vs. *Chlorinated Hydrocarbons*

Two general classes of insecticides, chlorinated hydrocarbons and organic phosphorus compounds, are used. The former have been recog-

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nized as having high residual activity and have often been blamed for fish mortality and other deteriorations of wildlife activity (*3, 22, 23, 24*). Recent concern in the United States is leading to decreased use of persistent chlorinated hydrocarbons—*e.g.*, DDT. The organic phosphorus insecticides are usually believed to have a low residual life in aqueous environments and are not particularly regarded as water contaminants. However, hydrolysis data (*25, 26*) indicate the stability and persistence of parathion and Diazinon. These compounds under natural water conditions are characterized by residual lives that vary between 3–6 months.

During the last decade parathion has been the most used organophosphorus insecticide. It has been proved to be valuable in crop protection (*27*). However, using this compound so much has also resulted in numerous accidental intoxications, and many have been lethal (*28*). In aquatic environments parathion hydrolyzes to yield *p*-nitrophenol or oxidizes to yield paraoxon (*25, 26*). Baker (*29*) has shown that substituted phenols affect the odor quality of drinking water. *p*-Nitrophenol may be chlorinated at a water treatment plant to produce an odorous product. The U. S. Public Health Service has adopted 1 μg/liter as a limit for phenolic compounds in water (*10*). Paraoxon is more toxic to insects and mammals than the parent compound parathion (*27*). The lethal dose (LD_{50}) for male white rats is 14 mg/kg for parathion while that determined for paraoxon is only 3 mg/kg (*30*). Bioassay studies with fathead minnows indicated a Median Tolerance Limit (TL_m) (96 hours) for parathion of 1.4 mg/liter and 0.3 mg/liter for paraoxon.

To evaluate the overall oxidation reaction of parathion, the kinetics of chemical hydrolysis of parathion and paraoxon first had to be investigated. Then the kinetics of chemical oxidation of *p*-nitrophenol, paraoxon, and parathion were studied with $KMnO_4$. This oxidant was chosen partially because of its accepted use to reduce tastes and odors caused by organic compounds (*31, 32, 33, 34*); potassium permanganate also is easily applied, and its reduction products are filtered from the finished water. Chlorine and chlorine dioxide were tested for their efficiencies in oxidizing parathion and paraoxon.

Chemical Hydrolysis of Parathion and Paraoxon

Experimental Procedure. Hydrolysis reactions were conducted in a thermostatically controlled water bath (±0.2°C) in diffused light. Into a one liter volumetric flask, an aliquot of the insecticide stock solution was pipetted. The solution was reduced to near dryness with a gentle stream of N_2 gas. Water (900 ml), distilled twice, was added to the flask and placed on a shaker for at least one hour to dissolve the insecticide completely. Into another flask, exactly 100 ml of the orthophosphate

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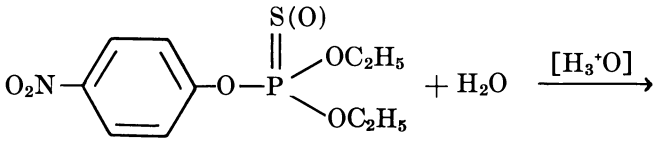
buffer solution (0.2*M*) was added. Both flasks were placed in the water bath to reach temperature equilibrium, after which the buffer solution was mixed with the insecticide solution. A stop watch was started at the initial pouring. At various time intervals, aliquots of the reaction solution were withdrawn to determine residual insecticide concentrations. These aliquots were immediately poured into a 250-ml separator to which was previously added enough acid ($\simeq 5N$ H_3PO_4) to adjust the pH to 1.0–1.5 before solvent extraction. This separator also contained a desired volume of ethyl acetate for extraction of the residual insecticide (1:1 solution–solvent). After 5 minutes of shaking, the lower aqueous layer was removed. The solvent layer was passed through a two-inch column containing approximately 5 grams of granular anhydrous sodium sulfate into a 50-ml volumetric flask. The separator and the column were washed three times with 2 ml of solvent. These washings were added to the eluate. The final volume of the extract was adjusted to 50 ml. A Microtek MT-200 gas chromatograph was used with a 10-mc Ni^{63} electron-capture detector at 250°C. Operating and chromatographic conditions are as follows:

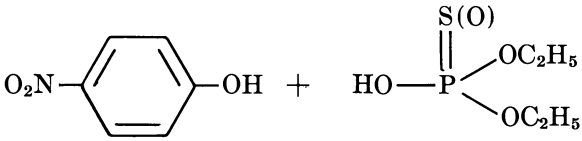
1. Liquid phase = 1.5% silicone (GE, XE-60) plus 1.5% silicone (DC, QF-1)
2. Solid support = gas-chrom Q, 80-100 mesh
3. Inlet temperature = 200°C
4. Column aging = 4 days at 240°C under normal flow rate.
5. Column temperature = 185°C
6. Column dimension = 4-feet glass, ¼-inch O.D., 40-mm I.D.
7. Detector temperature = 200°C
8. Flow rate of carrier gas (N_2) = 65 ml per minute
9. Recorder speed = 0.3 inch per minute

Figure 1 shows the isothermal separation of parathion and paraoxon. The insecticide concentration was calculated in each sample in the hydrolysis series from standard curve of peak area *vs.* concentration. Each experiment was repeated three times.

Results. The rates of hydrolysis of parathion and paraoxon were dependent upon pH:



Parathion or Paraoxon



(1)

p-Nitrophenol

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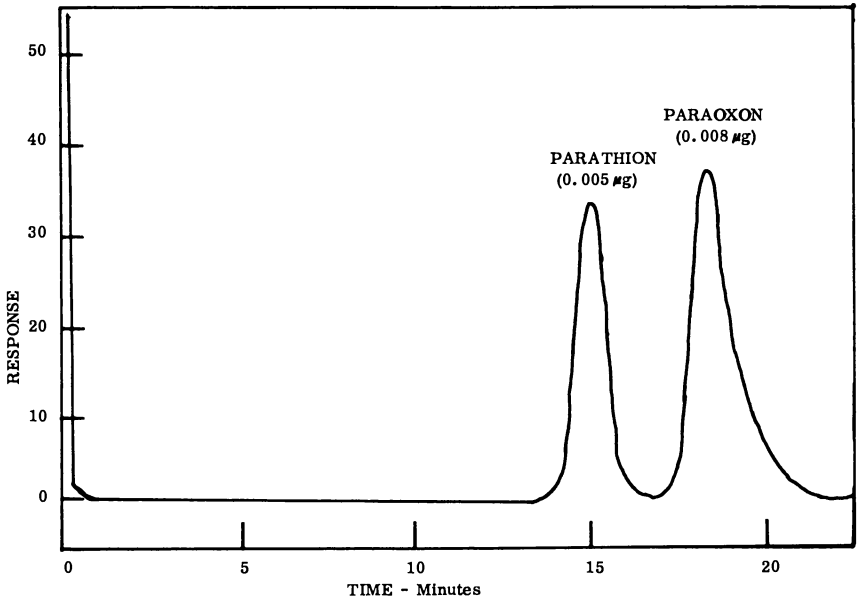

Figure 1. Isothermal separation of parathion and paraoxon

By the law of mass action, the velocity depends on the concentration of the two reactants:

$$-\frac{dC_{\text{Ins}}}{dt} = KC_{\text{Ins}}C_{\text{Cat}} \tag{2}$$

where, $C_{\text{Ins.}}$ is the residual concentration of insecticide (mole/liter) at time, t. $C_{\text{Cat.}}$ is the concentration of catalyst—*i.e.*, either $H^{+}{}_{3}O$ or OH^{-} in solution (mole/liter). Since the amount of catalyst used in the reaction is negligible, its concentration is constant. The velocity equation then takes the form:

$$-\frac{dC_{\text{Ins}}}{dt} = K_{ob}C_{\text{Ins}} \tag{3}$$

so that the rate is proportional to the residual concentration of the insecticide. Thus, the process should be first-order kinetics which was experimentally verified. Integrating Equation 3 yields:

$$\log C_{Ins} = \log C^{\circ}_{\text{Ins}} - \frac{K_{ob}}{2.303}t \tag{4}$$

where, $C^{\circ}_{\text{Ins.}}$ is the initial concentration of insecticide (mole/liter). K_{ob} is the observed rate constant (t^{-1}) and t is the time (hours).

Table I shows the data obtained upon hydrolyzing parathion at five pH values. The calculated first-order rate constants (Equation 4) at

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Table I. Effect of pH on the Rate

Sampling Time (hours)	*pH 3.1*		*pH 5.0*	
	C_t[b]	$K_{ob} \times 10^{-4}$[c]	C_t	$K_{ob} \times 10^{-4}$
0	11.50	—	11.50	—
2	—	—	—	—
4	—	—	—	—
6	—	—	—	—
8	—	—	—	—
12	—	—	—	—
24	—	—	—	—
48	11.41	1.96	11.39	1.94
96	11.31	1.72	11.30	1.90
144	11.18	1.64	11.20	1.86
192	11.14	1.68	11.09	1.92
240	11.07	1.60	11.00	1.84
480	10.66	1.59	10.55	1.80

[a] Average value of three experimental runs at the indicated pH.
[b] C_t is the parathion concentration at time t (mg/liter).

each sampling time at the indicated pH values are nearly constant. Since first-order kinetics are observed, relative rates are represented by the half life—*i.e.*, the time in which one-half of the original concentration has been hydrolyzed. Table II shows the hydrolysis rate constants and half-lives of parathion and paraoxon at five pH values and at 20°C.

The hydrolysis of parathion proceeds slightly faster under acidic or neutral conditions of pH. The reverse is observed under alkaline conditions where the hydrolysis of paraoxon is approximately 7.5 times faster than parathion at pH 9.0 and 5.5 times faster at pH 10.4.

The reaction order was confirmed by repeating the reaction at pH values of 3.1 and 10.4 using three insecticide concentrations. Equation 4

Table II. Rate Constants of Hydrolysis of Parathion and Paraoxon at 20°C (25)

pH	*Parathion*[a]		*Paraoxon*[b]	
	K_{ob} *(hr.$^{-1}$)*	$t_{1/2}$ *(hrs.)*	K_{ob} *(hr.$^{-1}$)*	$t_{1/2}$ *(hrs.)*
3.1	1.65×10^{-4}	4182	1.46×10^{-4}	4726
5.0	1.88×10^{-4}	3670	1.66×10^{-4}	4156
7.4	2.66×10^{-4}	2594	2.00×10^{-4}	3450
9.0	1.32×10^{-3}	523	9.87×10^{-3}	69.9
10.4	2.08×10^{-2}	33.2	1.15×10^{-1}	6.0

[a] Initial parathion concentration was $3.95 \times 10^{-5}M$.
[b] Initial paraoxon concentration was $4.81 \times 10^{-5}M$.

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Constant of Hydrolysis of Parathion[c]

pH 7.4		*pH 9.0*		*pH 10.4*	
C_t	$K_{ob} \times 10^{-4}$	C_t	$K_{ob} \times 10^{-3}$	C_t	$K_{ob} \times 10^{-2}$
11.50	—	11.50	—	11.50	—
—	—	—	—	11.04	2.06
—	—	—	—	10.63	1.98
—	—	—	—	10.07	2.21
—	—	—	—	9.75	2.07
—	—	—	—	9.00	2.04
—	—	11.14	1.34	6.90	2.13
11.36	2.68	10.81	1.30	—	—
11.22	2.62	10.07	1.39	—	—
11.06	2.72	9.54	1.30	—	—
10.92	2.70	9.01	1.27	—	—
10.79	2.66	—	—	—	—
10.15	2.60	—	—	—	—

[c] K_{ob} is the observed first order rate constant ($hour^{-1}$).

shows that the hydrolysis kinetics still obey the first-order expression by constant K_{ob} values (Table III).

Another objective of this study determined how temperature affects the rate constants, which resulted in calculating the activation energy of the hydrolysis reactions. Reactions were conducted in a thermostatically controlled water bath to ±0.2°C in diffused light. The rate constant, K_{ob}, was evaluated at 10°, 20°, 40°, and 60°C from the slope of a plot of log C_{Ins} as a function of time (Equation 4) for each experimental run. Table IV shows that the velocity of the reactions vary with temperature.

The Arrhenius equation was used to calculate the observed activation energy, E_{ob}, from a plot of the logarithm of the rate constant against the reciprocal of the absolute temperature:

Table III. Verification of Order of Hydrolysis Reaction[a]

		K_{ob}[b] *($hour^{-1}$)*	
Insecticide	*Insecticide Conc., M*	*pH 3.1*	*pH 10.4*
Parathion	7.90×10^{-5}	1.71×10^{-4}	.021
	3.95×10^{-5}	1.65×10^{-4}	.021
	1.97×10^{-5}	1.61×10^{-4}	.019
Paraoxon	9.62×10^{-5}	1.40×10^{-4}	.126
	4.81×10^{-5}	1.46×10^{-4}	.115
	2.41×10^{-5}	1.52×10^{-4}	.121

[a] Temperature = 20° ± 0.2°C.
[b] Average values of three experimental runs at the indicated pH.

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$$\log_{10} K_{ob} = \log_{10} A_{ob} - \frac{E_{ob}}{2.303\ RT} \quad (5)$$

The observed activation energy is calculated from the slope $-E_{ob}/2.303RT$ (Table V).

It seems that the reaction rate approximately doubled for each 10-degree temperature increase. The parent compound and its oxon are characterized by nearly equal activation energies at pH 3.1. However, under alkaline condition the E_{ob} value calculated for paraoxon is approximately 2.5 kcal mole^{-1} smaller than that calculated for the parent compound, parathion.

Table IV. Hydrolysis Rate Constants of Parathion[a] and Paraoxon[b] at Different Temperatures

Temp., °*C*	*pH 3.1*		*pH 9.0*	
	[c] K_{ob}, *hours*$^{-1}$	$t_{1/2}$, *hours*	K_{ob}, *hours*$^{-1}$	$t_{1/2}$, *hours*
Parathion				
10	5.20×10^{-5}	13327	5.41×10^{-4}	1281
20	1.65×10^{-4}	4182	1.32×10^{-3}	523
40	8.58×10^{-4}	808	5.47×10^{-3}	127
60	3.83×10^{-3}	181	2.65×10^{-2}	26.2
Paraoxon				
10	5.01×10^{-5}	13832	3.83×10^{-3}	181
20	1.46×10^{-4}	4726	9.87×10^{-3}	69.9
40	8.05×10^{-4}	861	3.81×10^{-2}	18.2
60	4.02×10^{-3}	172	1.19×10^{-1}	5.8

[a] Initial parathion concentration was $3.95 \times 10^{-5}M$.
[b] Initial paraoxon concentration was $4.81 \times 10^{-5}M$.
[c] Average values of three experimental runs at the indicated pH. Ionic strength was $0.02M$.

Ketelaar (*35*) reported an activation energy of 16.6 kcal mole^{-1} for parathion hydrolysis in 50% alcohol–water mixture $1N$ in sodium hydroxide. Ketelaar and Gersmann (*36*) studied the hydrolysis of parathion and paraoxon in 50% acetone–water mixture. The activation energies were reported for parathion's hydrolysis as 22.7 kcal mole^{-1} and for paraoxon as 20.5 kcal mole^{-1}. The calculated activation energies for parathion and paraoxon in buffered water (Table V) are much lower than those reported by the two investigators for the mixed solvent systems.

Potassium Permanganate Oxidative Kinetics

Experimental Procedure. Reactions were conducted in a thermostatically controlled chamber at 20° ± 0.2°C. in diffused light. To a one-liter volumetric flask was added the desired concentration of oxidant

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and buffer solution. The desired quantity of compound under investigation was added to another one-liter flask. After both flasks reached temperature equilibrium, the contents of each flask were simultaneously poured into the reaction vessel. A blank solution of oxidant was used under the same conditions. A stop watch was started at the initial pouring. After various time intervals aliquots of the reaction and blank solutions were withdrawn to determine the residual oxidant and pesticide concentrations. Each experiment was repeated three times. Concentrations of parathion and paraoxon were determined using a Microtek MT-200 gas chromatograph equipped with a 10-mc Ni^{63} electron-capture detector at 250°C. The operating and chromatographic conditions used for determining *p*-nitrophenol and its oxidative products, using a flame ionization detector, are described above. Two exceptions are inlet temperature of 225°C and detector parameters of 225°C, air at 0.6 CFM and hydrogen gas at 30 ml/min.

Figure 2 shows the isothermal separations of *p*-nitrophenol and two of its intermediate oxidative products, 2,4-dinitrophenol and 2-hydroxy-5-nitrobenzoic acid. A standard curve of peak area *vs.* concentration was constructed for *p*-nitrophenol and 2,4-dinitrophenol.

After determining the residual concentrations of the compound under investigation and its major intermediate oxidative products in the extract with gas–liquid chromatography techniques, the volume of each sample was reduced to 2 ml by flash evaporation. These concentrates were subjected to other chromatographic and spectrophotometric analyses to identify further any intermediate and final products of oxidation.

Results. REDOX REACTION MODELS OF PARATHION, PARAOXON, AND *p*-NITROPHENOL OXIDATIONS BY $KMnO_4$. Before proceeding to the kinetic studies, computations and experiments were conducted to determine the fate of the reactants under acidic and alkaline conditions. Assumptions were made concerning the oxidation states of the various elements:

(a) MnO_4^- is reduced to MnO_2 and not to Mn^{2+},
(b) carbon is oxidized to CO_2,
(c) the aromatic nitro group is oxidized to NO_3^-, and
(d) equilibrium is obtained between the reactants and the products.

Steward (*37*) reported that many organic compounds are degraded to CO_2 by potassium permanganate oxidation although in basic solution oxalate is isolated frequently as a major reaction product. This is because oxalate suffers further rapid oxidation only in acid solution. Assuming that organic phosphorus and sulfur groups become PO_4^{-3} and SO_4^{-2}, the following hypothetical redox reactions represent the degradation of

Table V. Activation Energies of the Hydrolysis Reactions

Compound	*pH*	E_{ob}, *kcal. mole*$^{-1}$
Parathion	3.1	16.4
	9.0	14.5
Paraoxon	3.1	16.4
	9.0	12.0

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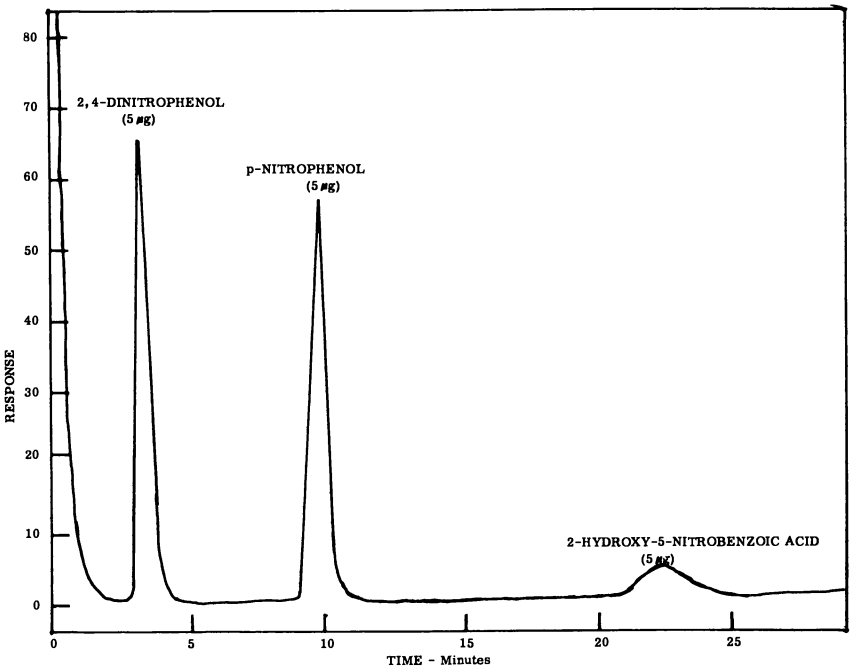

Figure 2. Isothermal separation of p-*nitrophenol and some intermediate oxidation products*

parathion, paraoxon, and *p*-nitrophenol under acidic and alkaline conditions:

Acid Medium

$$C_{10}H_{14}O_5NSP + 20\ MnO_4^- + 14\ H^+ = 20\ MnO_2 + 10\ CO_2 + SO_4^{-2} + NO_3^- + PO_4^{-3} + 14\ H_2O \quad (6)$$

Parathion

$$3C_{10}H_{14}O_6NP + 52\ MnO_4^- + 40\ H^+ = 52\ MnO_2 + 30\ CO_2 + 3\ NO_3^- + 3\ PO_4^{-3} + 41\ H_2O \quad (7)$$

Paraoxon

$$3C_6H_5NO_3 + 28\ MnO_4^- + 25\ H^+ = 28\ MnO_2 + 18\ CO_2 + 3\ NO_3^- + 20\ H_2O \quad (8)$$

p-Nitrophenol

Alkaline Medium

$$3C_{10}H_{14}O_5NSP + 50\ MnO_4^- = 50\ MnO_2 + 15\ C_2O_4^{-2} + 3\ NO_3^- + 3\ SO_4^{-2} + 3\ PO_4^{-3} + 2\ OH^- + 20\ H_2O \quad (9)$$

Parathion

$$C_{10}H_{14}O_6NP + 14\ MnO_4^- = 14\ MnO_2 + 5\ C_2O_4^{-2} + NO_3^- + PO_4^{-3} + 7\ H_2O \quad (10)$$

Paraoxon

$$3C_6H_5NO_3 + 22\ MnO_4^- = 22\ MnO_2 + 9\ C_2O_4^{-2} + 3\ NO_3^- + OH^- + 7\ H_2O \quad (11)$$

p-Nitrophenol

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The oxidations of parathion ($3.95 \times 10^{-6}M$), paraoxon ($4.81 \times 10^{-6}M$), and *p*-nitrophenol ($7.18 \times 10^{-5}M$) were conducted by adding excess $KMnO_4$ ($2.0 \times 10^{-3}M$). These reactions were conducted under acidic and alkaline conditions (pH 3.1 and 9.0). After contact times of 2–5 days, the amount of $KMnO_4$ used in oxidation and the oxidizing power of the precipitated MnO_2, expressed as the iodine liberated, were determined separately by adding acidified KI. The ratio:

$$\frac{\text{Iodine value of precipitated oxides}}{\text{Iodine value of complete sample}} = \frac{T' - T_\infty}{T_0 - T_\infty} \qquad (12)$$

should be equal to 0.4 if MnO_4^- is reduced to MnO_2 and should be equal to zero if it is reduced to Mn^{2+} ion. Also in this equation T_∞ is the amount in milliliters of thiosulfate required to titrate the test solution after filtering MnO_2. T_0 is the amount of thiosulfate required to titrate $KMnO_4$ blank solution, and T' is the amount of thiosulfate needed to titrate the test solution without filtering MnO_2.

The experimental values of the ratio are given in Table VI. From the same experiment the number of moles of $KMnO_4$ required to oxidize completely 1 mole of compound (parathion, paraoxon, or *p*-nitrophenol) was calculated (Table VI). The observed experimental data agree well with the hypothetical reactions proposed to oxidize completely parathion, paraoxon, and *p*-nitrophenol (Equations 6, 7, 8, 9, 10, 11).

Table VI. Potassium Permanganate Consumed by the Oxidation of Parathion, Paraoxon, and *p*-Nitrophenol[a] (25)

Compound	*pH*	*Contact Time, hours*	*Ratio*[b]	*Mole MnO_4^-/Mole Compound*	
				Experimental	*Calculated*[c]
Parathion	3.1	120	0.386	19.48	20.00
Paraoxon	3.1	120	0.364	16.69	17.33
p-Nitrophenol	3.1	96	0.404	9.10	9.33
Parathion	9.0	48	0.392	17.08	16.66
Paraoxon	9.0	48	0.403	14.17	14.00
p-Nitrophenol	9.0	96	0.367	7.62	7.33

[a] Temperature = 20° ± 0.2°C.
[b] Ratio determined using Equation 12.
[c] Ratio calculated from Equations 6, 7, 8, 9, 10, 11.

$KMnO_4$ OXIDATION OF PARATHION, PARAOXON, AND *p*-NITROPHENOL. The rates of oxidation of parathion, paraoxon, or *p*-nitrophenol by potassium permanganate depended upon pH. The oxidation rate is proportional to the product of the residual concentrations of both reactants. Determining the reaction order was done by fitting the data into the different kinetic equations. Regardless of the complex stoichiometry,

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Table VII. Oxidation of Parathion

Sampling Time (Min.)	*pH 3.1*			*pH 5.0*		
	$(KMnO_4)_t$ [b]	$(P)_t$ [c]	K_{ob} [d]	$(KMnO_4)_t$	$(P)_t$	K_{ob}
0	80.0	3.95	—	80.0	3.95	—
15	—	—	—	—	—	—
30	76.8	3.75	.415	78.0	3.83	.205
60	74.8	3.62	.420	76.9	3.76	.198
120	71.9	3.40	.409	75.1	3.63	.210
180	—	—	—	—	—	—
240	66.6	3.06	.388	71.55	3.41	.190
600	55.15	2.32	.354	64.6	2.95	.172
1200	35.75	1.32	.320	57.0	2.43	.161
2640	24.75	0.67	.300	50.0	1.86	.142
4080	—	—	—	—	—	—

[a] Temp. = 20° ± 0.2°C; ionic strength was 0.02*M*; average of three experimental runs.

[b] $(KMnO_4)_t$ = Residual concentration of $KMnO_4$ at time t in $M \times 10^{+5}$.

$KMnO_4$ oxidizes parathion, paraoxon, and *p*-nitrophenol and follows a second-order kinetic equation:

$$\frac{2.303}{C^\circ_{\text{Oxid}} - C^\circ_{\text{Compd}}} \log \frac{C^\circ_{\text{Comp}} C_{\text{Oxid}}}{C^\circ_{\text{Oxid}} C_{\text{Compd}}} = K_{ob}t \qquad (13)$$

where, K_{ob} is the observed rate constant of the reaction (liter mole^{-1} min.$^{-1}$), t is the time in minutes, C°_{Oxid} is the initial molar concentration of $KMnO_4$, C_{Oxid} is the residual molar concentration of permanganate at time t, C°_{Compd} is the initial molar concentration of compound under investigation, and C_{Compd} is the residual molar concentration of compound under investigation at time t.

The second-order equation deviates as the reaction proceeds over a long period of time. This deviation means that intermediate products

Table VIII. Verification of Order of Parathion–$KMnO_4$ Reactions [a]

pH	K_{ob} *Values (liter mole^{-1} min^{-1})*		
	Original Conc.	*Ten-fold Dilution*	*Hundred-fold Dilution*
3.1	.415	.403	.392
5.0	.205	.220	.190
7.4	.088	.086	.082
9.0	7.84	7.92	7.08

[a] Average values of three experimental runs; Temperature = 20° ± 0.2°C; Ionic strength was 0.02*M*.

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by $KMnO_4$—Effect of pH[c]

pH 7.4			*pH 9.0*		
$(KMnO_4)_t$	$(P)_t$	K_{ob}	$(KMnO_4)_t$	$(P)_t$	K_{ob}
80.0	3.95	—	80.0	3.95	—
—	—	—	73.4	3.32	7.79
78.8	3.88	.088	68.8	2.84	7.84
—	—	—	61.0	2.11	7.79
77.1	3.78	.086	47.25	1.15	7.70
—	—	—	36.8	0.65	7.53
75.95	3.69	.080	26.65	0.35	7.21
73.4	3.49	.079	—	—	—
69.3	3.20	.074	—	—	—
63.35	2.71	.071	—	—	—
59.15	2.37	.067	—	—	—

[c] $(P)_t$ = Residual Parathion concentration at time t in $M \times 10^{+5}$.
[d] K_{ob} = Observed rate constant in Liter Mole^{-1} Min.$^{-1}$.

in the reaction are produced which are characterized by a slower degradation rate and will affect the observed rate constant of oxidation. To compare the efficiency of potassium permanganate for oxidizing parathion and its intermediate oxidation products, paraoxon and *p*-nitrophenol, under different environmental conditions, the observed rate constants determined after 30 minutes of reaction were used. This avoided complications resulting from interference by intermediate products formed during the oxidation of the parent compound.

Table VII shows the data obtained for parathion–$KMnO_4$ oxidations at different pH values. The observed rate constants in Table VII were obtained with initial concentrations of $8 \times 10^{-4}M$ $KMnO_4$ and $3.95 \times 10^{-5}M$ parathion. Ten- and hundred-fold dilutions of these concentrations obey the same rate expression (Equation 13), as shown by constant observed rate constants in Table VIII. Table VII shows that the observed rate constant of the parathion–$KMnO_4$ varies with pH. The rate constant of the oxidation reaction decreases as the pH value of the solution was increased from 3.1 to 7.4. A sharp increase in the oxidation rate constant occurred as the pH value was further increased from 7.4 to 9.0. For paraoxon–$KMnO_4$ oxidations, the overall rate of reaction at pH 9.0 is approximately 4,000 times faster compared with that determined at pH 7.4 (Table IX). However, the *p*-nitrophenol oxidation reaction proceeds faster under acidic, rather than alkaline conditions (Table X).

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Effectiveness of Chlorine and Chlorine Dioxide in the Oxidation of Parathion and Paraoxon

Since most water treatment plants practice pre- and post-chlorination, an attempt was made to determine the influence of various doses of chlorine on parathion and paraoxon and to study how pH affects the chlorine–insecticide oxidation reaction. Chlorine dioxide was tested under the same environmental conditions as chlorine to compare their oxidative capacities.

Effect of Oxidant Concentration. One-liter solutions of approximately 1 mg/liter of either parathion or paraoxon in a 0.02*M* phosphate buffer at pH 7.4 were treated with increasing amounts of Cl_2 or ClO_2 at 20°C. The residual concentrations of the insecticides and the oxidant were determined after a contact time of 60 minutes.

Parathion and paraoxon were oxidized in proportion to the amount of oxidant as seen in Figure 3. The required amounts of Cl_2 and ClO_2 required to oxidize completely 0.982 mg/liter of parathion were graphically determined to be 22.25 mg/liter and 20.0 mg/liter, respectively.

Table IX. Oxidation of Paraoxon

Sampling Time (Min.)	*pH 3.1*			*pH 5.0*		
	$(KMnO_4)_t$[b]	$(PO)_t$[c]	K_{ob}[d]	$(KMnO_4)_t$	$(PO)_t$	K_{ob}
0	80.0	4.81	—	80.0	4.81	—
15	—	—	—	—	—	—
30	78.9	4.74	.083	79.3	4.76	.032
60	—	—	—	—	—	—
90	—	—	—	—	—	—
120	—	—	—	—	—	—
150	—	—	—	—	—	—
180	—	—	—	—	—	—
240	76.85	4.55	.085	78.5	4.69	.032
600	74.2	4.31	.081	77.1	4.57	.035
1200	70.35	3.92	.086	74.9	4.38	.031
2640	64.7	3.30	.083	72.2	4.09	.030
4080	60.8	2.85	.081	70.05	3.80	.033
5520	57.8	2.52	.078	67.85	3.62	.029
6960	—	—	—	—	—	—
Graphical value of K_{ob}			.083			.032

[a] Temp. = 20° ± 0.2°C; ionic strength was 0.02*M*; average values of three experimental runs.
[b] $(KMnO_4)_t$ = Residual concentration of $KMnO_4$ at time t in $M \times 10^{-5}$.

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Using gas–liquid and thin layer chromatography techniques, the only intermediate product detected and identified during the oxidation of parathion with Cl_2 or ClO_2 was paraoxon. Paraoxon accumulates in the system from the parathion–Cl_2 or parathion–ClO_2 reactions, but not in a stoichiometric amount. The amounts of Cl_2 and ClO_2 required to oxidize completely 1.012 mg/liter paraoxon were determined graphically to be equal to 38.95 mg/liter and 44.50 mg/liter, respectively, within a contact time of 60 minutes.

Effect of pH. The effect of pH on the Cl_2 and ClO_2 oxidations of parathion and paraoxon was studied. Buffered solutions of either compound at pH values from 3.1–9.0 were treated with a fixed concentration of oxidant. The residual concentrations of the reactants were determined after a contact time of 60 minutes. The results are plotted in Figure 4. Generally, as the pH of the solution was increased, the oxidation rates of both compounds using Cl_2 or ClO_2 increased markedly. Paraoxon accumulates during the oxidation of parathion by Cl_2 or ClO_2 in the pH range 3.1–7.4. However, at pH 9.0, only trace amounts of paraoxon and *p*-nitrophenol were detected.

by $KMnO_4$—Effect of pH[a]

pH 7.4			*pH 9.0*		
$(KMnO_4)_t$	$(PO)_t$	K_{ob}	$(KMnO_4)_t$	$(PO)_t$	K_{ob}
80.0	4.81	—	80.00	4.81	—
—	—	—	71.53	3.54	17.4
—	—	—	64.65	2.64	17.2
—	—	—	52.76	1.47	17.0
—	—	—	41.98	0.80	16.9
—	—	—	38.42	0.52	16.5
—	—	—	35.10	0.33	16.4
—	—	—	32.92	0.22	16.3
79.25	4.76	.004	—	—	—
77.9	4.67	.005	—	—	—
76.5	4.58	.005	—	—	—
74.8	4.46	.005	—	—	—
72.1	4.27	.005	—	—	—
69.6	4.11	.004	—	—	—
68.2	4.01	.004	—	—	—
		.0046			17.0

[c] $(PO)_t$ = Residual Paraoxon concentration at time t in $M \times 10^{+5}$.
[d] K_{ob} = Observed rate constant (Liter Mole^{-1} Min.$^{-1}$).

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Table X. Rate Constants for the Oxidation of Parathion, Paraoxon, and *p*-Nitrophenol by $KMnO_4$ (25)

System	*Rate Constant (liter mole^{-1} min^{-1})*[a]			
	pH 3.1	*pH 5.0*	*pH 7.4*	*pH 9.0*
Parathion[b]	0.415	0.205	0.088	7.84
Paraoxon[c]	0.083	0.032	0.004	17.0
p-Nitrophenol[d]	18.6	9.24	8.64	4.14

[a] Temp. = 20° ± 0.2°C; ionic strength was 0.02*M*; rate constants are average values of three experimental runs.

[b] Initial concentration of parathion was $3.95 \times 10^{-5}M$, and $KMnO_4$ was $8.0 \times 10^{-4}M$.

[c] Initial concentration of paraoxon was $4.81 \times 10^{-5}M$, and $KMnO_4$ was $8.0 \times 10^{-4}M$.

[d] Initial concentration of *p*-nitrophenol was $7.18 \times 10^{-4}M$, and $KMnO_4$ was $2.0 \times 10^{-3}M$.

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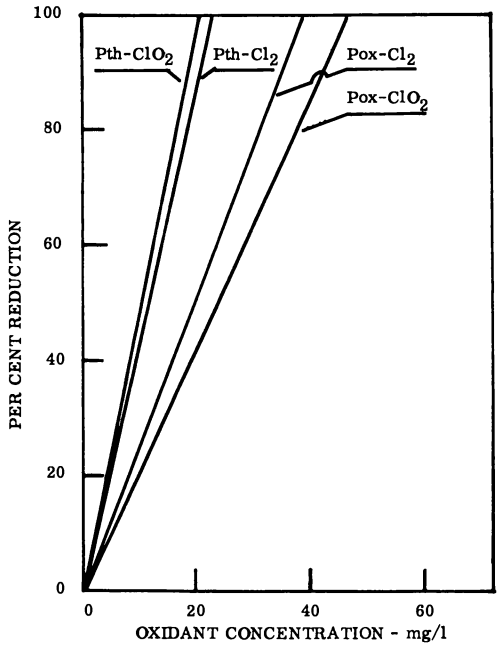

Figure 3. Oxidation of parathion and paraoxon by chlorine and chlorine dioxide

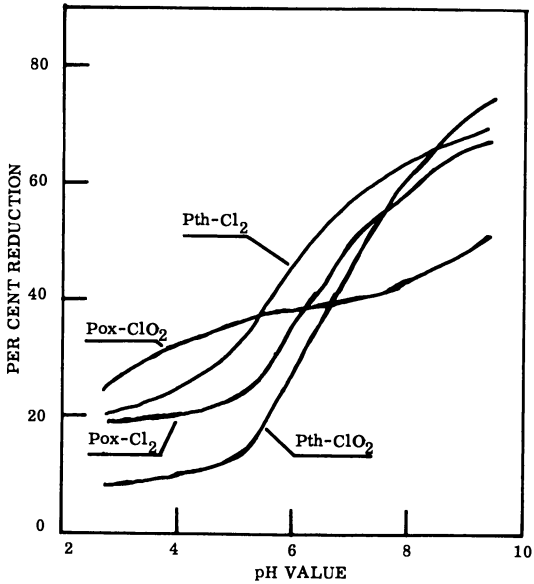

Figure 4. Effect of pH on the oxidation of parathion and paraoxon by chlorine and chlorine dioxide

Discussion

Potassium permanganate is a more effective oxidant of parathion or paraoxon in an alkaline medium than in an acid medium. The rate of reaction of parathion–$KMnO_4$ at pH 9.0 is about 19 times faster than at pH 3.1 and is about 89 times faster than at pH 7.4. pH affects the rates at which paraoxon–$KMnO_4$ reactions proceed much more than the parathion–$KMnO_4$ reaction rates. At a pH value of 9.0, the oxidation of paraoxon proceeds approximately 205 times faster than at pH 3.1 and about 4250 times faster than at pH 7.4.

From the data in Table X, it seems that $KMnO_4$ is a more effective oxidizing agent for *p*-nitrophenol under acidic than under neutral or alkaline conditions. The oxidative reaction rate decreases as the pH increases. The reaction rate at pH 3.1 is approximately 4.5 times as fast as that at pH 9.0.

Paraoxon is not the final oxidation product of parathion oxidized by $KMnO_4$ as reported by Robeck *et al.* (*21*) and Schiavone and Torrado (*38*). By comparing overall rates of paraoxon and *p*-nitrophenol oxidation with the rate determined for parathion, it is possible to explain the differences in their accumulation rates during the parathion oxidation under acidic, neutral, and alkaline conditions. Table X summarizes the rate constants of oxidations of the three compounds, parathion, paraoxon,

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and *p*-nitrophenol. The overall oxidation rates of parathion are faster than those of paraoxon under acidic or neutral conditions. The parathion–$KMnO_4$ reaction proceeds with a rate 5 times faster than the paraoxon–$KMnO_4$ reaction at pH 3.1 and about 22 times faster at pH 7.4. This may explain why paraoxon accumulates in the system as the parathion–$KMnO_4$ oxidation reaction proceeds either under acid or neutral conditions. The reverse is true under an alkaline condition (pH 9.0) where trace concentrations of the paraoxon are detected in the system. This last point is important because paraoxon is at least five times more toxic to fish and animals compared with the parent compound, parathion.

Theoretically, *p*-nitrophenol accumulates in the system after hydrolyzing or oxidizing parathion and paraoxon. However, the hydrolysis rates of parathion and paraoxon are slow under acid or neutral conditions (Table II). The *p*-nitrophenol that might be formed while oxidixing parathion would come from the paraoxon–$KMnO_4$ oxidation reaction. At a pH value of 3.1, the rate of *p*-nitrophenol–$KMnO_4$ oxidation is approximately 45 times faster than parathion and 225 times faster than paraoxon. Consequently, *p*-nitrophenol formed either from the hydrolysis or oxidation would immediately be oxidized without accumulating in the system. As the pH value of the system was increased from 3.1–9.0, the overall oxidation rate of *p*-nitrophenol decreased appreciably, while the overall rates of oxidation of parathion and paraoxon increased. Thus, at pH 9.0 the overall oxidation rate of parathion by $KMnO_4$ is about twice as fast as that determined for *p*-nitrophenol and $KMnO_4$. Also at pH 9.0, the paraoxon–$KMnO_4$ reaction proceeds with a rate approximately 4 times faster than the *p*-nitrophenol reaction. Consequently, *p*-nitrophenol coming either from the hydrolysis or oxidation of parathion or paraoxon would accumulate in the system. The oxidation of parathion and paraoxon at pH 9.0 is nearly complete within two hours, which is a short period of time compared with the hydrolytic half-lives of the two compounds at the same pH value (522 hours for parathion and 69 hours for paraoxon). Therefore, most of the *p*-nitrophenol accumulating in the system comes from the oxidative step and not from the hydrolytic step. Figure 5 represents the suggested mechanism of oxidation of parathion by $KMnO_4$.

Robeck *et al.* (*21*) studied the efficiency of Cl_2 in removing residual parathion from river water. A parathion formulation of 42.4% active ingredient was used. River water dosed with 10 μg/liter parathion was altered by 3 mg/liter of Cl_2 (15% reduction in parathion) and was altered more by 7 mg/liter of Cl_2 (97% reduction in parathion), over a contact time of 90 minutes.

From the data presented in Figure 3, it seems that 22.25 mg/liter Cl_2 are required to oxidize completely 1 mg/liter of parathion (99.5%

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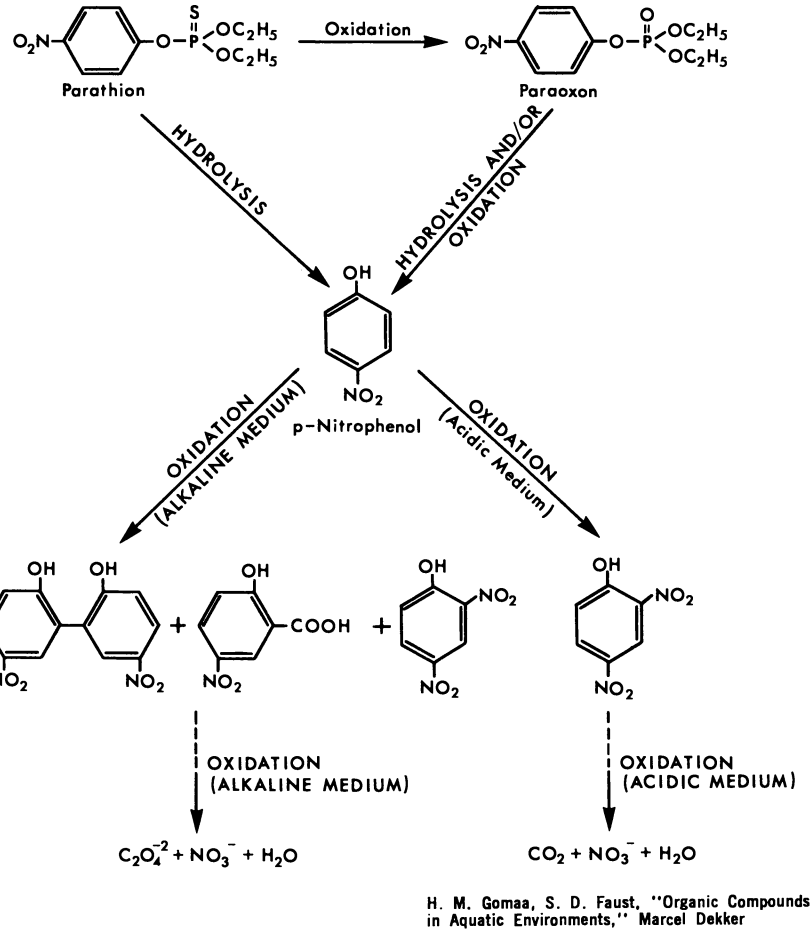

Figure 5. Suggested mechanism for parathion–$KMnO_4$ oxidative system (25)

active ingredient) over a contact time of 60 minutes in buffered distilled water.

The large difference between the optimum dose of Cl_2 determined in this study and that reported by Robeck *et al.* (*21*) may result from the amount of Cl_2 consumed in oxidizing formulating solvents, plus the chlorine demand of the river water which was characterized by a chemical oxygen demand of 5–35 mg/liter and a carbon–chloroform extract of 185–1320 μg/liter.

The optimum dosage determined for ClO_2 was nearly equal to that of Cl_2. Paraoxon was the only intermediate oxidative product formed during the oxidation of parathion by Cl_2 or ClO_2 at pH 7.4. Paraoxon is more resistant to oxidation by Cl_2 or ClO_2 as compared with the parent

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compound, parathion. The optimum concentrations of Cl_2 or ClO_2 required to oxidize completely approximately 1 mg/liter of paraoxon are almost double those determined for parathion under the same experimental conditions.

It seems that the pH of the reaction solution is important. Generally, the oxidation of either parathion or paraoxon by Cl_2 or ClO_2 proceeds much faster under alkaline conditions when compared with acid or neutral conditions. Trace concentrations of paraoxon and *p*-nitrophenol were detected and identified from the alkaline oxidation of parathion by Cl_2 and ClO_2. Still any *p*-nitrophenol which is formed might then be chlorinated (*39*) and thus affect the organoleptic properties of the treated water.

During parathion's oxidation by $KMnO_4$, several intermediate compounds were detected and identified. Besides paraoxon and *p*-nitrophenol, three intermediates were identified: 2,4-dinitrophenol, 2-hydroxy-5-nitrobenzoic acid, and 2,2′-dihydroxy-5,5′-dinitrodiphenyl (Figure 5). These compounds arise from inappropriate environmental conditions or from insufficient reaction times. The environmental hazards of these compounds are largely unknown, but they do represent the products of an incomplete reaction. The experimental details of these reactions are published elsewhere (*40*).

Water chemists face the problem that trace concentrations of organic pesticides are usually present in natural waters along with different groups of organic constituents that compete for the oxidant added to the water. Therefore, separating and identifying those constituents are essential steps to obtain their rates of degradation using a particular oxidant. However, chemical kinetic data collected in the laboratory help the water chemist to determine the best conditions for the rate of a specific reaction to be enhanced while other oxidation reactions of secondary importance are retarded.

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11

Studies of The Persistence of Some Carbamate Insecticides in The Aquatic Environment

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The various environmental factors that may influence the persistence of some carbamate insecticides in natural waters were investigated. The compounds studied were the monomethylcarbamate esters, Sevin and baygon, and the dimethylcarbamate esters, pyrolan and dimetilan. The hydrolysis of these compounds with various hydroxyl ion concentrations revealed that they were unstable under alkaline conditions. The adsorption of the four insecticides on the clay minerals, kaolinite and bentonite, was also investigated, as was the biodegradability of these carbamate insecticides. Sevin and baygon were amenable to biological degradation in natural surface waters. Attempts to obtain an acclimitized flora capable of utilizing pyrolan and dimetilan were unsuccessful. The hydrolysis products of both compounds, however, were readily used by microorganisms, indicating that the hydrolysis step is the limiting factor in their biodegradation in natural waters.

Developing the resistance of certain insect species to chlorinated hydrocarbon insecticides led to the recent discovery of the *N*-alkyl and *N,N*-dialkyl carbamate esters as useful broad spectrum insecticides. The best known insecticide of this class is Sevin (1-naphthyl-*N*-methylcarbamate) which is one of the most used insecticides. In Egypt Sevin has been extensively used to control cotton pests—*e.g.*, pink boll worm, boll weevil, and the cotton leaf worm—and also to control several other

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agricultural pests. Little information is known about the fate and persistence of carbamate insecticides in natural waters.

Here some of the chemical, physical, and biological factors that may influence the persistence of carbamate insecticides were studied. The physical and chemical factors studied included the hydrolysis rate, the effect of suspended solids in water, and the effect of ultraviolet light on the stability of these compounds. The compounds investigated were: Sevin (1-naphthyl-*N*-methylcarbamate), baygon (2-isopropoxyphenyl-*N*-methylcarbamate), pyrolan (1-phenyl-3-methyl-5-pyrazolyl-dimethylcarbamate), and dimetilan (2-dimethylcarbamyl-3-methyl-5-pyrazolyl-dimethylcarbamate).

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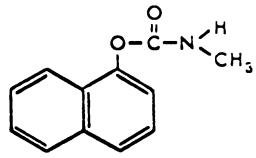
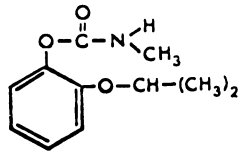
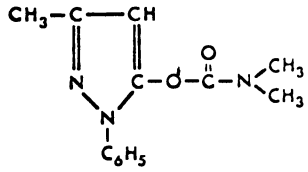
Sevin



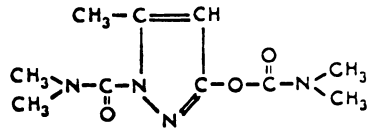
baygon



pyrolan



dimetilan



Hydrolysis of the Carbamate Insecticides

The hydrolysis rates of the four carbamate insecticides with different hydroxyl ion concentrations and solutions of different pH values were studied. The progress of the hydrolysis reaction was followed by estimating the amount of the corresponding hydroxy compound formed after measured time intervals. For Sevin and baygon the increase in the amount of hydrolysis product, 1-naphthol and *o*-isopropoxyphenol, respectively, was measured by determining the increase in light absorption at the wavelength of maximum absorbance of each phenol. The fact that phenolic compounds undergo bathochromic shift of the wavelength maximum in alkaline solutions because of the forming of phenolates was useful. Therefore, the hydrolysis of Sevin and baygon in strongly alkaline media was followed by measuring the increase in absorption at 320 and 290 mμ, respectively. For pyrolan and dimetilan the heterocyclic enols resulting from the hydrolysis were colorimetrically measured by the 4-aminoantipyrine method (*1*).

Kinetic Procedure. All solutions were brought to the desired temperatures by incubating in a water bath ($\pm$0.5°C) before mixing. Carbon dioxide, free distilled water, and sodium hydroxide solutions were always used. Buffer solutions covering the range between pH 4.0–10.0 were prepared by diluting 0.1 *M* standard phosphate buffer (a mixture of monobasic potassium phosphate and dibasic sodium phosphate) to obtain 0.01 *M* working solutions. The resultant solutions were titrated to the final desired pH with sodium hydroxide or phosphoric acid solutions.

Sevin and baygon were hydrolyzed in sodium hydroxide solutions according to the following procedure:

A sodium hydroxide solution of the desired hydroxyl ion concentration was prepared. Five millimeters of the alkaline solution were put into a 2 cm cell; then a methanolic solution of the insecticide was used to make a final concentration of about 0.12 mmole/liter. The concentration of methanol was about 2%. The solutions were immediately mixed by inverting the cell, and the change in absorbance was recorded on Carl Zeiss–Jena spectrophotometer using sodium hydroxide solution as a blank. The temperature in the cell was kept constant during the run. The release of 1-naphthol was followed at λ 320 mμ and that of *O*-isopropoxyphenol at λ 290 mμ.

For kinetic runs at low temperatures or in buffered solutions, the 4-aminoantipyrine method was used to analyze the released phenols by following the same procedure described for pyrolan and dimetilan.

By plotting the log (% residual ester) *vs.* time, a straight line was obtained corresponding to the pseudo first order rate constant. Concurrently by multiplying the slope of the line by -2.303, the rate constant, *k*, was obtained.

The half-life time was calculated according to the following equation:

$$t_{0.5} = \frac{0.693}{k_1}$$

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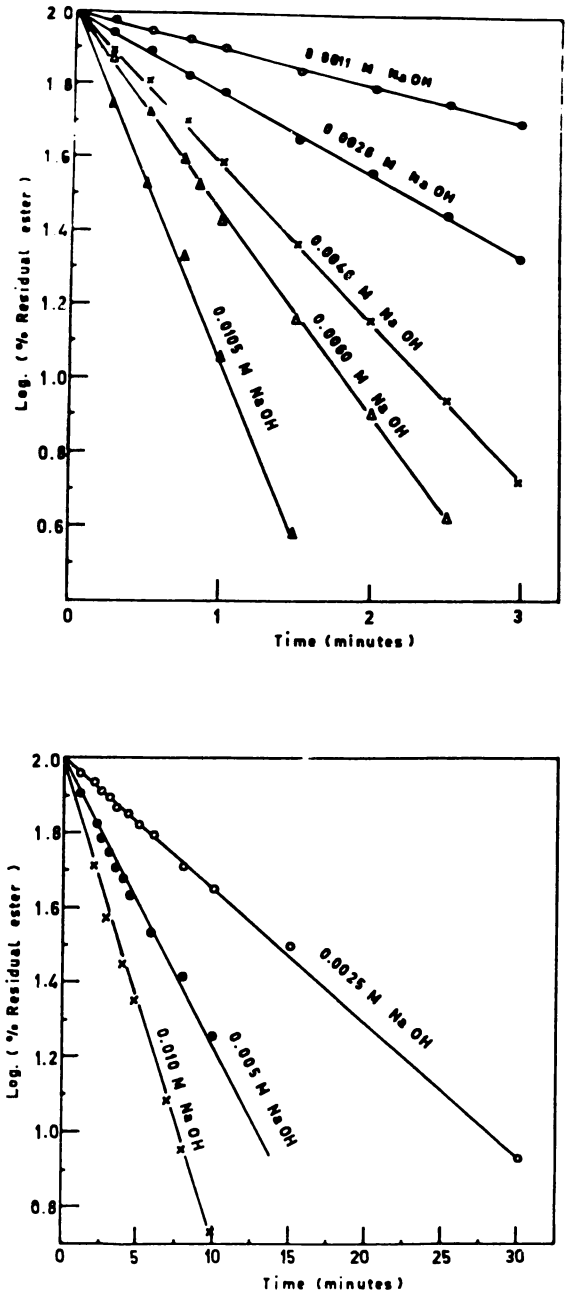

Figure 1. Hydrolysis of Sevin and baygon with various hydroxyl ion concentrations at 20°C

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The second order rate constant k_2 was calculated from the equation:

$$k_2 = \frac{k_1}{[OH^-]}$$

Results

Effect of Hydroxyl Ion Concentration. The hydrolysis rate of the four carbamate esters, Sevin, baygon, pyrolan, and dimetilan, at various hydroxyl ion concentrations at about 20°C are plotted according to the first order rate equation—*i.e.*, log (% residual ester) *vs.* time and are presented in Figure 1 for Sevin and baygon, respectively. Similar results were obtained for pyrolan and dimetilan. Straight lines were obtained for the four insecticides at the various hydroxyl ion concentrations which agree with the first order reaction rates. Pseudo-first order rate constants k_1 were determined from the slopes of these lines and are presented together with second order constants, k_2, in Table I. The observed first order rate constants, k_1, indicate that the four compounds are sensitive to hydroxyl ions in aqueous solutions. Sevin was the most sensitive to hydroxide ions so that at high concentrations of base 1-naphthol was liberated too fast to be measured by conventional methods. Figure 2 shows plots for k_1 for the four compounds *vs.* hydroxide ion concentration.

Table I. Kinetic Results for the Rate of Hydrolysis of the Carbamate Insecticides in Sodium Hydroxide Solutions

Compound	*Temp., °C*	*Molarity of NaOH*	k_1, (min^{-1})	k_2, (*liter* $mole^{-1}min^{-1}$)
Sevin	23	0.0009	1.84×10^{-1}	2.04×10^{2}
		0.0011	2.30×10^{-1}	2.09×10^{2}
		0.0023	4.6×10^{-1}	2.00×10^{2}
		0.0046	9.44×10^{-1}	2.05×10^{2}
		0.0060	1.24	2.07×10^{2}
		0.0105	2.16	2.06×10^{2}
Baygon	20	0.0025	8.0×10^{-2}	3.22×10
		0.0050	1.72×10^{-1}	3.44×10
		0.0100	3.04×10^{-1}	3.04×10
Pyrolan	20	0.0500	3.3×10^{-3}	6.7×10^{-2}
		0.1000	7.1×10^{-3}	7.1×10^{-2}
		0.2500	1.78×10^{-2}	7.1×10^{-2}
		0.5000	3.80×10^{-2}	7.6×10^{-2}
Dimetilan	20	0.1250	4.6×10^{-4}	3.7×10^{-3}
		0.2500	8.5×10^{-4}	3.4×10^{-3}
		0.5000	1.65×10^{-3}	3.4×10^{-3}

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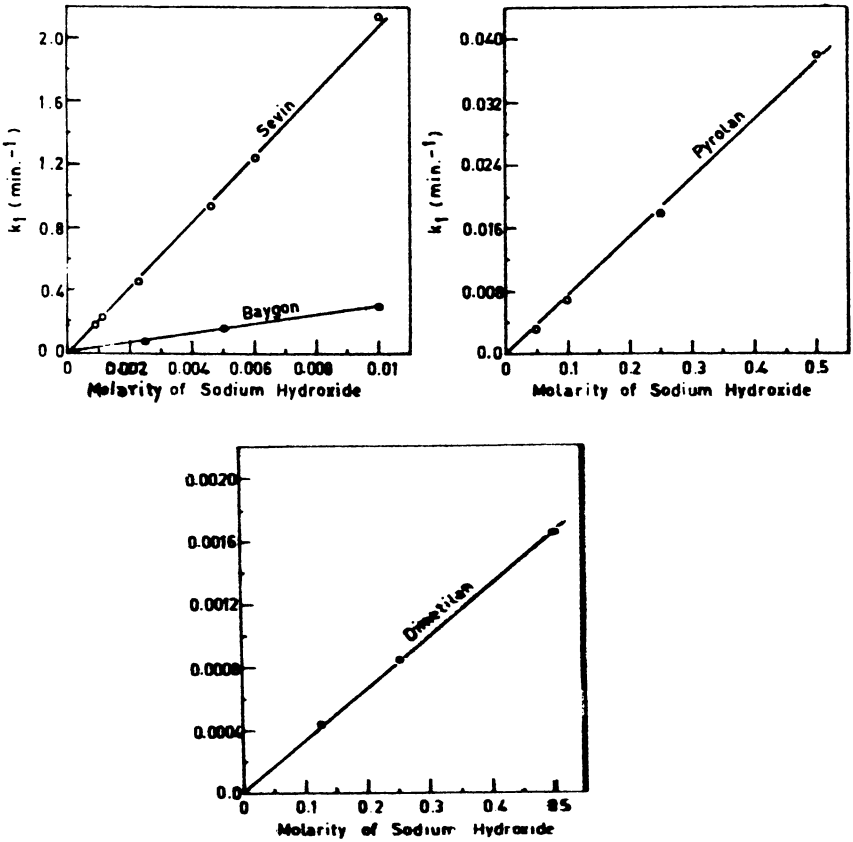

Figure 2. Effect of hydroxyl ion concentration on the hydrolysis rates of Sevin, baygon, pyrolan, and dimetilan

Straight lines passing through the origin were obtained showing that the reaction is first order with respect to hydroxide ions. The observed second order rate constants, k_2, show that the *N,N*-dialkylcarbamates are more stable towards alkaline hydrolyzing than the *N*-monoalkyl carbamates. Thus the value of k_2 at 20°C for Sevin is about 6×10^4 greater than that for dimetilan. The order of increasing stability of the four compounds towards alkaline hydrolysis was: Sevin <baygon <pyrolan <dimetilan.

Effect of pH on Hydrolysis. Hydrolysis of the four insecticides was also studied in buffered solutions at different pH values. Pyrolan and dimetilan were stable towards hydrolysis in the pH range of 6.0–10.0 used here. Thus at a concentration of 4.8 mg/liter and at pH 10 only 4% of dimetilan and 8% of pyrolan were hydrolyzed at the end of 100 days. Baygon was also stable towards hydrolysis over pH range of 3.0–7.0. However, at pH 8.0 measurable hydrolysis was observed which increased

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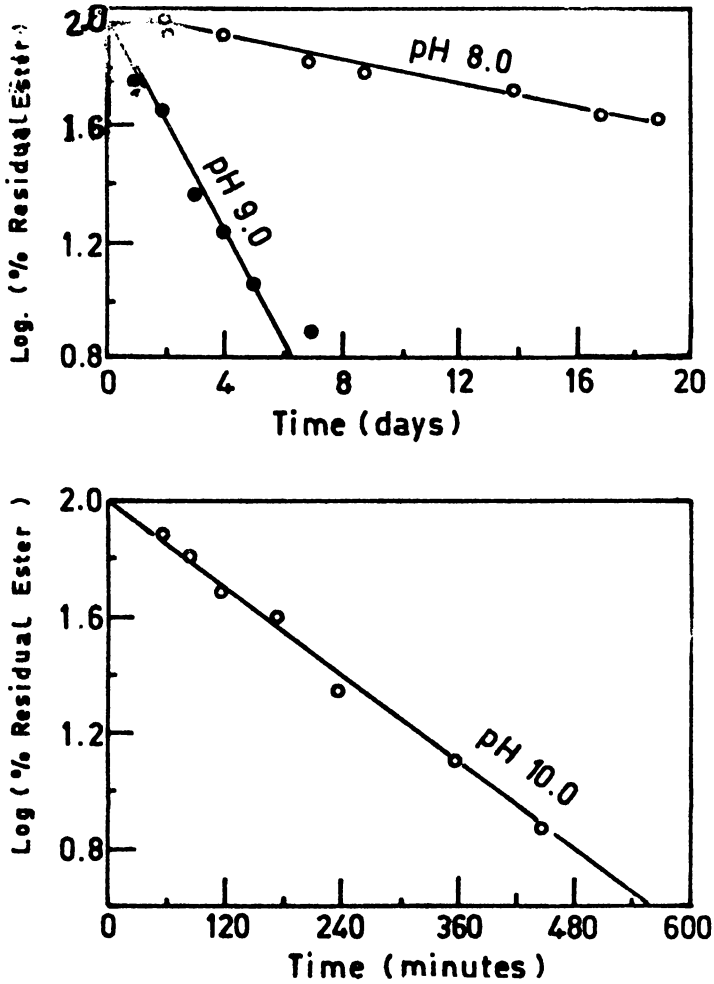

Figure 3. Effect of pH on the hydrolysis of baygon at 20°C

with increasing the pH. First order rate constants and the half-life time were therefore determined at pH 8, 9, and 10 at 20°C; the results are plotted in Figure 3.

The half-life time of baygon was 16 days at pH 8, 1.6 days at pH 9, and 0.17 day at pH 10. Sevin was also stable to hydrolysis at the acidic pH range of 3.0–6.0. However, at pH 7.0 quick rise in the hydrolysis rate was observed and increased with the increase of the pH. The first order rate constants of hydrolyzing Sevin were therefore determined over the pH range of 7.0–10.0; the data are plotted in Figure 4. The half-life time was 10.5 days at pH 7, 1.8 days at pH 8, 2.5 hours at pH 9, and only 15 minutes at pH 10. Table II shows the k_1 values and lifetimes of Sevin

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and baygon at different pH values. These results indicate that Sevin is the least stable compound towards hydrolysis in aqueous solutions at neutral and alkaline pH values. Baygon however is moderately stable while pyrolan and dimetilan are extremely stable to hydrolysis under these conditions.

Effect of Temperature. A series of kinetic experiments at different temperatures between 3°–40°C was carried out to study how the hydrolysis rate of the four insecticides depend upon temperature. The second order rate constants were calculated at each temperature and are presented in Table III. These results show that increasing the temperature results in increasing the reaction velocity. The increase of the second order rate constants, k_2, for each 10°C rise which is called the temperature coefficient, Q_{10} or $k_t + 10/k_t$, was calculated for the hydrolyzing of each of the four insecticides at 20° and 30°C, and the results are also shown in Table III. The temperature coefficients for the hydrolysis of these compounds range between 2.0–2.9—*i.e.*, the hydrolysis rate increases two to three times for each 10°C rise.

Figure 5 shows plots of the logarithm of the second order rate constants, k_2, *vs.* $1/T$ for Sevin, baygon, pyrolan, and dimetilan according to Arrhenius equation. The activation energy, E, for the hydrolysis of each system was calculated from the slopes of the straight lines (*see* Table III). The values are in the range of activation energies obtained by other investigators for hydrolyzing other carbamate esters (*2, 3*).

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Discussion

The hydrolysis of the four carbamate insecticides investigated in alkaline medium was a function of the hydroxyl ion concentration in the solution and was first order with respect to these ions. The second order rate constants, k_2, for the mono *N*-methyl substituted esters, Sevin and baygon, were much higher than those for the *N,N*-dimethyl substituted ones. Casida *et al.* (*4*), Dittert (*5*), and Christenson (*2*) also found that

Table II. Hydrolysis and Life Time of Sevin and Baygon at Different pH Values

Compound	*pH*	k_1	$t_{0.5}$	$t_{0.99}$
Sevin	7	4.6×10^{-5}	10.5 days	69.5 days
	8	3.7×10^{-4}	1.3 days	8.6 days
	9	4.6×10^{-3}	2.5 hr	16.7 hrs
	10	4.6×10^{-2}	15.0 min	100.0 min
Baygon	8	3.0×10^{-5}	16.0 days	106.6 days
	9	2.8×10^{-4}	1.6 days	11.4 days
	10	2.7×10^{-3}	4.2 hr	1.18 days

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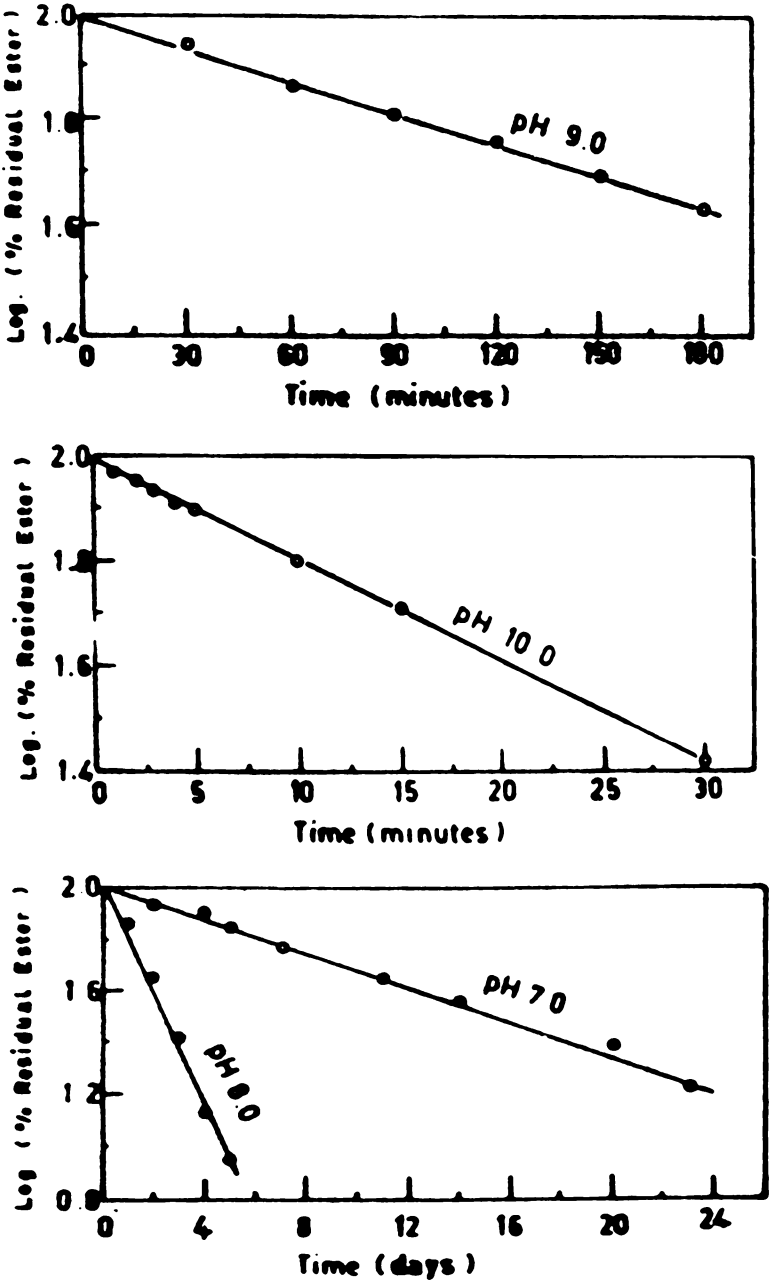

Figure 4. Effect of pH on the hydrolysis of Sevin at 20°C

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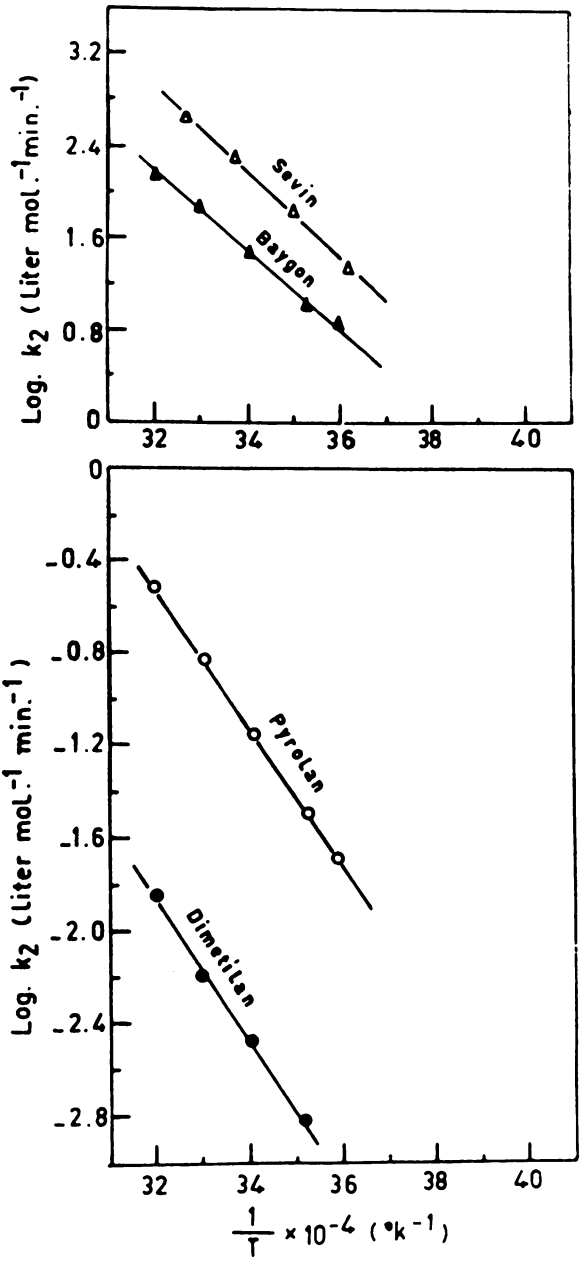

Figure 5. Effect of temperature on rate of hydrolysis of Sevin, baygon, pyrolan, and dimetilan

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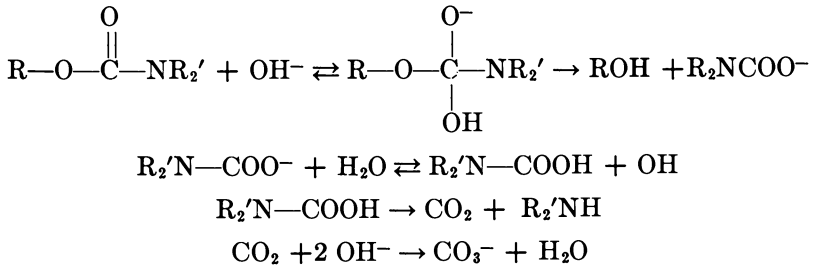
the *N,N*-disubstituted carbamates were more stable towards alkaline hydrolysis than the singly *N*-substituted esters. Dittert (*5*) suggested that hydrolyzing of the aromatic dimethylcarbamates proceeds according to the following mechanism:



$$R_2'N—COO^- + H_2O \rightleftarrows R_2'N—COOH + OH$$

$$R_2'N—COOH \rightarrow CO_2 + R_2'NH$$

$$CO_2 + 2\,OH^- \rightarrow CO_3^- + H_2O$$

Thus, the initial hydroxyl ion attack on the carbonyl carbon results in cleaving the CO–O bond. The carbamate ion formed then decomposes into an amine and carbon dioxide. Since Dittert found high velocity constants and extremely low apparent heats of activation for the hydrolyzing of aromatic nonsubstituted carbamates, he suggested that these esters decompose according to a different mechanism involving an isocyanate intermediate according to the following scheme:

Table III. Kinetic Data for the Effect of Temperature

Compound	*Temp., °C*	*Molarity of NaOH*	k_1, (min^{-1})	k_2, ($liter\ min^{-1}\ mole^{-1}$)
Sevin	3	0.0009	2.18×10^{-2}	2.42×10
	13		6.22×10^{-2}	6.91×10
	23		1.84×10^{-1}	2.04×10^{2}
	33		4.84×10^{-1}	5.37×10^{2}
Baygon	5	0.01	7.30×10^{-2}	7.37
	10		1.12×10^{-1}	1.12×10
	20		3.04×10^{-1}	3.04×10
	30		7.59×10^{-1}	7.59×10
	40		1.16	1.16×10^{2}
Pyrolan	5	0.1	2.00×10^{-3}	2.00×10^{-2}
	10		3.20×10^{-3}	3.20×10^{-2}
	20		7.00×10^{-3}	7.00×10^{-1}
	30		1.49×10^{-2}	1.49×10^{-1}
	40		2.99×10^{-2}	2.99×10^{-1}
Dimetilan	10	0.5	7.60×10^{-4}	1.50×10^{-3}
	20		1.65×10^{-3}	3.40×10^{-3}
	30		3.25×10^{-3}	6.50×10^{-3}
	40		7.14×10^{-3}	1.43×10

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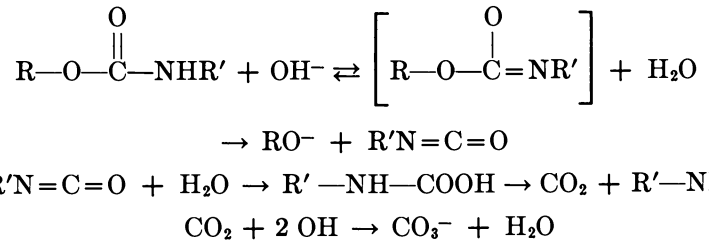

$$\rightarrow RO^- + R'N=C=O$$

$$R'N=C=O + H_2O \rightarrow R'-NH-COOH \rightarrow CO_2 + R'-NH_2$$

$$CO_2 + 2\,OH \rightarrow CO_3^- + H_2O$$

Because of the low heats of activation, he considered that probably the first step in above scheme—*i.e.*, ionizing of the ester—might have a negative temperature coefficient.

Casida (*4*) reported a second order rate constant of 7.7 × 10 liter mole^{-1} min^{-1} for the hydrolyzing of Sevin, which is much lower than the value of k_2 reported here, (2.04 × 10^2) liter mole^{-1} min^{-1}. This result occurs because the Sevin formulation used in Casida's work was not completely soluble in the reaction media.

Hydrolyzing the four insecticides in buffered solutions in the pH range between 3.0–10.0 showed that pyrolan and dimetilan completely resisted hydrolysis in this pH range. Baygon however was susceptible to hydrolysis at pH 8.0 with hydrolysis rates increasing with increase in pH.

on the Hydrolysis of the Carbamate Insecticides

$Q=\frac{(k_t+10)}{k_t}$	*Heat of Activation, k.cal/mole*
2.9	16.9
2.49	15.8
2.22	13.7
1.91	14.0

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Below pH 8.0, however, this compound resisted hydrolysis. Sevin was the most susceptible insecticide to hydrolysis. Measurable hydrolysis started at pH 7.0 and increased with increase in pH. In acidic pH medium, however, the compound resisted hydrolysis.

The hydrolysis rates of the carbamate insecticides also depended upon the temperature of the medium. As shown in Table III, the second order rate constants for hydrolysis increased two to three times when temperature rose from 20° to 30°C.

The salt content of natural waters (ionic strength) seems to be an important factor affecting the hydrolysis rate of the carbamate insecticides. Fukoto *et al.* (3) reported that the observed first order rate constants, k_1, for the hydrolysis of *p*-nitro-*N*-methylcarbamate increased upon decreasing the ionic strength of the phosphate buffer. He suggested that phosphate ions do not participate in the hydrolytic reaction and the lowering of the rate constant by increasing the ionic strength resulted from decreasing activity of the hydroxide ion or the carbamate. Therefore, Sevin and baygon would be expected to be more stable in waters of high salt content such as sea or ocean waters, and the hydrolysis would be expected to be more rapid in waters of low salt content.

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Adsorption of Carbamates on Clay Minerals

Suspended solids in rivers and streams are important in decontaminating natural waters through adsorption processes. Much of these suspended solids is composed of clay materials. These substances are characterized by having high surface area and therefore are expected to contribute substantially to the adsorptive properties of natural turbidity. Clay minerals also constitute a major portion of the colloidal fraction of soils, and therefore contaminated natural or waste waters percolating through the soils may react with clay minerals through adsorption. Thus, these substances may be important in the removing of contaminants from surface and underground waters.

Here the adsorption of the carbamate insecticides and 1-naphthol on kaolinite and bentonite was studied. Adsorption isotherms for Sevin, 1-naphthol, baygon, pyrolan, and dimetilan on bentinite and kaolinite (hydrogen forms) were determined. The adsorption isotherms for the bentonite system are found in Figure 6. These isotherms are similar to those usually encountered in the majority of cases of adsorption of organic solutes from dilute solutions. These types of isotherms are represented according to the classical Freundlich equation:

$$X/m = K C^{1/n}$$

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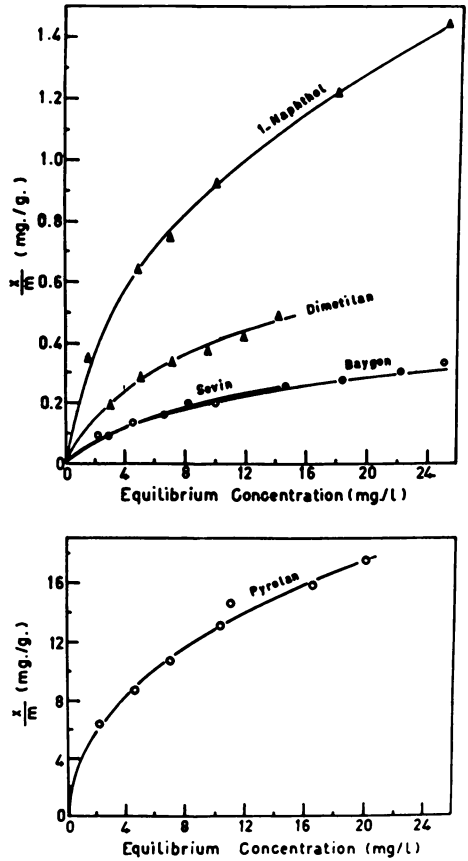

Figure 6. Adsorption isotherms for Sevin, 1-naphthol, baygon, pyrolan, and dimetilan on bentonite at 20°C

where X = the amount of solute adsorbed, m = weight of adsorbent, C = equilibrium concentration of the solute, and K and $1/n$ are constants for the particular system.

In its logarithmic form, the equation becomes:

$$\text{Log } X/m = \text{Log } K + 1/n \text{ Log } C$$

By plotting log X/m *vs.* log C, a straight line is obtained where the slope is $1/n$ and its intercept at $C = 1$ gives the value of K.

Plots of the Freundlich adsorption isotherms for Sevin, 1-naphthol, baygon, pyrolan, and dimetilan on kaolinite are shown in Figure 7; similar plots were obtained for the bentonite system. All the insecticides studied showed equilibrium adsorption on the clay minerals according to

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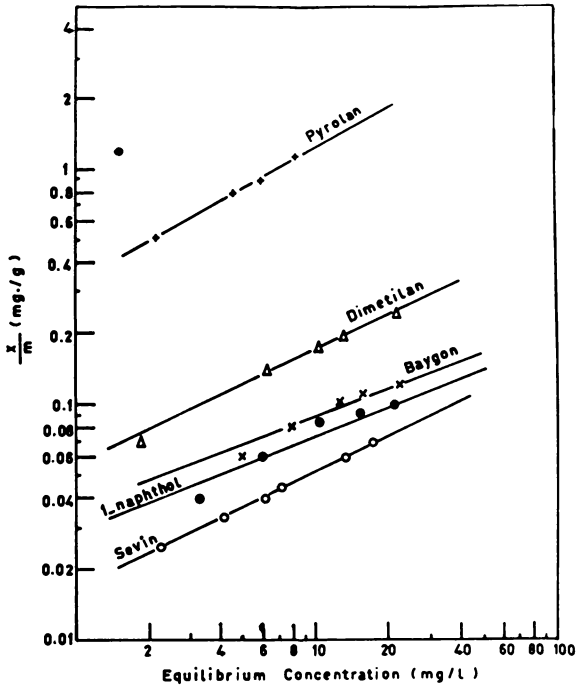

Figure 7. Freundlich adsorption isotherms for Sevin, 1-naphthol, baygon, pyrolan, and dimetilan on kaolinite

the Freundlich equation. The constants K and $1/n$ for each system were determined and are presented in Table IV.

Comparing the values of K and $1/n$ obtained with the two minerals may give some idea about the effectiveness of each adsorbent. The higher the K value is, the greater the degree of adsorption; the higher the $1/n$ values, the greater will be the efficiency of the adsorbent. However, since both constants are usually different with different systems, comparing the capacity of one absorbent for adsorption of different solutes or the relative adsorption of the same solute on different adsorbents is difficult unless a single numerical expression is used. Therefore, it was decided to compare the amount of each clay required to reduce the concentration of each insecticide from a high concentration to an arbitrary low value. Such computation will include the constants, K and $1/n$, and all the factors influencing adsorption from solution—*i.e.*, the properties of the adsorbent, adsorbate, and solvent—and the equilibria among them. This computation was accomplished by modifying the Freundlich equation into:

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$$\frac{C_o - C_f}{m} = K C_f^{1/n}$$

where C_o = the initial concentration of the solute (mg/liter) and C_f = the equilibrium concentration of the solute (mg/liter). The only unknown in the equation will be the value of m which is easily calculated. The higher the computed amount of adsorbent required to reduce the concentration of a particular solute, the less efficient is the adsorbent while lower computed values indicate higher efficiency of adsorption.

The amount of kaolinite and bentonite required to reduce the concentration of each insecticide from initial concentrations of 5–1 mg/liter (the range of concentration which may be encountered in natural waters) to a concentration of 0.1 mg/liter were calculated and are presented in Table V.

These results indicate that bentonite showed much higher capacity for adsorption of all the insecticides studied than kaolinite. The relative order of adsorption of the four insecticides was the same on kaolinite and bentonite. Thus the sequence of adsorption in decreasing order was: pyrolan > dimetilan > baygon > Sevin. 1-Naphthol however occupied an intermediate level of adsorption between baygon and Sevin for kaolinite, and between pyrolan and dimetilan for bentonite. Pyrolan showed relatively high levels of adsorption on both clays. Thus the amount adsorbed on kaolinite ranged between 0.35–1.12 mg/gram of kaolinite; whereas for bentonite the amounts adsorbed ranged between 6.5–17 mg/gram on bentonite.

Discussion. The adsorption isotherms obtained for Sevin, baygon, pyrolan, and dimetilan on bentonite and kaolinite conformed with the Freundlich adsorption equation.

Table IV. Parameters of Freundlich's Isotherm for Sevin, 1-Naphthol, Baygon, Pyrolan, and Dimetilan on Kaolinite and Bentonite

Clay	*Compound*	k	$\frac{1}{n}$
Kaolinite	Sevin	0.017	0.49
	1–Naphthol	0.030	0.40
	Baygon	0.038	0.37
	Pyrolan	0.340	0.57
	Dimetilan	0.058	0.48
Bentonite	Sevin	0.046	0.68
	1–Naphthol	0.260	0.55
	Baygon	0.060	0.52
	Pyrolan	4.200	0.48
	Dimetilan	0.110	0.54

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Bentonite showed higher capacity for adsorption of the four carbamate esters than kaolinite. This may occur because bentonite possesses large surface area (600–800 sq meters/gram). Bentonite is also characterized by the tendency of the lattice to expand in the presence of water or other organic molecules resulting from intermolecular adsorption of complete molecules. Kaolinite however possesses low cation exchange capacity and small surface area. Adsorption of organic molecules occurs only on the surface of the mineral, and the organic molecules do not penetrate between the unit layers as they do in bentonite and are retained only around the edges and exterior surface of the particles.

Sevin, 1-naphthol, baygon, and dimetilan generally showed low levels of adsorption on both clays. The amount sorbed was small and ranged between 0.03–0.19 mg/gram of clay at an applied concentration of 5.0 mg/liter. The amount of kaolinite or bentonite required to remove 1.0 mg/liter of these compounds ranged between 12–163 grams. However, pyrolan was more adsorbed on both clays than the other insecticides. This behavior was more pronounced for bentonite where only 0.65 gram of this clay was required to remove 1 mg/liter of the insecticide and 3.5 grams were required to remove 5 mg/liter.

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Photodecomposition of the Carbamate Insecticides

Among the environmental factors that influence the persistence of the carbamate insecticides in the aquatic environment is the decomposing of these compounds when influenced by solar radiations. Many organicides undergo changes after they are exposed to ultraviolet light (uv) and artificial or natural sunlight (*7*, *8*, *9*, *10*). Therefore, the effect of

Table V. Amount of Clays Required to Reduce the Concentration of Sevin, 1-Naphthol, Baygon, Pyrolan, and Dimetilan to 0.1 mg/liter

Clay	*Initial Conc.* C_o *mg/liter*	*Amount of Clay Required*[a]				
		Sevin	*1-Naphthol*	*Baygon*	*Pyrolan*	*Dimetilan*
Kaolinite	1	163	75	56	9.1	47
	2	345	158	118	19.3	100
	3	527	241	181	29.5	152
	4	709	325	243	39.8	205
	5	890	408	306	50.0	257
Bentonite	1	93	12	50	0.65	28
	2	198	26	105	1.37	58
	3	302	40	161	2.09	89
	4	406	54	216	2.80	120
	5	510	68	273	3.53	151

[a] Units in grams.

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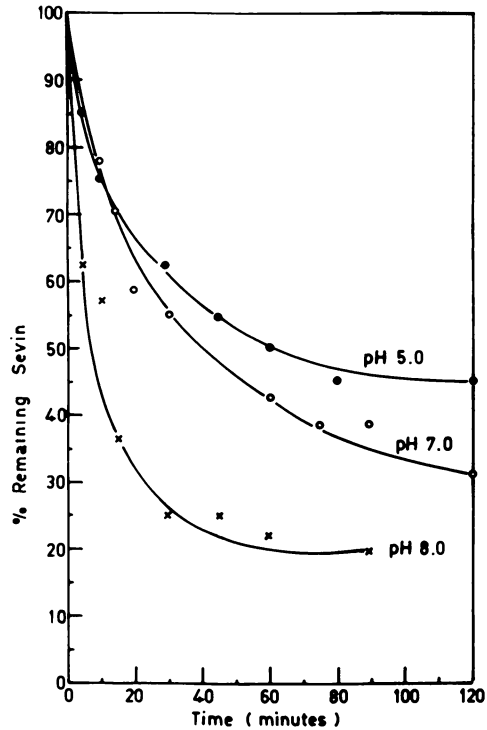

Figure 8. Effect of pH on photodecomposition of Sevin

ultraviolet irradiation upon the stability of Sevin, baygon, pyrolan, and dimetilan in aqueous solutions was studied.

Irradiation Procedure. Aqueous solutions of the carbamate insecticides in different phosphate buffer solutions at pH 5.0, 7.0, and 9.0 received ultraviolet irradiation for various time periods. The irradiation source was two 15-Watt germicidal tubes which produce peak radiation at 254 mμ. The tubes were mounted, 10 cm apart, in an exposure cabinet lined with reflecting shields of aluminum sheets. Solutions of the insecticides, 20 mg/liter, were prepared in 0.1*M* phosphate buffer (pH 6.8) and adjusted to the desired pH value by adding sodium hydroxide on phosphoric acid solutions. They were irradiated in open 9 cm petri dishes placed at a distance of about 5 cm from the light source. Aliquots were periodically withdrawn and analyzed for the parent insecticides and the hydrolysis products, using the 4-aminoantipyrine colorimetric method (*6*). The degrading was also followed by measuring the ultraviolet absorption spectra of solutions irradiated in 2-cm quartz cells at different time intervals. The temperature was kept constant by circulating air through the exposure cabinet.

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Effect of pH on the Photodecomposition. The effect of ultraviolet irradiation on aqueous solutions of Sevin, baygon, pyrolan, and dimetilan was studied at various pH values.

The results of photodecomposition of Sevin at pH 5.0, 7.0, and 8.0 at increasing time intervals are shown in Figure 8. Generally the concentration of Sevin decreased upon increasing the irradiation time; however, the photolysis process progressed at a decreasing rate after prolonged exposure. The photodecomposition proceeded at increasing rates as the pH value of the solutions was increased. Thus, after an exposure time of 60 min only 50% of Sevin was decomposed at pH 5.0 while 57% was decomposed at pH 7.0 and 78% at pH 8.0. 1-Naphthol appeared as a decomposition product after 5 min of exposure in all the irradiated solutions of Sevin. Similar results were obtained for the baygon photolysis.

The photodecompositions of pyrolan and dimetilan at pH 5.0, 7.0, and 9.0 are shown in Figures 9 and 10, respectively. Decomposing of the two carbamate esters progressed more rapidly than Sevin and baygon. The pH of the irradiation medium did not seem to affect the photodecomposing of the two compounds. The times required for 50%

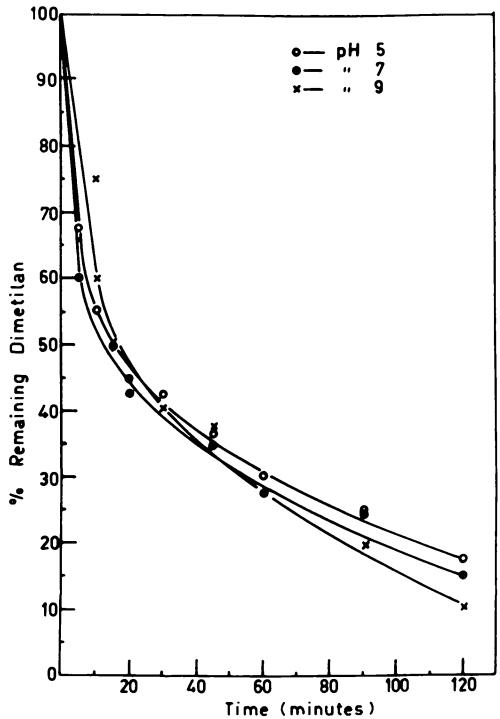

Figure 9. Effect of pH on photodecomposition of pyrolan

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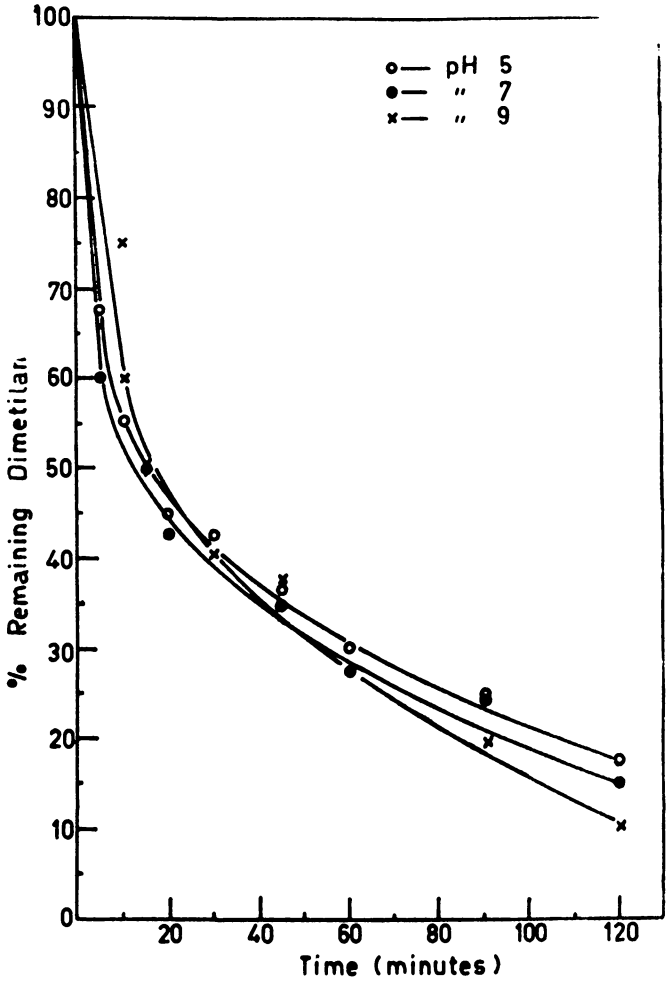

Figure 10. Effect of pH on photodecomposition of dimetilan

decomposition of pyrolan and dimetilan at the three pH values were about 6.5 min and 15 min, respectively. The photodecomposing of both compounds produced heterocyclic enol forms that were colorimetrically detected. However after irradiating 60 min, the enols were completely decomposed.

The amounts of phenols or hetercyclic enols produced during the irradiating of Sevin, baygon, pyrolan, and dimetilan are shown in Table VI. Table VII summarizes the times required for 50% decomposition of Sevin, 1-naphthol, baygon, pyrolan, and dimetilan at the different pH values.

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Table VI. Concentrations of Phenols or Heterocyclic Enols Formed during the Irradiation of Sevin, Baygon, Pyrolan, and Dimetilan at Different pH Values[a]

Time, min	*Compound Irradiated*[b]			
	Sevin	*Baygon*	*Pyrolan*	*Dimetilan*
pH 5.0				
0	0.0	0.0	0.0	0.0
10	2.0	1.5	1.0	3.0
15	3.0	3.0	1.0	2.0
20	3.0	—	1.0	1.5
30	—	4.0	2.0	0.8
45	2.0	9.0	2.0	0.0
60	2.0	8.0	1.0	0.0
90	1.0	8.0	—	0.0
pH 7.0				
0	0.0	0.0	0.0	0.0
10	1.0	4.0	1.0	2.5
15	1.0	5.0	2.0	3.0
30	2.0	7.0	2.0	1.0
45	2.0	9.0	1.5	0.0
60	2.0	8.0	0.8	0.0
90	2.0	7.0	—	0.0
pH 9.0				
0	—	0.0	0.0	0.0
10	—	7.0	0.0	2.5
15	—	7.5	1.0	1.5
30	—	8.0	1.0	0.0
45	—	7.0	1.0	0.0
60	—	7.0	0.0	0.0

[a] Initial concentration of each 20 mg/liter.
[b] Concentration of phenol or heterocyclic enol produced (mg/liter).

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Qualitative Changes During Photodecomposition. The qualitative changes occurring during the ultraviolet irradiating of aqueous solutions of Sevin, 1-naphthol, baygon, pyrolan, and dimetilan were studied by estimating the changes in the ultraviolet absorption spectra of these compounds during exposure.

Figure 11 shows the absorption spectra of aqueous solutions of Sevin (2 mg/liter) at pH 7.0 and 8.0 before and after exposing them to ultraviolet light irradiation. Sevin showed two adsorption maxima; one at 280 mμ and a second at 220 mμ. After irradiating, absorption at the wavelength of 220 mμ decreased, indicating gradual decomposing of the original compound. The irradiated solutions acquired yellowish-brown coloration, and increased absorption occurred at 250–260 mμ. After 90 min of exposure, the absorption spectrum of Sevin at pH 8.0 was completely changed, showing that the compound lost its identity. Similar

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changes in the ultraviolet spectra of baygon, pyrolan, and dimetilan were observed during the irradiating.

Discussion. The results of this study indicate that carbamate insecticides in water photodecompose under ultraviolet light. The pH value of the aqueous medium was important in determining the photolysis rate of Sevin and baygon, being slow at low pH values and tending to increase with rise of pH. However, the decomposing of pyrolan and dimetilan was not affected by the pH of the irradiated medium. The primary effect of the ultraviolet light irradiation seems to cleave the ester bond, producing the phenol or heterocyclic enol of the four carbamate esters. The effect of pH on the photolysis of Sevin and baygon is analogous to that observed with 2,4-dichlorophenoxyacetic acid (*6*) where the alkaline photodecomposed much faster than neutral or acidic media.

Crosby *et al.* (*7*) studied the photodecomposing of some carbamate esters using thin layer chromatography and the cholinesterase-inhibition method to detect these products. They showed that the photodecomposition of Sevin yielded, besides 1-naphthol, several cholinesterase inhibitory substances which indicate that these compounds retained the intact carbamate ester group and that irradiation resulted in changes at other positions in the molecule. Similar results were reported for the irradiation products of other carbamate esters (*8, 9, 10*). Crosby *et al.* (*8*) also reported that irradiating of ethanolic or hexane solutions of baygon was only slightly affected by ultraviolet light. Here the irradiated aqueous solutions of baygon resulted in the rapid decomposing of the insecticide. This supports the view that photodecomposing of the carbamate esters is affected by the nature of the solvent.

By comparing the half-life times for the photodecomposing of the four carbamate insecticides under comparable conditions (Table III), we see the order of decomposing was pyrolan > dimetilan > baygon > Sevin.

Table VII. Irradiation Time Required for 50% Decomposition of Sevin, 1-Naphthol, Baygon, Pyrolan, and Dimetilan[a]

	Irradiation Time (minutes)			
Compound	*pH 5*	*pH 7*	*pH 8*	*pH 9*
Sevin	60.0	39.0	8.00	—
1-Naphthol	120.0	60.0	43.	7.5
Baygon	19.0	17.5	—	9.0
Pyrolan	7.5	6.0	—	6.0
Dimetilan	15.0	15.0	—	15.0

[a] Initial Concentration: 20 mg/liter.

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Pyrolan which showed the fastest rate of photodecomposing shows a wavelength of maximum absorption at 248 mμ which is close to the peak radiation (254 mμ) of the ultraviolet light source used here. Dimetilan, baygon, and Sevin showed relatively lower absorption values at this wavelength. These results suggest that the light absorption characteristics of the insecticide influences the extent of its photodecomposing by a specific light source. The ultraviolet spectrum of sunlight ranges between 292–400 mμ, and therefore the photodecomposition rate and the nature of degradation products induced by sunlight is expected to be different from those observed here. Eberle and Gunther (9) showed that pyrolan was rapidly decomposed when ethanolic or hexane solutions were exposed to short-wave ultraviolet light (254 mμ) while natural sunlight did not induce any photodecompositing; however, ultraviolet light and natural sunlight caused decomposing of Sevin (8) and dimetilan (9). The extent of photodecomposition, particularly for Sevin, was not the same under the

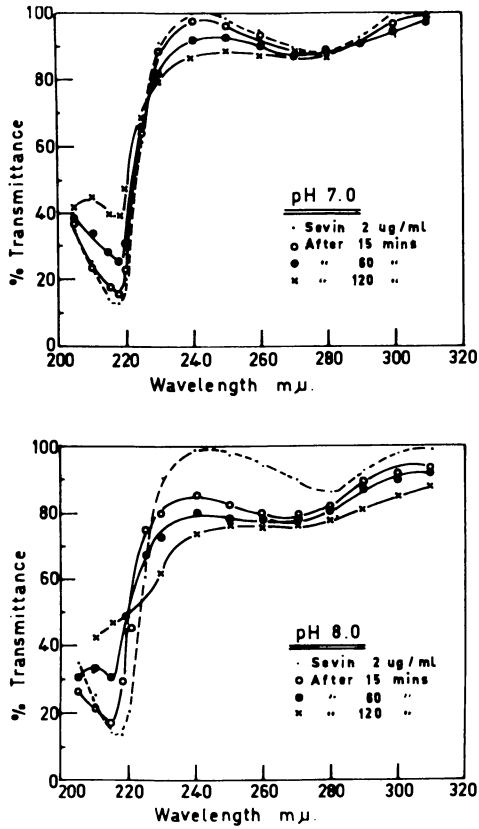

Figure 11. Ultraviolet absorption spectra of Sevin before and after irradiating

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different irradiation conditions. Intense ultraviolet irradiation generally resulted in forming more degradation products.

Therefore, photodecomposition may reasonably be suggested to account for some loss of the carbamate insecticides in clear surface waters exposed to long periods of sunlight illumination. However, photolysis may be a minor factor in decomposing these compounds in highly turbid waters where the light penetration is greatly reduced.

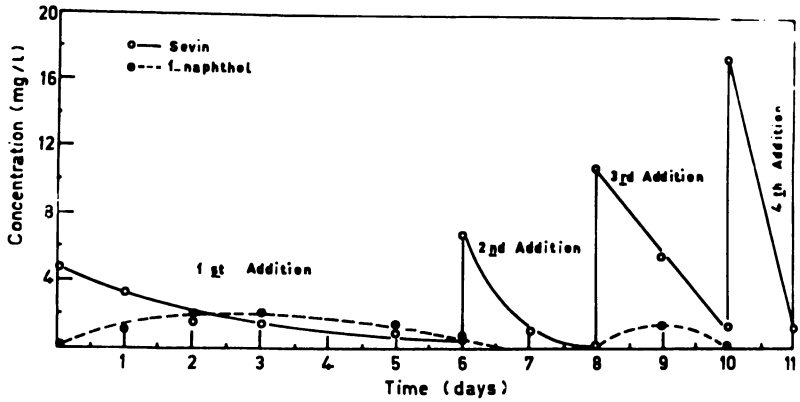

Figure 12. Degrading of Sevin in the Nile River water

Biological Degradation of the Carbamate Insecticides

The biochemical activities of bacteria constitute the most important phase of self-purification of polluted streams. It was essential, therefore, to study the biodegradability of Sevin, 1-naphthol, baygon, pyrolan, and dimetilan.

Procedures. Solution of each of Sevin, 1-naphthol, baygon, pyrolan, and dimetilan were prepared in Nile River Water in concentrations of about 4.0 mg/liter. A phosphate buffer was added to maintain a pH of 7.2 ± 0.1. Ten liter portions of each solution were placed in 5 gal containers and kept at room temperature, 25 ± 2°C. Aerobic conditions were kept in the solutions by bubbling a gentle stream of air. Samples were periodically withdrawn and analyzed for the concentration of the insecticide and its enol form. For experiments lasting for long periods of times, two liter portions were withdrawn weekly and replaced by the same volume of solutions of the insecticide in fresh Nile River water containing 1% of settled sewage to supply trace nutrients and new microorganisms.

When the chemical analysis showed that the insecticide was almost completely oxidized, one half of the contents of the bottles was syphoned off and then replaced with buffered Nile River water and redosed with aqueous solutions of the insecticide of the desired concentration. The disappearing of the compound was then followed to check possible acclimatization.

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Biological degrading of these compounds was also studied by measuring the oxygen uptake for solutions of each compound in Nile River water and 50% sewage in BOD dilution water (*11*) by using the manometric technique (*11*). At the end of each run the residual concentration of each compound and its hydrolysis products were determined.

Biological Degradation of Sevin. The decrease in concentration of Sevin in river water with time is shown in Figure 12. The concentration decreased progressively with time and 89% of the added amount of Sevin (4.75 mg/liter) disappeared in 6 days. However, 1-naphthol appeared as a degradation product during the biological oxidation of Sevin, and a concentration of 2.2 mg/liter was detected after 2 days which was subsequently reduced to 0.8 mg/liter after 6 days. This amount of 1-naphthol did not result from chemical hydrolysis of Sevin since a sterile buffered solution of the ester showed negligible hydrolysis at the end of this incubation period and a half-life of 16 days was obtained. Therefore, the hydrolysis product of Sevin was produced because of biological activity of the microorganisms in the river water. The concentration of the formed 1-naphthol decreased with time, indicating the biological degrading of this compound. Subsequent additions of increasing concentration of Sevin disappeared in shorter periods of time, and there was no high buildup of 1-naphthol in the oxidation bottles. At the fourth addition, 17.5 mg/liter of Sevin disappeared almost completely after one day, and no 1-naphthol was detected in the solution, indicating the forming of acclimatized flora able to use Sevin and 1-naphthol.

The biological breakdown of Sevin in Nile River water and 50% sewage was also studied by measuring the oxygen uptake with the Warburg Respirometer (*see* Figure 13). Sevin in concentration of 40 mg/liter was rapidly oxidized in Nile water after a lag period of one day, and the oxygen uptake reached 95% of the theoretical amount required

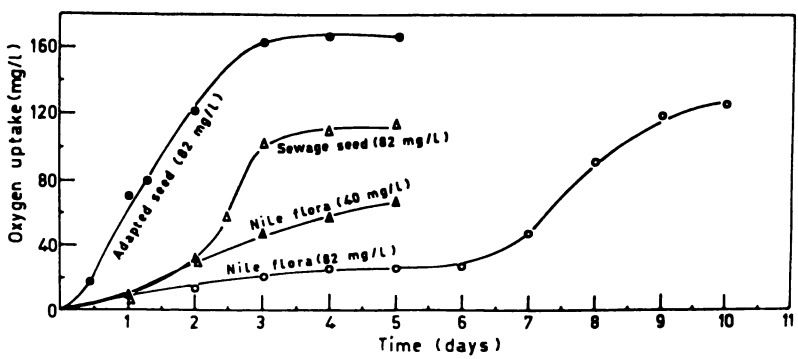

Figure 13. Oxygen uptake curves for Sevin in Nile River water and sewage

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to oxidize it completely in five days. At a concentration of 82 ml/liter, it oxidized at a low rate for six days followed by rapid oxygen uptake, and after 10 days 74% of the theoretical amount of oxygen was used. In 50% sewage however oxidizing of the same concentration of Sevin, 82 mg/liter was more rapid than in river water, and 66% of the compound was oxidized in five days at a lag period of one day. By using flora adapted for the biological breakdown of Sevin, the oxidizing of 82 mg/liter progressed rapidly without a lag period, and 96% oxidation was achieved in six days.

These results show that natural waters and sewage contain microorganisms capable of oxidizing Sevin and 1-naphthol. The relatively rapid decomposing in the presence of sewage may be attributed to the higher number of microorganisms capable of using these compounds than those present in Nile River water.

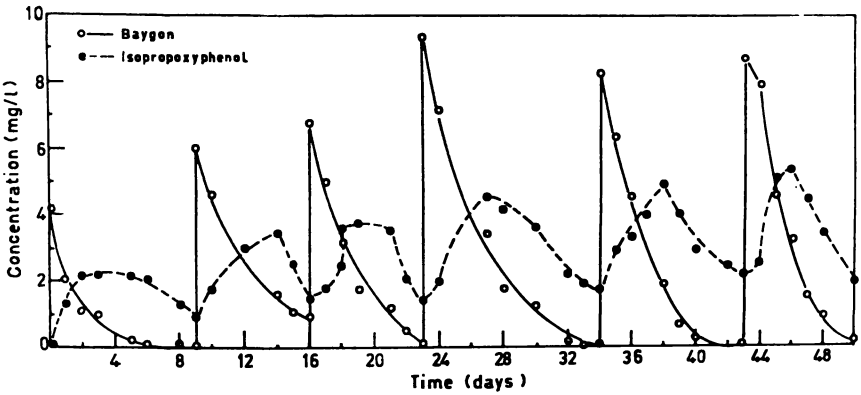

Figure 14. Degrading of baygon in Nile River water

Biological Degradation of Baygon. The results of the disappearing of baygon in the Nile River water are shown in Figure 14. The concentration of baygon decreased continuously with time; thus starting with a concentration of 4.2 mg/liter, only 0.2 mg/liter were left after 5 days (95% disappearance). However, the hydrolysis product, *o*-isopropoxyphenol, was detected in a concentration of 0.8 mg/liter in the system after the first day of adding the ester, and its concentration increased to 2.2 mg/liter in the second day then decreased gradually with incubation time. Subsequent additions of increasing concentrations of baygon disappeared also in short periods of time, but there was always a slight buildup of *o*-isopropoxyphenol in the system which again disappeared with time. The producing of phenol under the conditions of these experiments where the pH of the water was maintained at pH 7.2 cannot be attributed to chemical hydrolysis of this ester since it has previously been shown that

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baygon is resistant to chemical hydrolysis at this pH value. These results were also confirmed by running a blank experiment by aerating baygon solutions in phosphate buffer at pH 7.2 containing sodium azide at a concentration of 0.01% where no noticeable hydrolysis was observed. Therefore, the hydrolysis of baygon in the oxidation bottles is attributed to enzymatic action of bacterial flora present in the Nile River water which subsequently used the produced phenol.

Trying to obtain acclimatized flora capable of rapidly using baygon and *o*-isopropoxyphenol, increasing concentrations of the ester were added to settled sewage, and aerobic conditions were maintained. Rapid decrease in concentration of baygon was always observed, but there was always a slight buildup of isopropoxyphenol in the medium which subsequently disappeared with aeration time. It seems, therefore, that biodegradation of baygon proceeds first by biologically hydrolyzing the ester to the corresponding phenol, which is subsequently used by the microorganisms. The rate of the hydrolysis step seems to be faster than the rate of using of the phenol.

Biodegrading of baygon was also studied by measuring the oxygen uptake for different concentrations of the ester, 22.0, 50.0, and 80 mg/liter in 50% sewage. The results are plotted in Figure 15. A short lag period of 2–3 days was observed with the concentrations of 22.0 and 50.0 mg/liter of baygon which was followed by rapid oxygen uptake, and 95% of the theoretical oxygen demand for these two concentrations was

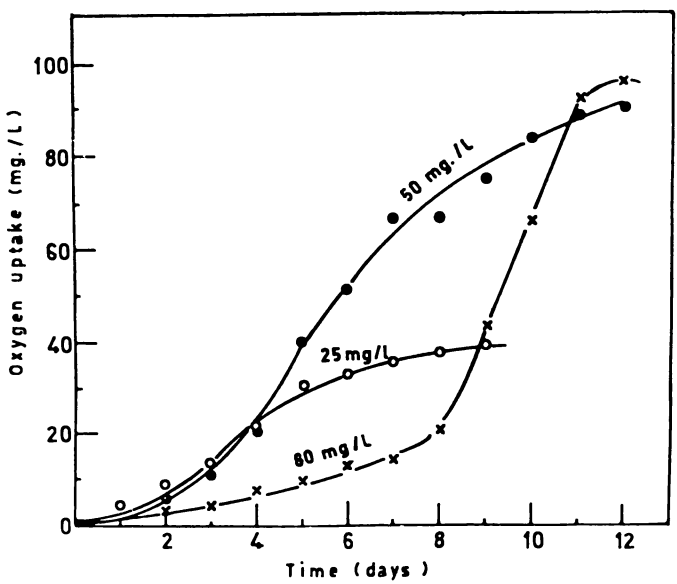

Figure 15. Oxygen uptake curves for baygon in sewage

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used in 9 and 12 days, respectively. When a concentration of 80.0 mg/liter of the ester was used, a long lag period of 7 days was observed after which oxygen was used rapidly, and 63% of the ester was oxidized in 12 days.

Biological Degradation of Pyrolan and Dimetilan. Pyrolan and dimetilan, 4.0 mg/liter each, in Nile River water did not change concentrations nor the producing of their hydrolysis products over a period of 120 days. The same results were obtained when solutions of either insecticide in concentrations of 4.0 mg/liter were prepared in 50% or 100% sewage.

These results suggest that pyrolan and dimetilan were not biologically degraded under these conditions. These results were further confirmed by measuring the oxygen uptake of pyrolan and dimetilan in concentrations of 20, 40, and 60 mg/liter in 50% sewage solutions. Pyrolan showed some inhibiting effect on the sewage miroflora as shown by generally lower oxygen uptake levels than that of the control. Dimetilan however did not show inhibitory effects on the sewage microflora but was not biologically oxidized since the oxygen uptake level was always the same as the control.

Analyzing the residual pyrolan and dimetilan in the Warburg flasks at the end of the run by the colorimetric and ultraviolet methods revealed that the concentrations of either compound did not change during the incubation period (9 days). Extracts of these solutions were also examined by thin layer chromatography. The chromatograms yielded a single spot in each case having the same R_f value as the initial insecticide, and no other degradation product was obtained when different developing solvents were used.

Whereas pyrolan and dimetilan resisted biological degradation, their hydrolysis products, 1-phenyl-3-methylpyrazolone and 2-dimethylcarbamoyl-3-methyl-5-pyrazolone, respectively, were readily available to biological degradation. Figure 16 shows the progress of biological degradation of 1-phenyl-3-methyl-5-pyrazolone in Nile River water. Similar results were obtained for the dimetilan hydrolysis product.

Discussion. The biological degradation of Sevin in natural surface water and in sewage took place in a relatively short period of time and has been confirmed by respirometric and chemical techniques. Repeated addition of Sevin to Nile River water resulted in the buildup of flora capable of decomposing higher concentrations of this compound. The intermediate 1-naphthol was formed during the biooxidation of Sevin but subsequently disappeared on further incubation. The rapid producing of 1-naphthol during serial additions of Sevin to water rich in adapted microflora indicates that enzymatic hydrolysis rather than chemical

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hydrolysis occurred since the latter is known to be comparatively slow under the same experimental conditions.

Baygon also yielded to biological oxidation in natural waters. Its hydrolysis product, *o*-isopropoxyphenol, was rapidly produced during the metabolic degradation processes and was then used by the microorganisms. The bacterial hydrolysis rate of the ester seems to be faster than the rate of using the phenol produced. The slow rate of biological oxidizing of *o*-isopropoxyphenol may be attributed to presence of the etheral linkage and the branched side chain of the isopropoxy group (*12*).

These results suggest that the primary step in bacterial degradation of Sevin and baygon is the hydrolyzing of the carbamic acid ester group, yielding 1-naphthol or *o*-isopropoxyphenol, respectively, as well as methylamine. The hydrolysis products are further oxidized by bacteria to yield

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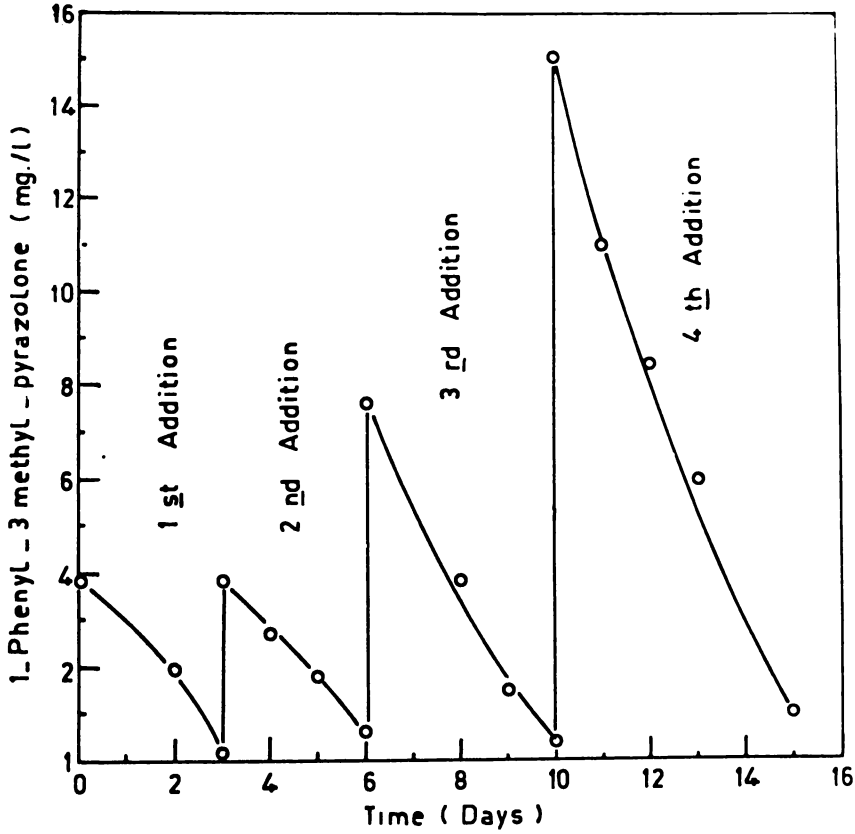

Figure 16. Degradation of 1-phenyl-3-methyl-pyrazolone in Nile River water

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carbon dioxide and ammonium salts. More than one criterion supports this hypothesis:

1. The rapid formation of the phenols during biodegradation has been shown by the colorimetric analysis.

2. Sevin was rapidly decomposed on incubating with microflora previously adapted to the biodegradating of 1-naphthol.

While Sevin and baygon were readily biodegraded, pyrolan and dimetilan resisted biological oxidation under the same experimental conditions. Pyrolan at relatively high concentrations (20.0 mg/liter or more) exerts some inhibitory effect on sewage microflora. Attempts to obtain acclimatized flora from Nile waters or sewage that could use these compounds were unsuccessful. However, the hydrolysis products of both insecticides were readily available to biological degradation in natural waters. Previously the hydrolysis mechanism of the dialkylcarbamates (pyrolan and dimetilan) was shown to be different from the monoalkyl esters (Sevin and baygon). The lack of the presence of an enzymatic system capable of hydrolizing pyrolan and dimetilan accounts for their resisting biological breakdown and emphasizes that the hydrolysis step is the limiting step in their metabolism by the microorganisms. Both pesticides therefore are expected to persist for long periods of time in natural waters.

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General Discussion

The persistence and fate of the organic insecticides reaching the aquatic environment depend upon various chemical, physical, and biological processes operating singly or in sequence. There are many factors that influence the chemical and biological changes in a stream. The rates of such changes depend upon the nature of the compound and the particular conditions to which it is subjected.

The investigated carbamate insecticides were susceptible to chemical hydrolysis in alkaline media. The hydrolysis rates of the monomethylcarbamates, Sevin and baygon, were much higher than those of the dimethylcarbamates, pyrolan and dimetilan. The pseudo-first order rate constants for hydrolyzing Sevin and baygon increased with the rise of the pH of the medium.

The pH of natural waters generally lies in the range of 5.0–8.0 and is expected to influence the chemical stability of these insecticides. In slightly acidic waters all the compounds will be stable and persist for long periods of time. However, with waters at pH 7.0 at 20°C, Sevin decomposes slowly, and the compound would be almost completely hydrolyzed (99%) in about 70 days, and at pH 8.0 it would be completely hydrolyzed in 9 days. Baygon would be more stable in neutral

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waters, but in slightly alkaline waters the compound is hydrolyzed, and 99% decomposition would occur in about 107 days at pH 8.0. In highly alkaline waters Sevin and baygon are expected to decompose in short periods of time. Pyrolan and dimetilan are expected to be stable to hydrolysis within the pH range usually encountered in natural waters.

The temperature variations of natural waters are also expected to be important in the stability of the carbamate insecticides. As shown in Table IV, the second order rate constant for hydrolysis increases two to three times with a temperature rise from 20°–30°C. Therefore, the stability in natural waters is expected to depend largely on the temperature. In cold waters, the compounds would persist for longer periods of time while at higher temperatures they hydrolyze rapidly.

The salt content of natural waters (ionic strength) seems also to be important, affecting the rate of hydrolysis of the carbamate insecticides possibly resulting from decreasing the activity of the hydroxyl ions and the carbamates (*2*). Karinen *et al.* (*13*) reported that about 50% of Sevin in sea water at 20°C and pH 8.0 was hydrolyzed in 4 days. However, in dilute solutions the same ratio of hydrolysis has been achieved under similar conditions within 1.3 days only. Therefore, Sevin and baygon, which hydrolyze at the slightly alkaline pH range, are expected to be more stable towards hydrolysis in waters of high salt contents than in brackish or sweet waters.

The suspended solids in rivers and streams which are largely composed of clay minerals do not seem important in decontaminating waters polluted with Sevin, 1-naphthol, baygon, or dimetilan by adsorptive processes. The amounts of these compounds adsorbed on kaolinite and bentonite ranged between 0.03–0.19 mg/gram of clay from an initial concentration of 5.0 mg/liter. The amounts of clay needed to remove 1.0 mg/liter of these compounds from the water ranged between 12–163 grams. Such amounts of suspended solids are rarely encountered in natural waters. Pyrolan, however, is more easily adsorbed on both clay minerals than other tested insecticides. The level of adsorption on bentonite was higher than on kaolinite. Thus 0.65 gram of bentonite was needed to remove a 1 mg/liter of pyrolan while 3.5 grams of this clay were required to remove 5.0 mg/liter. Such clay concentrations may be present in turbid natural waters high in suspended solids, and pyrolan is removed to an appreciable extent by adsorption on mineral particulate matter rich in montmorillonite content.

Ultraviolet light induced marked changes in the structure of the four carbamate insecticides. The primary effect of ultraviolet irradiation was to cleave the esteric bond to form the phenol or heterocyclic enols of the carbamate esters which were further decomposed after prolonged exposure. The photodecomposition rate and the nature of the

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degradation products induced by the sunlight ultraviolet radiations (ranging between 292–400 mμ) is expected to be different from those produced by shorter wavelength irradiations used here. However, there is sufficient evidence (*8*, *9*, *10*) to suggest that photodecomposition may account for some loss of the carbamate insecticides in clear surface waters subjected to sunlight irradiation for long periods. However, in highly turbid waters where light penetration is greatly reduced, photolysis may be a minor factor in decomposing these compounds.

Sevin and baygon were amenable to biological degrading in Nile water and sewage as a result of the activities of microorganisms. Rivers and streams receiving continuous supply of Sevin or baygon are expected to develop an acclimatized flora able rapidly to use high concentrations of these compounds. Pyrolan and dimetilan, however, resisted biological oxidizing in Nile waters or sewage. Trying to obtain an acclimatized flora from Nile water or sewage capable of using these insecticides has not been successful. These two particular compounds are expected to persist in natural waters for long periods. The primary step in the microbial degradation of carbamate insecticides seems to be the enzymatic hydrolysis of the ester yielding the corresponding phenol or heterocyclic enols. Sevin and baygon seem to be readily hydrolyzed by the microbial actions, and the hydrolysis products were used further by the flora present in Nile water and sewage. Pyrolan and dimetilan, however, resist such biodegradation possibly because of the lack of a specific enzymatic system capable of hydrolyzing these compounds. This view is supported by the fact that the hydrolysis product of both insecticides was used rapidly by the microorganisms present in Nile River waters.

Thus, the persistence of the carbamate insecticides, Sevin and baygon, in natural water is affected by the different environmental conditions. The two compounds are readily hydrolyzed in slightly alkaline waters; they are also slightly adsorbed on mineral particulate matter common in streams and are slowly decomposed by solar ultraviolet radiation. Also, these compounds and their hydrolysis products are readily used by the microbial flora present in natural waters. Pyrolan and dimetilan, however, are expected to persist for long periods of time in natural waters; these compounds are resistant to chemical hydrolysis under normal pH conditions of stream waters and are not readily used by the aquatic microorganisms. Still, pyrolan is partially removed by adsorption on mineral suspended solids of a high montmorillonite content.

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Summary

The various environmental factors that may influence the persistence of some carbamate insecticides in natural waters were investigated. The

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compounds investigated were the monomethylcarbamate esters, Sevin (1-naphthyl-*N*-methylcarbamate) and baygon (2-isopropoxyphenyl-*N*-methylcarbamate), and the dimethylcarbamate esters, pyrolan (1-phenyl-3-methyl-5-pyrazolyl-carbamate) and dimetilan (2-dimethyl-carbomyl-3-methyl-5-pyrozolyl-dimethylcarbamate). Hydrolyzing these compounds with various hydroxyl ion concentrations revealed that they were unstable under alkaline conditions and that the reaction was first order with respect to the hydroxyl ion concentration. The observed second order rate constants were 2.04×10^2, 3.04×10, 7×10^{-1}, and 3.4×10^{-3}, respectively. The effect of pH on the hydrolysis rate showed that measurable hydrolysis of Sevin and baygon started at pH 7.0 and 8.0, respectively. The rate of hydrolysis increased with the rise of the pH value of the medium. Pyrolan and dimetilan, however, did not hydrolyze in the pH range of 4.0–10.0.

Adsorption of the four insecticides on the clay minerals kaolinite and bentonite, which constitute the sum of the major portion of the colloidal suspended solids in streams, was also studied. Equilibrium adsorption isotherms were constructed, and the amounts of Sevin, baygon, and dimetilan adsorbed on both clays were so small as to exclude the adsorption on particulate matter in streams as an important factor in decontamination of these compounds in natural waters. Pyrolan, however, showed appreciable adsorption on both clays which suggests that this insecticide may be removed to a great extent from natural waters by adsorption on suspended solids of high clay content.

Studies on the biodegradability of these carbamate insecticides showed that Sevin and baygon yielded to biological degradations in natural surface waters or synthetic medium seeded with sewage flora. Pyrolan and dimetilan, however, were biologically stable under these conditions. Efforts to obtain an acclimatized flora capable of using these compounds were unsuccessful. The hydrolysis products of both compounds, however, were readily used by microorganisms, indicating that the hydrolysis step is the limiting factor in the biodegrading of pyrolan and dimetilan in natural waters.

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Diazinon Degradation in Submerged Soil and Rice-Paddy Water

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Diazinon persisted for about 15 days in a flooded soil (pH 6.6) that had been treated previously with the insecticide; but, in a flooded soil that had never been exposed to diazinon, it persisted for about 60 days. Similarly, water from a diazinon-treated rice field inactivated the insecticide within 5 days after incubation. Microorganisms that developed in response to insecticide application accelerated its hydrolysis and the subsequent mineralization of the hydrolysis product, 2-isopropyl-6-methyl-4-hydroxy pyrimidine, to CO_2. A Flavobacterium *sp., isolated from water of a treated rice field, had exceptionally high capability to metabolize diazinon as sole carbon source. This provides unequivocal evidence that microbes are involved in the rapid inactivation of diazinon in rice fields.*

Flooded soils differ from unflooded soils in physical, chemical, and microbiological properties. The presence of highly oxidized compounds and various aerobic microorganisms characterizes unflooded soils while anaerobic microorganisms are dominant in submerged soils. A flooded soil consists principally of a predominantly reduced soil layer and a thin oxygen-rich surface soil with a column of water generally 2–5 cm over the soil surface.

Recent studies indicate that a compound that persists in unflooded environments does not persist necessarily in flooded conditions, and a compound which persists in flooded environments does not persist necessarily

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Table I. Stability of Diazinon and Certain Other Organic Pesticides in Unflooded and Flooded Soils[a]

	Persistence	
Pesticide	*Unflooded*	*Flooded*
Diazinon	180 days (*1*)	60 days (*2*)
Heptachlor	9 years (*3*)	30–90 days (*4*)
DDT	4–10 years (*3*)	60–180 days (*4, 5*)
Lindane	11 years (*3*)	30–90 days (*6, 7*)

[a] Summarized from reported work.

in unflooded conditions. The relative persistence of diazinon has been compared with that of other insecticides in flooded and unflooded soils (Table I). Diazinon [O,O-diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate] decomposed more rapidly in flooded soils than in unflooded soils. Soil type (*2, 8*), moisture (*8, 9*), pH (*2, 9, 10*), and certain constituents (*11*) affect the persistence of diazinon in soils. Certain chlorinated hydrocarbons [γ-, α-, β-, and δ-isomers of benzene hexachloride (*6, 7*), DDT (*4, 5*), methoxychlor (*4*), and heptachlor (*4*)] have been also reported to break down rapidly in submerged soils. However, the mechanism in the degradation of these insecticides differ from that of diazinon.

The fate of diazinon in submerged soil and paddy water with emphasis on its metabolism by microorganisms is reviewed. The first part of this paper deals with the fate of diazinon in submerged soil which has never been exposed to diazinon. The detailed experimental procedures and results of this phase have been reported elsewhere (*2, 12*). The second part will center largely on enhanced diazinon metabolism in submerged soil and paddy water following repeated applications at levels and intervals recommended for rice pest control.

Diazinon Degradation in Soils

Diazinon persists for six months or longer in nearly neutral unflooded soil (*1, 8*). Its life is shorter in acid soils (*9*) because of the rapid hydrolysis under acid conditions (*10, 13, 14*). Diazinon applied to a nearly neutral flooded soil persists only for 2 months (*2*). When applied to an acid soil (Luisiana clay with an initial pH 4.7) immediately after submergence, its persistence is shortened considerably (*2*). In such an acid soil if the application of diazinon is delayed to two or three weeks after submergence, the insecticide is not degraded rapidly because soil pH rises by about two units after reduction in waterlogged soils. In fact, diazinon controlled rice pests for 15 days after it was applied to Luisiana clay that was kept submerged for four weeks before application (*15*).

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Microbial vs. *Chemical Role in Diazinon Degradation*

Bro-Rasmussen *et al.* (*8*) studied the interaction of diazinon concentration, soil type, and water regime in sterile and nonsterile systems. They found that heat treatment increased the persistence of diazinon irrespective of moisture level, soil type, and insecticide concentration. They concluded that microorganisms in the soil decomposed the insecticide applied to the soils that they tested. However, Getzin (*9*) and Lichtenstein *et al.* (*16*) observed similar degradation rates in autoclaved and nonautoclaved soils, indicating abiotic degradation of diazinon in such soils. Konrad *et al.* (*10*) presented also strong evidence for chemical hydrolysis of diazinon. Certain chemical constituents of those soils accelerate the chemical hydrolysis of diazinon as suggested by a recent report of catalytic hydrolysis of diazinon by Cu II (*11*).

In our studies, diazinon was applied to autoclaved and nonautoclaved samples of an acid soil (Luisiana clay) and two neutral soils (Maahas clay and a clay loam), and the soils were flooded. The insecticide disappeared from both autoclaved and nonautoclaved acid soils, indicating that degradation was nonbiological. Degradation was more rapid in the nonautoclaved sample than in the autoclaved sample of the other two soils (*2*). The half-lives of diazinon in the nonautoclaved and autoclaved Maahas clay were 8.8 and 33.8 days, respectively; the corresponding values for the clay loam were 17.4 and 43.8. The increased breakdown of diazinon in nonautoclaved soils of neutral pH can be attributed to microbial participation, but some of the insecticide was lost from the autoclaved lots of these soils as well as a result of chemical degradation and volatilization.

Thus in nonautoclaved flooded soils diazinon is degraded by a combination of biological and nonbiological phenomena. In the biological breakdown, the microorganisms may attack the insecticide molecule directly through specific enzyme systems or indirectly by generating a condition such as reduction of the submerged soil, which favors chemical degradation.

In both flooded and nonflooded soils, the first step in the degradation of diazinon is hydrolysis at the P–O–pyrimidine bond, but the rate of hydrolysis is faster in flooded soil than in unflooded soil (*12*). Furthermore, the pyrimidinyl moiety of the hydrolysis product persists in flooded soil, but it mineralizes readily in unflooded soils. As a result, the hydrolysis product tends to accumulate in submerged soils and only 0.4–0.7% of the added ^{14}C as diazinon was recovered as $^{14}CO_2$ during the 50 day incubation period (*12*). In unflooded soils a significantly higher proportion of the radioactivity added as ^{14}C-diazinon was released as $^{14}CO_2$ (*1*). Further oxidation of the hydrolysis product is retarded or arrested in the

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absence of molecular oxygen in predominantly anaerobic submerged soil if an oxygenase is involved in the reaction.

Biological Degradation Enhanced by Repeated Applications

Diazinon applied to paddy water at 2 kilogram/ha active ingredient every 20 days has controlled for several years common insect pest of rice at the International Rice Research Institute. After its continuous use for three and a half years, its efficiency for controlling rice brown planthoppers (*Nilaparvata lugens* Stål) declined. Preliminary studies indicated that biodegradation might be involved. Detailed studies were undertaken and reported elsewhere (*17*). However, brief descriptions of the procedures used will be provided for better clarity to the reader.

The persistence of diazinon in soil from a rice field that had never been exposed to diazinon before and in soil from a previously treated field was studied under flooded conditions. The treated fields received granular applications of diazinon (*17*) at rates and intervals recommended for rice pest control *viz.* 2 kilogram/ha active ingredient every 20 days. Soils (Maahas clay, pH 6.6) were collected from three treated and three untreated fields 12 days after the third application. Soils were air-dried and screened (2mm); 20 gram samples of these soils were placed in test tubes and flooded with 25 ml of aqueous diazinon solution. The insecticide residues from the soils incubated at 30°C were extracted periodically with hexane–acetone (*2*) and analyzed in a gas chromatograph fitted with a cesium bromide detector as described earlier (*18*).

Analyses of residues in the soils after incubation showed that the persistence of diazinon was considerably shorter in the previously treated soil than in the untreated soil. The half-life value for diazinon in previously treated soil was 1.7 days while in the untreated soil it was 9.9 days. Most of the insecticide added to the previously treated soil was lost within 10 days. Paddy water from the same fields were tested also for diazinon-degrading activity (*17*). Again water from a rice field treated previously with diazinon inactivated the insecticide more rapidly than did the water from an untreated field. In the water from the previously treated field the insecticide dissipated completely within 3–5 days of incubation after an initial lag of 1–2 days (*17*, *18*). Table II summarizes the results of the study on the stability of diazinon in soil and paddy water. The data indicated clearly that a factor capable of degrading diazinon developed in rice fields of the Institute farm after insecticide applications. The diazinon-degrading factor, found in the diazinon-treated rice fields in the Institute farm, was noticed also in three other locations in the Philippines (*19*).

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Table II. Stability of Diazinon in Soil and Paddy Water

System	*Source treated previously with diazinon*	*Period of persistence*
Unflooded soil	No	6 months (*1*)
Flooded soil (Maahas clay)	No	2 months (*2*)
Flooded soil (Maahas clay)	Yes	10 days (this report)
Paddy water (from Maahas clay)	No	2 months (*17*)
Paddy water (from Maahas clay)	Yes	3–5 days (*17*)

In addition, the following results (*see 17*) indicated that the factor was biological:

1) An initial lag preceded rapid degradation (Figure 1).

2) The pH of the incubation mixture (paddy water or soil plus diazinon solution) ranged from 7.1–7.8 (*17*) at which diazinon is known to be chemically stable (*13, 14*).

3) Aerobic conditions during incubation favored the degradation although some degradation occurred also under anaerobic conditions (*17*). Perhaps, facultative anaerobes are involved in the degradation. This view is supported by the observation that a *Flavobacterium* sp. isolated from paddy water of treated field could degrade diazinon under aerobic and anaerobic systems but more rapidly under aerobic conditions (*20*).

4) Autoclaving, Millipore filtration, and the presence of streptomycin retarded the degradation (*17*).

5) Degradation was rapid at 23° and 30°C but not at 0° and 40°C (*21*).

6) When radioactively labelled diazinon was incubated with water from a diazinon-treated field, more than 66% of the added ^{14}C was liberated as $^{14}CO_2$ in five days (Figure 1). Adding streptomycin to this incubation mixture, however, prevented the breakdown of the diazinon molecule and the formation of $^{14}CO_2$. No appreciable degradation of diazinon was evident on its incubation with water from untreated field.

In attempts to characterize the factor that developed in the rice fields of the Institute farm, we enriched paddy water from treated fields with specific diazinon-degrading microorganisms (*17*). The insecticide in aqueous solution was incubated with paddy water from a treated field at a one to one ratio. When the insecticide disappeared from this mixture, 5 ml of this incubation mixture was incubated again with 5 ml of aqueous diazinon solution. During a 10 day incubation period, five transfers were made. Following the first transfer, the insecticide disappeared from the incubation mixture between 96–120 hours, but in less than 6 hours after the fifth transfer (*17, 22*). Evidently, the factor originally

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present in the water of the treated field proliferated following additions of diazinon, causing enhanced inactivation of the insecticide with each transfer (*22*). During the same incubation period (10 days), no appreciable degradation of diazinon occurred after the first addition of insecticide to water from an untreated field (*17*).

A dilution (10^{-4}) of the enriched culture thus prepared from water of a treated field was mixed with a mineral agar medium (*17*) containing diazinon as sole carbon source and 2% agar. Bacterial isolates appearing on this medium were transferred to sterile mineral solution plus aqueous diazinon solution. None of the colonies degraded diazinon (*17*). When the same colonies were transferred to the mineral solution but supplemented with diazinon dissolved in ethyl alcohol, several isolates decomposed the insecticide (*17*). The most active isolate, identified as *Arthrobacter* sp., metabolized diazinon only in the presence of additional carbon source (Table III). It has been reported earlier that an *Arthrobacter* sp., isolated from diazinon-treated soil, also metabolized diazinon only when dissolved in ethyl alcohol (*23*, *24*) or in the presence of an additional carbon source (*23*). Furthermore, the same *Arthrobacter* sp. decomposed diazinon by a synergistic action when incubated together with a *Streptomyces* sp. isolated also from diazinon-treated soil (*24*). No change in the diazinon molecule was evident when these two organisms were incubated separately.

Table III. Degradation of Diazinon in the Presence of Additional Carbon Source by an *Arthrobacter* sp. Isolated from Paddy Water of a Diazinon-Treated Field[a]

	Diazinon (p.p.m.) recovered at 6 days after incubation	
Mineral medium +	*Inoculated*	*Uninoculated*
Aqueous diazinon	22.4	22.9
Aqueous diazinon + 0.5% glucose	0	22.9
Diazinon dissolved in alcohol	9.0	18.9

[a] Adapted from Sethunathan and Pathak (*17*).

Bacteria were isolated also from paddy water of diazinon-treated fields in Maligaya Rice Research and Training Center, Philippines, following the procedures used in the isolation of bacteria from the Institute rice fields. The most active isolate, *Corynebacterium* sp., decomposed diazinon in mineral solution only in the presence of ethyl alcohol or glucose (*25*).

The inability of these several bacterial isolates (among these, only two isolates were identified as *Arthrobacter* sp. and *Corynebacterium* sp.)

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to decompose diazinon as sole carbon source was surprising. The factor that developed in the diazinon-treated field was able to inactivate the insecticide within 3–5 days without any additional carbon source.

We were interested in isolating a microorganism from paddy water of treated field, capable of decomposing diazinon as sole carbon source by using a maximum dilution frequency technique. Enrichment cultures from paddy water of diazinon-treated field were prepared as before. The enriched culture was diluted serially (10^{-12} as against 10^{-4} in the previous test). Each dilution was tested for its diazinon-degrading activity by incubating 1 ml of each dilution with 9 ml of mineral solution plus aqueous diazinon solution. Dilution 10^{-7} appeared to be the maximum dilution point for the degrading factor; dilutions beyond this point did not retain the degrading principle (*20*). The degrading agent in dilution 10^{-7} was further enriched by incubating 1 ml of this dilution with 9 ml of mineral solution plus aqueous diazinon solution. After 3 days of incubation, a loop of this mixture was spread on a modified Wakimoto agar, mineral agar, and potato–dextrose agar. Wakimoto's original medium (*26*) was modified by substituting potato with ferrous sulfate. Modified Wakimoto medium, used in this Institute to isolate *Xanthomonas oryzae*, a bacterial pathogen of rice, was composed of calcium nitrate (0.5 gram), sodium phosphate (2.0 grams), peptone (5.0 grams), sucrose (20.0 grams), ferrous sulfate (0.5 gram), and distilled water (1000 ml). Clear yellow and white bacterial colonies developed only on modified Wakimoto agar. Diazinon was degraded when yellow bacterial colonies were transferred to the mineral solution containing aqueous diazinon as sole carbon source (Table IV).

The yellow bacterium decomposing diazinon as sole carbon source was gram-negative, flagellate, rod-shaped, and facultative anaerobe. The bacterium was identified as *Flavobacterium* sp. by J. F. Bradbury of Commonwealth Mycological Institute, England. This bacterium grew well on modified Wakimoto agar but not on original Wakimoto agar. The metabolism of diazinon as sole carbon source by *Flavobacterium* sp. is being investigated.

Table IV. Degradation of Diazinon in a Mineral Medium with Diazinon as the Sole Carbon Source by a *Flavobacterium* sp.[a] Isolated From Paddy Water of a Diazinon-Treated Field

Incubation, Hours	*Diazinon recovered, p.p.m.*	
	Inoculated	*Uninoculated*
0	26.3	26.7
24	4.8	25.7
48	0.01	26.5

[a] Isolated by maximum dilution frequency method.

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Table V. Bacteria Capable of Decomposing Diazinon in Pure Culture

a. *In the presence of additional carbon source*
   1. *Pseudomonas melophthora* (*27*)
   2. *Trichoderma viride* (*28*)
   3. *Arthrobacter* sp. (*17, 23*)
   4. *Streptomyces* sp. (*2*)
   5. *Corynebacterium* sp. (*25*)

b. *By the synergistic action of 2 microorganisms*
   1. *Arthrobacter* sp. + *Streptomyces* sp. (*24*)

c. *As a sole carbon source*
   1. *Flavobacterium* sp. (this report)

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Isolating *Flavobacterium* sp. with exceptionally high ability to metabolize diazinon as sole carbon source and other bacteria (*Arthrobacter* sp. and *Corynebacterium* sp.), which could degrade diazinon only in the presence of additional carbon source, provides strong evidence that microbes rapidly inactivate diazinon in the rice field.

Earlier reports show that microorganisms metabolize diazinon either in the presence of additional carbon source (*2, 17, 23, 27, 28*) or synergistically by the action of two microorganisms (*24*). Bacteria capable of degrading diazinon are listed in Table V. These studies show clearly that attempts to isolate a bacterium utilizing diazinon as sole carbon source have been unsuccessful. In this report, using a maximum dilution-frequency technique, we have succeeded in isolating a *Flavobacterium* sp. from paddy water of diazinon-treated fields that could metabolize diazinon as sole carbon source.

Biochemical Hydrolysis Enhanced by Repeated Applications

Isotope studies were conducted to determine the biochemical pathway of enhanced diazinon metabolism observed in paddy water of treated fields. In these studies, diazinon labelled at 4-position on the pyrimidine ring was incubated with paddy water from diazinon-treated and untreated fields as described earlier (*17*). The enclosed CO_2-free system was utilized to measure the $^{14}CO_2$ production, and the radioactivity in the evolved $^{14}CO_2$ was assayed by liquid scintillation counting (*17*). Diazinon residues were analyzed by gas–liquid chromatography after extraction with hexane. The results are summarized in Figure 1. Water from treated rice fields was capable of metabolizing 4-carbon atom on the pyrimdine ring, releasing more than 66% of the added radioactivity as $^{14}CO_2$ within five days of incubation. Such rapid metabolism was not observed with water from untreated field.

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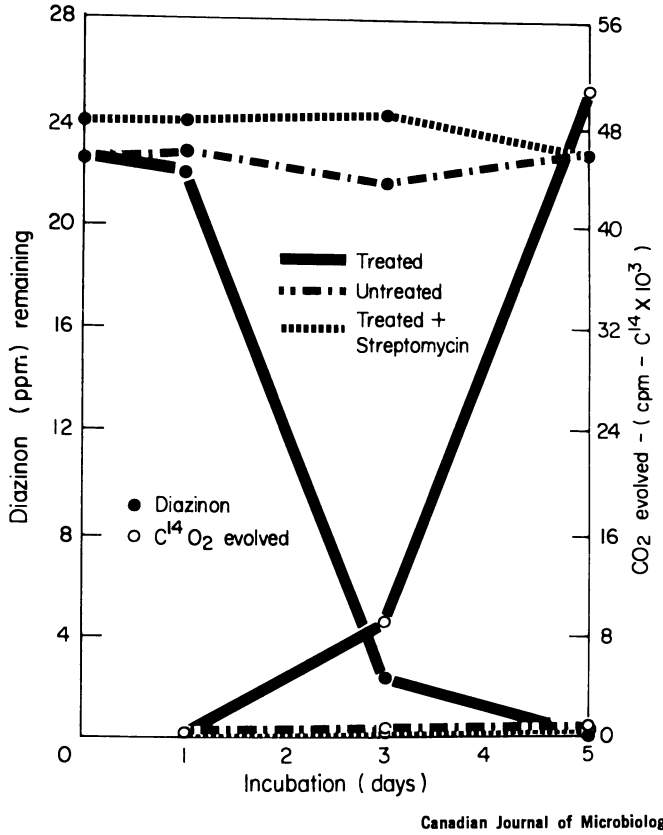

Figure 1. Diazinon degradation after its incubation with water from a rice field treated previously with diazinon and from an untreated rice field (17)

This study indicated also that within three days of incubation with water from treated field, diazinon was converted to a metabolite (s) which was mineralized to CO_2 within the next two days. To study the nature of the metabolite (s), the residue in the incubation mixture (paddy water from treated field plus ^{14}C-diazinon) were extracted with chloroform–diethyl ether (one to one) and analyzed by cochromatography and radioautography (*12*). Detailed procedures and results of this study will be published (*19*). In summary, these studies indicate that diazinon is rapidly hydrolyzed by a biological action in paddy water of treated fields. The hydrolysis product, 2-isopropyl-6-methyl-4-hydroxypyrimidine increased with a corresponding decrease in diazinon levels in the incubation mixture until 75 hours and thereafter declined (Figure 2). No other radioactive metabolite was detected in the autoradiograph of the incubation mixture. Addition of streptomycin to this incubation mixture

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blocked the formation of 2-isopropyl-6-methyl-4-hydroxypyrimidine indicating microbial participation in the initial hydrolysis of diazinon. The pH of the incubation mixture without streptomycin was 7.8, and with streptomycin it was lowered to 7.3. However, these pH differences cannot account for the rapid hydrolysis of diazinon in paddy water when streptomycin is not present. No appreciable hydrolysis occurred when diazinon was incubated with paddy water from untreated fields for five days.

Formation of 2-isopropyl-6-methyl-4-hydroxypyrimidine by chemical hydrolysis of diazinon in soils has been reported earlier (*1, 10, 12*). The initial step in diazinon degradation in soils appeared to be chemical hydrolysis principally (*1, 9, 10*) and soil microflora attack the products of the chemical reaction, the pyrimidine and diethyl-thiophosphoric acid, rather than intact diazinon (*23*). Based on these results, Kearney and Helling (*29*) in their review on reactions of pesticide in soils included hydrolysis of diazinon as a clear example for chemical transformation of pesticide in soil. In contrast, the data summarized here demonstrated the rapid biological hydrolysis of diazinon molecule which occurs when

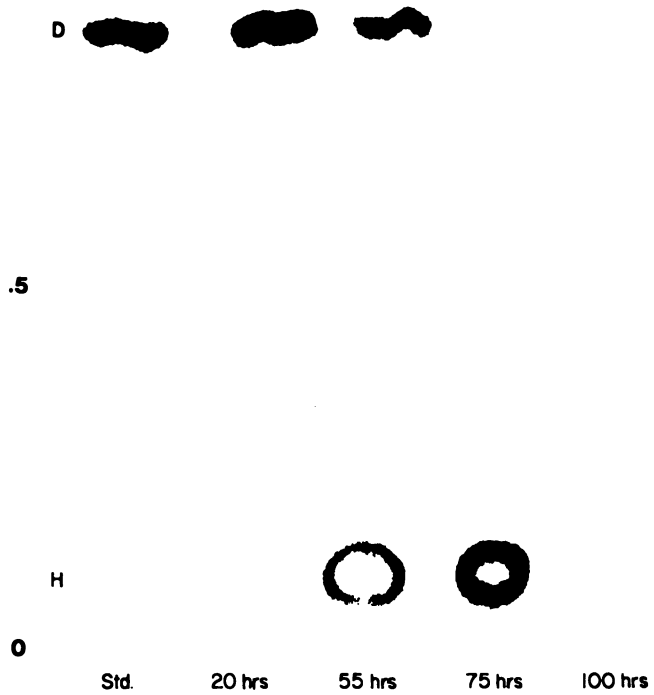

Figure 2. Formation of hydrolysis product, 2-isopropyl-6-methyl-4 hydroxy pyrimidine (H) from ^{14}C–diazinon (D) incubated with water from a rice field treated previously with diazinon (19)

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populations of appropriate microorganisms build up in paddy water following repeated applications.

The mechanism through which diazinon-degrading microorganisms build up in rice fields after repeated applications is not clear. Audus (*30*) offers two major possibilities for this phenomenon: chance mutation or adaptive enzymes. However, our results suggest that microbial systems with constitutive enzymes are involved. For example, *Flavobacterium* sp. retained its diazinon-degrading activity when introduced into a medium with diazinon as sole carbon source, even after repeated subcultures on modified Wakimoto agar (*20*). Also, the resting cells and cell-free suspensions of the bacterium decomposed the insecticide without a lag phase. The lag phase in diazinon breakdown in paddy water (Figure 1) could be attributed to the time required for the proliferation of appropriate constitutive microorganisms to levels which effect detectable rates of degradation.

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13

Degradation of Chlorinated Hydrocarbons under Anaerobic Conditions

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Chlorinated hydrocarbons are degraded slowly in the environment. Some degradation could be anaerobic, but except for DDT, the direct evidence is small. The major reaction of DDT is reductive dechlorination to DDD. It occurs with many microorganisms at equal rates with either o,p′- *or* p,p′- *DDT. Other analogs of DDT do not undergo this reaction. The degradation of DDT always yields varying amounts of unidentified polar compounds. Metabolic pathways for formation of DDA and dichlorobenzophenone from DDT have been proposed, but supporting evidence has not been conclusive. Pentochlorocyclohexane and* CO_2 *have been suggested as products of anaerobic BHC degradation. Some microbial cultures degrade aldrin, dieldrin, and endrin, but all cultures were studied aerobically. Anaerobic degradation of the other chlorinated hydrocarbons has not been studied.*

The chlorinated hydrocarbons are the most stable pesticide residues in the environment. The other pesticides in use break down rapidly so that measurable quantities rarely exist many months after their application. The most common residues are DDT (Table I) and dieldrin, followed by lindane, chlordan, heptachlor, and aldrin (*1*). Prevalence of a residue is a result of the amount of pesticide used and the resistence of the pesticide to degradation.

Polychlorinated biphenyls (PCB), while not pesticides, are chlorinated hydrocarbons. Many chemical and toxicological characteristics of PCB's are similar to those of the chlorinated hydrocarbon pesticides (*2*). PCB's are distributed widely, but their significance as residues has not been established.

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The average persistence in the environment is greatest with DDT and dieldrin with lesser times for the other chlorinated hydrocarbons (*1*). Chemical and biological factors are involved in the environmental degradation of pesticides. It is difficult to evaluate the contribution of each factor to the degradation of the chlorinated hydrocarbons.

Microbiologists have been agreed generally that microorganisms either exist or can be adapted, which can metabolize any organic compound. Thus, no pesticide should be considered totally resistent to possible microbial degradation. The persistence of the chlorinated hydrocarbons does suggest that proper organisms and/or conditions are not prevalent.

This review summarizes some of the proposed products and pathways of the anaerobic degradation of the chlorinated hydrocarbon pesticides. Some aerobic work is included because the organisms studied existed anaerobically in the environment. The most work has been conducted with DDT and related compounds. There is some information on dieldrin with less on endrin and lindane. The other chlorinated hydrocarbons have received little attention.

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Table I. Common Names, Abbreviations, and Chemical Names

Aldrin—1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-*endo, exo*-5,8-dimethanonaphthalene
BA—*p*-chlorobenzoic acid
BHC—Mixed isomers of 1,2,3,4,5,6-hexachlorocyclohexane
Chlordan—1,2,4,5,6,7,10,10-octachloro-4,7,8,9-tetrahydro-4,7-methyleneindane
DBH—*p,p'*-dichlorobenzhydrol
DBP—*p,p'*-dichlorobenzophenone
DDA—bis(*p*-chlorophenyl) acetic acid
DDD—1,1-dichloro-2,2-bis(*p*-chlorophenyl) ethane
DDE—1,1-dichloro-2,2-bis(*p*-chlorophenyl) ethylene
DDMS—1-chloro-2,2-bis(*p*-chlorophenyl) ethane
DDMU—1-chloro-2,2-bis(*p*-chlorophenyl) ethylene
DDNU—1,1-bis(*p*-chlorophenyl) ethylene
DDT—1,1,1-trichloro-2,2-bis(*p*-chlorophenyl) ethane
Dieldrin—1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo, exo*-5,8-dimethanonaphthalene
DPM—*p,p'*-dichlorodiphenylmethane
Endrin—1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo, endo*-5,8-dimethanonaphthalene
Heptachlor—1,4,5,6,7,8,8-heptachlor-3a,4,5,5a-tetrahydro-4,7-*endo*-methanoindene
Kelthane—1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethanol
Lindane—gamma isomer of 1,2,3,4,5,6-hexachlorocyclohexane
Methoxychlor—1,1,1-trichloro-2,2-bis(*p*-methoxyphenyl)ethane

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Lindane

Lindane (γBHC) undergoes anaerobic degradation by microorganisms; however, the quantity and identity of degradation products has not been established.

MacRae *et al.* (*3*) found that both the γ and β isomers of BHC were degraded within 30 days in unsterilized flooded soils. The compounds were stable in sterilized soils implying microbial action. When ^{14}C labeled γ-BHC was incubated with soil, $^{14}CO_2$ was produced. This requires breakage of the ring. The reaction may not be of great importance because the amount of $^{14}CO_2$ evolved was small compared with the loss of BHC.

Allen (*4*) attributed the loss of activity of BHC in cattle dips to microbial action. Gases produced from cultures of *Clostridium sporagenes* and *Escherichia coli* in suspensions of γ-BHC yielded benzene as well as *m*-dinitrobenzene. Quantitative data were not presented.

A microorganism isolated from submerged soil, *Clostridium* sp., anaerobically converted ^{14}C-γ-BHC to a metabolite that was further degraded (*5*). The metabolite was not the dehydrochlorination product, γ-pentachlorocyclohexene, found in aerobic degradation. Reasoning by analogy with DDT degradation, it was suggested that the metabolite was the reductive dechlorination product, γ-pentachlorocyclohexane.

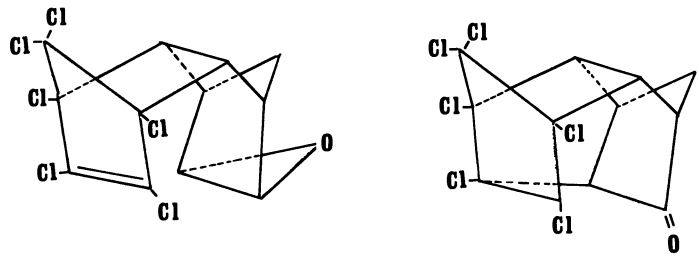

Figure 1. Keto-endrin, identified by Matsumura et al. (7) *as a product of endrin degradation by soil microorganisms*

Endrin and Dieldrin

The cyclodiene pesticides, dieldrin and endrin, are degraded by microorganisms. Many of the isolates tested were obtained from soils that had been treated with dieldrin. Generally, this work was carried out aerobically, but the cultures were not aerated. Some facultative anaerobes may have similar reactions under oxygen-deficient and anaerobic conditions. One study included organisms that are anaerobic in

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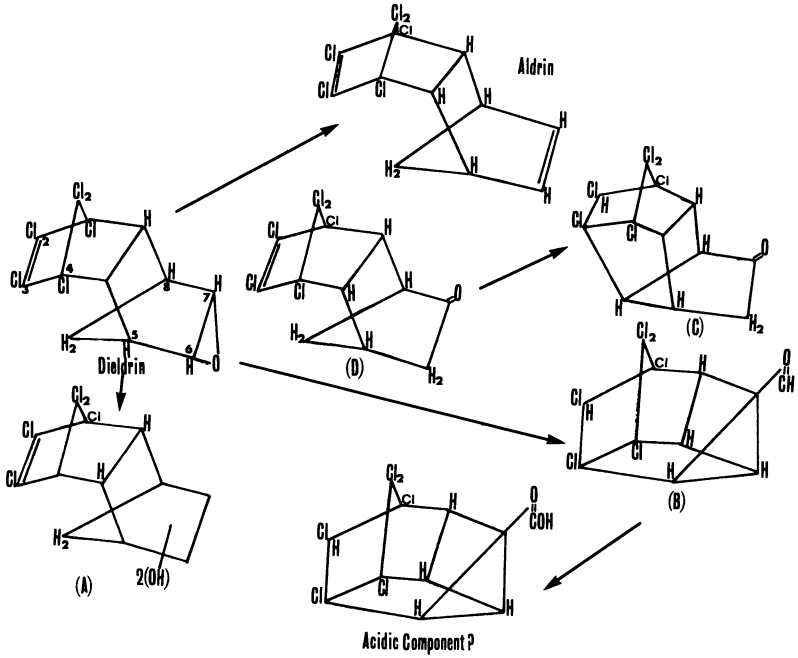

Figure 2. Dieldrin degradation pathways by the soil microorganism, Pseudomonas *sp., as proposed by Matsumura* et al. (10). *The structures of D and C were established. The structures shown for B and the acidic component were considered the most likely ones. The arrangement of the two hydroxyl groups in D is unknown except that one of them is at the 6-carbon position.*

their natural states. Therefore, one cannot rule out the possibility that some of the reactions described occur anaerobically.

Patil *et al.* (*6*) isolated a number of organisms from soil capable of degrading endrin. No product was identified definitely. All organisms capable of degrading dieldrin were capable also of degrading endrin. This should not be unexpected because endrin is an endo-endo isomer of dieldrin. More recently Matsumura *et al.* (*7*) studied a series of soil microorganisms and isolated five metabolites. The only metabolite which was identified positively was keto-endrin (Figure 1), and this was the most common metabolite. It occurred in all of the cultures which degraded endrin and in many cases was the major metabolite. The other metabolites appeared to be either ketones or aldehydes with five or six chlorine atoms.

Matsumura and Boush (*8*) incubated ^{14}C-dieldrin with microorganisms isolated from soil. A number of the isolates degraded dieldrin, and several products were obtained. The only product identified was 6,7-

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trans-dihydroxydihydroaldrin. Wedemeyer (*9*) reported the same product with aerobic degradation of dieldrin by *Aerobacter aerogenes*.

Matsumura *et al.* (*10*) in a detailed study of one of the previous isolates, *Pseudomonas* sp., proposed the products shown in Figure 2. In contrast to the previous study (*8*) 6,7-*trans*-dihydroxy-dihydro-aldrin was not identified. The finding of aldrin is interesting because aldrin is converted to dieldrin by many microorganisms aerobically (*11*).

Several strains of microorganisms isolated from lake water, lake bottom silt, rat intestine contents, and rumen contents, as well as the previously described soils (*8*, *10*), produce photodieldrin (Figure 3) from dieldrin (*12*). The conditions in the rumen, rat intestine, and lake bottom silt would be anaerobic normally. The tests were conducted under oxygen deficient conditions; however, because the reaction is a simple rearrangement, there is no reason to believe it could not occur anaerobically.

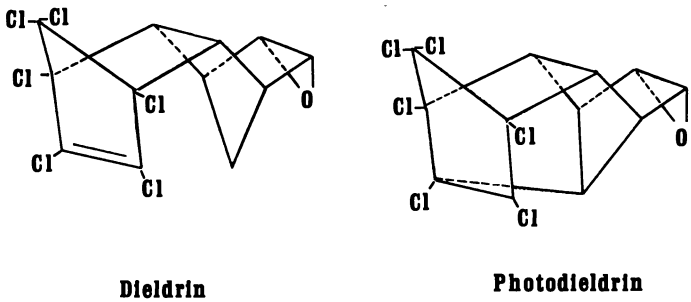

Figure 3. Photodieldrin, found by Matsumura et al. (12) *as a product of dieldrin metabolism by microorganisms from several sources*

There is evidence that the source of isolate or the exact experimental conditions may influence the results. For example, the soil fungus, *Trichoderma viride*, is effective (*13*) and ineffective (*14*) in degrading dieldrin.

Polychlorinated Biphenyls

The possible anerobic degradation of PCB's has not been studied directly. However, we have analyzed samples of silage containing the PCB, Aroclor 1254. The silage had been stored for several months and had undergone normal fermentation. The gas chromatogram of the standard is identical to the chromatogram of the sample obtained from silage (Figure 4). If anaerobic degradation had occurred, it was uniform for all components. It is unlikely that uniform degradation would occur.

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In contrast, when the silage is fed to cows, many of the peaks with the lower retention time are removed by the animal (Figure 4). The silage fermentation may not be a good test of possible anaerobic degradation. We found much less degradation of DDT in silage than is usual for other anaerobic systems (*15*).

DDT and Related Compounds

Most studies of the anaerobic degradation of chlorinated hydrocarbons have been carried out with DDT and related compounds. Various microorganisms were studied either as pure cultures or as mixed cultures from environmental sources. In appropriate cases the organisms were studied under anaerobic and aerobic conditions. In many cases the two conditions yielded similar end products.

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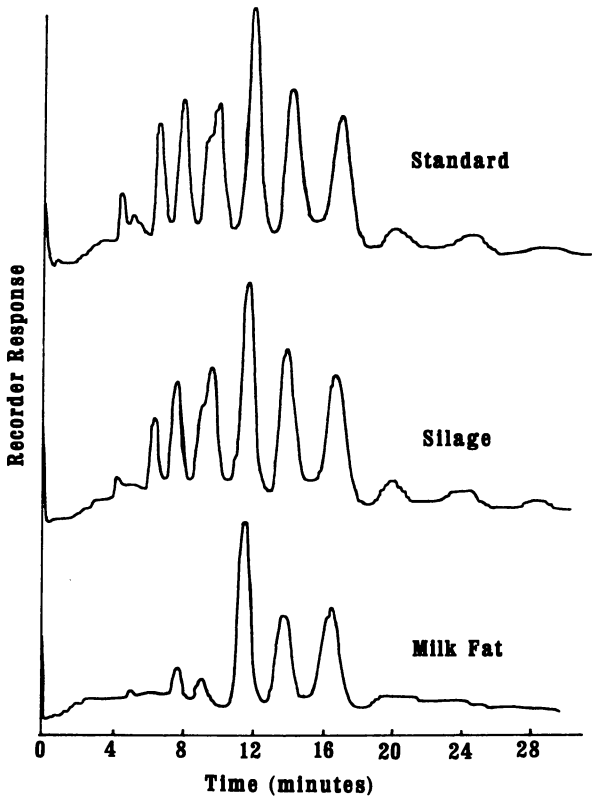

Figure 4. Gas chromatograms of the polychlorinated biphenyl. Aroclor 1254, recovered from silage and milk fat of cows fed the silage.

Table II. Investigations of the Degradation

Investigators	*Organism or Source*
Wedemeyer (*16, 18, 26*)	*Aerobacter aerogenes*
Plimmer *et al.* (*24*)	*Aerobacter aerogenes*
Mendel *et al.* (*17*)	*Aerobacter aerogenes*
Mendel and Walton (*21*)	*A. aerogenes* & *E. coli*
Barker *et al.* (*22*) and Barker and Morrison (*28*)	*Proteus vulgaris*
Braunberg and Beck (*30*)	Pure cultures—Rat G.I.
Miskus *et al.* (*33*)	Lake water
	Rumen
Fries *et al.* (*25*)	Rumen
Stenersen (*20*)	Pure cultures—fly excreta
Johnson *et al.* (*19*)	Pure cultures—plant sources
Kallman and Andrews (*23*)	Yeast
Ko and Lockwood (*31*)	Soil
Chacko *et al.* (*14*)	Soil–Fungi
	Soil–Actinomycetes
Patil *et al.* (*6*)	Pure cultures—soil
Matsumura and Boush (*13*)	*Trichoderma viride*
Guenzi and Beard (*29*)	Soil
Fries *et al.* (*15*)	Silage

[a] Studies are listed aerobic if it is not clear from the authors description or the organisms used that the system was anaerobic.
[b] Most investigators also found undergraded DDT. When recovery data was given, the formation of unidentified products was implied.

Recent investigations of the degradation of DDT by microorganisms are listed in Table II. Some of the papers have one or more deficiencies that make their evaluation difficult. It was not always possible to determine whether the systems were aerobic or anaerobic. The expression of results on a qualitative basis or as a percent of the products found without recovery data does not allow one to evaluate properly the significance of a given reaction. The final deficiency is the use of inconclusive means of identification, particularly for minor products.

DDD is the major product when DDT is incubated anaerobically with microorganisms. This reductive dechlorination has occurred in many but not all of the aerobic studies. *Aerobacter aerogenes* has been studied aerobically and anaerobically in parallel experiments. In some cases the reaction was similar under both conditions (*16, 17*), but it was suggested that anaerobic conditions increased the yield of DDD (*18*). In contrast

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of DDT by Microorganisms

Conditions[a]	*Products Reported*[b]
Aerobic	DDD, DDE, DDMU, DDMS, DDNU
Anaerobic	DDD, DDE, DDMU, DDMS, DDNU, DDA, DPM, DBH, DBP
Anaerobic	DDD
Aerobic	DDD[c]
Aerobic	DDD
Anaerobic	DDD[c]
Aerobic	DDD, DDMU, DDMS
Anaerobic	DDD, DDE
Anaerobic	DDD
Anaerobic	DDD
Anaerobic	DDD[d]
Aerobic	None
Anaerobic	DDD, DDE
Aerobic	None
Anaerobic	DDD
Aerobic	DDD
Anaerobic	DDD
Aerobic	None
Aerobic	DDD
Aerobic	DDD, Kelthane, DDA
Aerobic	DDD, DDE, Kelthane
Anaerobic	DDD, DDE, Kelthane, DDA, DBP, DPM, BA
Anaerobic	DDD

[c] *o,p'*-DDT was used.
[d] Both *o,p'*- and *p,p'*-DDT were used.

Johnson *et al.* (*19*), using pure cultures from plant sources, found that no organism including *A. aerogenes* produced DDD under aerobic conditions. Most of these organisms produced DDD under anaerobic conditions.

The studies of Stenersen (*20*) suggest an explanation for the failure of some aerobic cultures to produce DDD. Several cultures of facultative anaerobes formed DDD under a nitrogen atmosphere (anaerobic) or in unshaken cultures (oxygen deficiency). However DDD was not formed when the cultures were aerated fully. The investigators reporting no DDD aerobically aerated their cultures by shaking (*14*, *19*). To the extent that it can be determined, the investigators reporting DDD did not aerate their cultures (*6*, *13*, *16*, *17*, *21*, *22*). Thus, one may conclude that while anaerobic conditions are not strictly necessary for the reductive dechlorination of DDT to DDD, the presence of oxygen tends to inhibit the reaction.

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Small amounts of DDE have been reported in some studies (Table II). The quantity rarely exceeded 5% of the recovered products. In the more common case the amount of DDE recovered did not exceed the amount in the uninoculated controls. The occurrence of DDE as a product shows no consistent relationship to organisms or conditions studied. DDE can be formed easily by the chemical dehydrochlorination of DDT. Therefore, it is reasonable to conclude that DDE is not a normal product of microbial metabolism. The pH of the media may be a factor affecting the formation of DDE. The information given in most of the studies is not sufficient to determine if this could be the case.

At times it has been suggested that DDE was an intermediate in the formation of DDD from DDT. Two lines of evidence have eliminated this possibility. DDD has never been a product when DDE was the substrate (*16, 18, 23, 24*). More conclusive evidence was provided by Plimmer *et al.* (*24*); they used DDT labelled with deuterium in the 2-position of the trichloroethane group. The DDD produced contained the deuterium label which rules out DDE as an intermediate.

The groups on the phenyl rings appear to have some effect on the reductive dechlorination of the trichloroethane. Thus, *o,p'*-DDT is dechlorinated reductively to *o,p'*-DDD by mechanisms and rates similar to the reductive dechlorination of *p,p'*-DDT (*17, 25*). In contrast, Mendel *et al.* (*17*) were unable to obtain reductive dechlorination when the phenyl chlorine atoms of *p,p'*-DDT were replaced by ethyl or methoxy groups. It is interesting, however, that they were unable to recover completely the methoxychlor. This indicates anaerobic degradation of this compound by some other route.

When one considers the further metabolism of DDT, the picture becomes more confusing. Wedemeyer (*16, 26*) has proposed the pathway from DDD to DBP shown in Figure 5. This pathway is similar to that proposed originally for rats by Petersen and Robinson (*27*). It was developed by detecting the succeeding metabolites after incubating the various proposed intermediates with *A. aerogenes*.

There are several reasons to question the significance or even the existence of this pathway in its present form. Some of the steps in the sequence were worked out using aerobic conditions. However, it was necessary to use anaerobic conditions to convert DDNU to DDA and DDA to DBP (*16*). It is also significant that it was not possible to obtain a product beyond DDNU when DDT, DDMU, or DDMS were used as starting materials.

Some discrepancies appear also in the study of the steps from DDA to DBP (*26*). When DDA was incubated with *A. aerogenes* for seven days, the recovery of DDA decreased from 260 to 47 μg. The recovery of DPM rose to 250 μg at four days and decreased to 10 μg at

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seven days. However, the recoveries of DBH and DBP were never more than 1 μg. This would be an unlikely situation if DBP were a stable end product of DDA degradation. One must conclude that most of the DDA was metabolized to an undetected product by a different pathway.

With a few exceptions, no other investigators have reported the intermediates shown in the pathway. After incubating DDD with *Proteus vulgaris* for 84 days, Barker and Morrison (*28*) found DDMS (<1%) and DDMU (about 10%). The cultures became alkaline with age suggesting that the DDMU could have been formed by chemical dehydrochlorination of DDD. Guenzi and Beard (*29*) incubated ^{14}C-DDT with soil and reported finding DDA, DBM, and DBP. However, the quantities were less than 1% of the original DDT, and thin layer chromatography was the only means of identifying them.

In the other studies reviewed, DDD and occasionally DDE were listed as the only products detected. The methods used should have detected compounds such as DDMU that can be extracted with nonpolar solvents. In some cases failure to find the proposed intermediates was stated more explicitly (*24*, *30*).

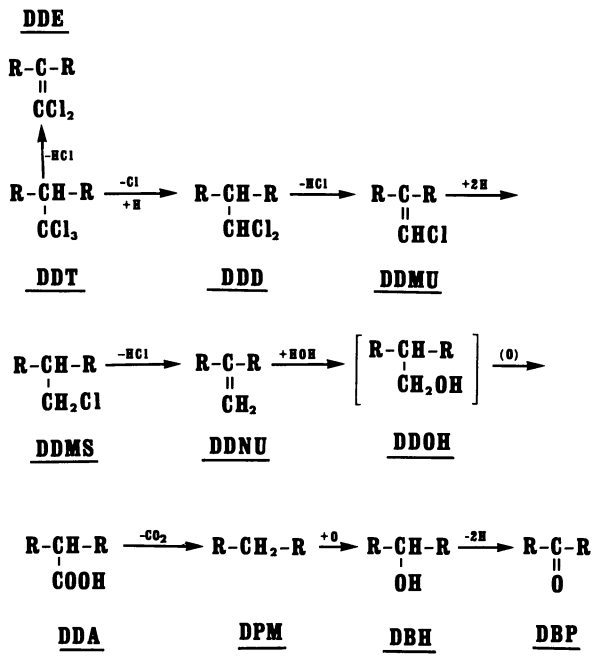

Figure 5. DDT degradation pathways by Aerobacter aerogenes *as proposed by Wedemeyer* (16, 26). *The* p-*chlorophenyl groups are represented by R.*

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Complete recovery of the starting material was not obtained in any of the studies that included recovery data. When unlabelled DDT was used, it was impossible to determine whether the extraction methods were inadequate or whether the material has been converted to polar or volatile compounds. However when ^{14}C-DDT was used, there was no evidence of volatile products (*29*) and evidence was presented that most of the unextracted ^{14}C was associated with the cell debris (*24, 25*). We concluded that most of the ^{14}C was present as polar compounds because it was not possible to extract the dehydrochlorination products of DDT and DDD after digesting the cell debris with KOH (*25*).

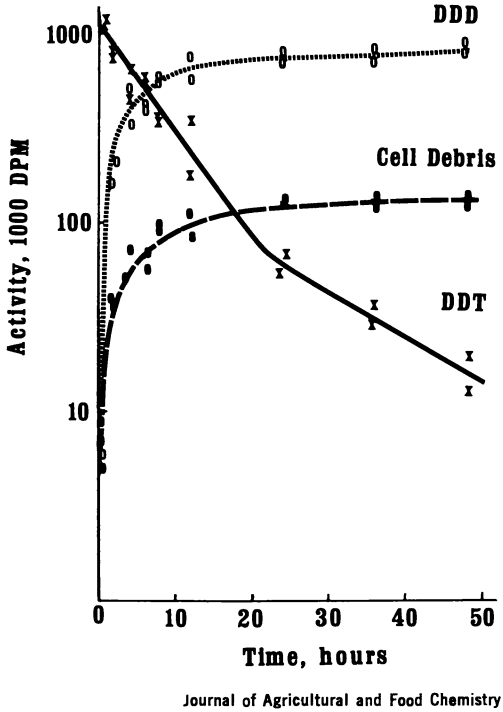

Figure 6. ^{14}C in the DDT, DDD, and cell debris fractions recovered from incubation of ^{14}C-DDT with rumen microorganisms (25)

Measuring the undegraded DDT and the products formed at several time intervals during an incubation will frequently provide information that cannot be obtained by measurement at a single time. As an illustration, our study (*25*) of the degradation of ^{14}C-DDT by rumen microorganisms is shown in Figure 6. The amount of ^{14}C-DDD increased, reached the maximum, and remained at this level. The picture was

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similar for ^{14}C in the cell debris. The amount of ^{14}C in the cell debris was a constant ratio to the amount of ^{14}C-DDD. Thus, the material in the cell debris appears to arise by a pathway that did not involve DDD. If it arose through a pathway involving DDD, one would expect DDD concentration to rise to a peak and then decline. The ^{14}C in the cell debris would continue to increase as long as DDD was present.

The mechanism of the reductive dechlorination of DDT to DDD has not been delineated. Typically when uninoculated cultures are used as a control, the only material found is unaltered DDT (*17, 21, 29, 30, 31*). Reduced cytochrome oxidase has been suggested as a cellular agent in the reductive dechlorination of DDT to DDD (*18*). However, there are a number of nonbiological processes that degrade DDT to DDD and other products. DDT was converted to DDD and DDE in heparinized chicken blood stored at −20°C (*32*). Reduced porphyrins (*33*), photolysis (*34, 35*), chromous chloride (*36*), and elevated temperature (*37*) have catalyzed the conversion of DDT to DDD. It is interesting also that many of the compounds in Figure 4 were also products of these chemical systems (*34, 35, 36, 37*). Thus, whether the conversion process is purely biochemical or chemical cannot be stated clearly. Regardless of the catalyst, it appears that the microorganisms are a significant contributor to the reaction when they are used.

The free radical mechanism has been suggested to account for the various end products of photolysis of DDT (*35*). The work of Miller and Narang (*34*) on the induced photolysis of DDT is of particular interest for application to biological systems. Their work was based on the use of a sensitizer which is photoexcited first and then transfers an electron to organic halides. This should produce dissociation of the organic halide in analogy with a large number of reactions of the type

$$\mathrm{A} \xrightarrow{h\nu} \mathrm{A}^*$$

$$\mathrm{A}^* + \mathrm{RCl} \rightarrow \mathrm{A}^{\cdot\cdot} + \mathrm{R}\cdot + \mathrm{Cl}^-$$

The decomposition of DDT induced by photolysis of diethylanaline produced DDD, DDE, and dichlorobenzophenone. All have been suggested as products of anaerobic degradation of DDT.

In microbial fermentation the oxidation of organic matter would result in the reduction of a number of oxidation–reduction systems. Glass (*38*) has proposed that these systems could provide an electron for the dissociation of DDT to form a free radical. A generalized scheme, using this electron source in place of the photoinduced charge transfer, is illustrated in Figure 7. Reactions analogous to those proposed for photolysis (*34*) could produce other products.

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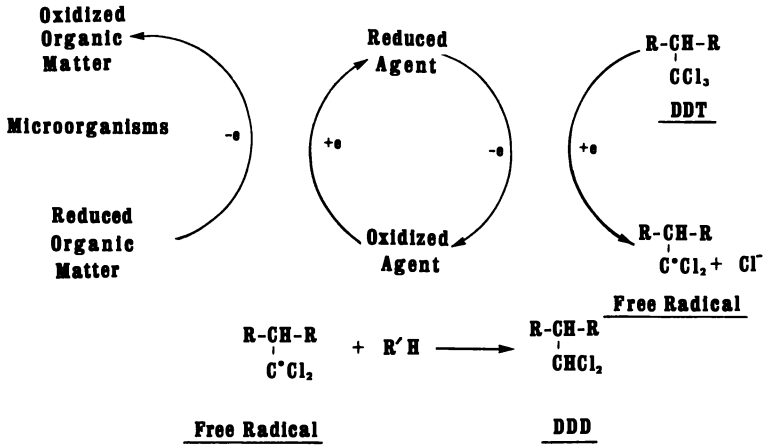

Figure 7. A possible mechanism for the reductive dechlorination of DDT to DDD, adapted from a proposal by Glass (38). *The* p*-chlorophenyl groups are represented by R.*

At present there are no experimental data to determine whether this is a mechanism of DDT degradation by microorganisms. However, it is consistent with our studies (25) in which end products other than DDD were formed without DDD as an intermediate.

Conclusions

Chlorinated hydrocarbons present more serious residue problems than the other pesticides. This is a result of two characteristics of these compounds: they are nonpolar and are relatively resistant to degradation by either chemical or biological means in the environment. Regardless of their future use, these compounds will be present in the environment for many years.

Because the chlorinated hydrocarbons are nonpolar, they are relatively immobile in the environment. They will concentrate in biological systems, and because of resistance to degradation, their concentration will be magnified as one moves up the food chain.

Anaerobic degradation is one means of reducing the residues in the environment. With the exception of DDT anaerobic degradation of chlorinated hydrocarbons has not been the subject of significant study. The emphasis on DDT is appropriate because it is the most abundant residue. However, even in this case, little has been established except that DDD is a major product of DDT degradation.

Several factors should be considered when designing studies of degradation of pesticides. Often studies will be encountered in which the organism was isolated from an anaerobic environment but was studied

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aerobically. While the results may be interesting, it is not always possible to apply them to the environment.

Quantitative data should be obtained whenever possible. Identification of a product is only the first step in evaluating its significance. The quantity produced and its chemical and biological characteristics must be determined also. Lack of recovery data will leave the possibility that the major product was overlooked completely.

In the studies reviewed, the nonpolar products have received the most emphasis. This is appropriate because these nonpolar products can present residue problems as serious as those presented by the parent compound. The polar products generally will be less serious because they will be dispersed rather than concentrated in the environment.

Despite the residue significance of the nonpolar products, these compounds have received much less study than the parent compounds. DDE is a striking example. It is the major residue in the organisms at the higher levels of the food chain; however, compared with the number of studies of DDT, its possible degradation by biological systems seldom has been studied.

Because the chlorinated hydrocarbons are the most significant residues, it is important to obtain information on their degradation. This information must be applied ultimately to the situation as it exists in the environment. Therefore, the studies should be designed with this ultimate purpose in mind.

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