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MODELING OF PESTICIDES IN THE AQUEOUS ENVIRONMENT

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INTRODUCTION

The United States Environmental Protection Agency has recently proposed water quality criteria for pesticides which are much stricter than any that have been applied before. For example, the U.S. EPA has proposed that the recommended maximum limit in whole (unfiltered) water for DDT be 0.002 ug/l. The recommendation for parathion and toxaphene are 0.004 ug/l and 0.01 ug/l, respectively. They have also recommended that general standard of $0.001 \times 96 \text{ hr LC}_{50}$, where 0.01 is the application factor which relates acute to chronic toxicity.

These criteria are based on acute and chronic toxicity of pesticides as well as accumulation of some of them in food webs, which can result in potentially significant concentrations in organisms of higher trophic levels. These new proposed criteria require a much better understanding of the environmental behavior of pesticides in order to predict their concentrations in aquatic systems and their impact on biological communities.

Pesticides manufacturers and environmental quality control regulatory agencies must develop a systematic approach for reviewing for each potential source the environmental behavior of all existing, and especially, new pesticides. This paper discusses the use of environmental chemistry models to predict the potential environmental behavior and impact of new pesticides.

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PREVIOUS ATTEMPTS TO MODEL PESTICIDE BEHAVIOR

Two reports have been published recently of attempts to mathematically describe DDT behavior in the environment. These models focus on a pesticide already in the environment. However, a model that successfully predicts DDT behavior might be useful in predicting behavior of future pesticides.

The first model is one proposed by Harrison et al. (1970). This model is essentially an attempt to describe DDT behavior in a food web. Since it deals primarily with DDT in organisms, it is concerned with only a small fraction of the DDT present in the environment. Harrison et al. derived an expression for the flow of DDT through what they call the substrate, which includes soil, water, and sediment; however, it has no practical use since it does not include terms for volatilization, sorption-desorption, and microbial decomposition, the factors that are probably most important in controlling DDT movement and persistence.

The equations presented to describe DDT movement in a food web are based on the assumption that the sole source of DDT to a trophic level is that contained in material ingested by organisms of that trophic level, and that the means of elimination of DDT from a trophic level are death of an organism in that level, excretion, and metabolism. No consideration is given to the possibility that the rates of excretion and metabolism are dependent on the concentration of DDT in an organism. The basic limitation of this model is that it fails to take into account the possibility of partitioning of DDT between lipids in an organism and the surrounding water. Hamelink, Waybrandt, and Ball (1971) found that algae, crustaceans, and fish were able to accumulate DDT directly from water and, in the case of crustaceans, concentrations of DDT in the organisms declined when DDT concentrations in water were reduced. Johnson et al. (1971) have found that crustaceans concentrate DDT from water and, in the case of *Daphnia magna*, can accumulate levels of over 100,000 times the DDT concentration in water. Oysters are also quite effective at concentrating DDT and in at least one instance (Westlake and Gunther, 1966) removed DDT from water with a calculated efficiency of about 90 percent.

Although it appears that many invertebrates are very effective at concentrating DDT from water, this process may not be as important in fish. Macek and Korn (1970) compared rates of accumulation of DDT from water and from food by brook trout. They found that at concentrations to which the trout would be exposed in the environment, DDT was accumulated about ten times more rapidly from food than from the surrounding water. Thus, while direct exchange of DDT between organisms and water is probably very important for organisms in lower trophic levels, such as algae and crustaceans, it may be less important for higher trophic levels containing fish.

Harrison et al. (1970) make further assumptions to simplify their equation and arrive at the conclusion that the time required to reach an "equilibrium" concentration in a trophic structure "lies between four times the average life span of the longest-lived species and the sum of the life spans for all trophic levels," a conclusion that has been widely quoted in the literature. A careful examination of some of the simplifying assumptions, that organisms retain all DDT ingested and that they neither metabolize nor excrete DDT, indicates however, that the assumptions and thus the conclusion are probably in error. Macek et al. (1970) found that rainbow trout retained only 20 to 24 percent of ingested DDT, and Macek and Korn (1970) found that brook trout retain about 35 percent after 120 days and that the amount retained decreased with time. Thus, it appears unlikely that organisms retain all DDT that they ingest. A number of aquatic organisms, including crustaceans (Hamelink, Waybrandt, and Ball, 1971; Johnson et al., 1970) and fish (Macek et al., 1970) are capable of metabolizing and/or excreting DDT. Even if the prediction of this model is correct, it does not represent a significant advance since it predicts a time limit for an "equilibrium" rather than what ultimate DDT levels will occur in organisms.

The objective of Harrison et al., to reliably predict DDT behavior in organisms, is a necessary goal for any attempt to model the environmental impact of a pesticide. Unfortunately, they fall far short of their objective and succeed instead in mathematically obscuring the obvious, that some part of the DDT ingested by an organism will be retained by it, while ignoring other vital factors that control DDT distribution.

Another model of DDT movement has recently been proposed by Woodwell, Craig, and Johnson (1971). This model is an attempt to predict what will eventually happen to DDT in the environment on a global scale. Their approach is to estimate residence times of DDT in soil, in the atmosphere and in the upper, mixed layer of the ocean, which they feel are the major DDT reservoirs. They then use these to predict movement of DDT from soil to the atmosphere to the upper layer of the ocean, and finally to the abyss.

After consideration of estimates of the amount of DDT that has been applied to soils in the United States and the amount that is remaining in these soils, Woodwell, Craig, and Johnson (1971) calculate a DDT soil residence time of about five years. They estimate further that less than one percent of DDT is transported from the point of application by harvest with the crop and about 0.1 percent is lost in water runoff. They assume that biochemical degradation is insignificant and that volatilization is the chief mode of removal from soil. Although it is possibly true that degradation is insignificant compared to volatilization of DDT in soil, there is no hard evidence to support this assumption. If degradation is

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significant, this would affect an estimate of the amount of DDT entering the atmosphere but would have no effect on their estimate of residence time in soil.

For atmospheric residence time, Woodwell, Craig, and Johnson assume a time constant of about four years. They base this assumption on an estimated concentration in rain of 60 ng/l, which may be too high, and an average annual rainfall of one meter. This yields an atmospheric residence time of 3.3 years. They also base it on the time constant for carbon dioxide transfer from the atmosphere to the ocean, which is about seven years. As they point out in their paper, the estimated time constant of four years is probably an upper limit. Photochemical degradation of DDT while in the atmosphere, which is not considered in this estimate, may be significant and could shorten the residence time considerably.

For the oceans the assumptions made are that the abyss is infinite for the purposes of the model and that the rate of transfer of DDT from the upper mixed layer into the abyssal region approximates the rate of carbon dioxide transfer, which is about four years. It is not known how closely DDT transfer follows carbon dioxide transfer; however, there does not seem to be any other data available.

Woodwell, Craig, and Johnson have used their model for two sets of conditions. First, that DDT use will decline to zero by 1974, and second, that DDT use will increase. Assuming that use declines to zero, the model predicts that DDT concentration reached a peak in 1964, that DDT in the air reached a peak in 1966 and will decline to ten percent of its peak concentration by 1984, and that DDT in the mixed layer of the ocean reached a peak in 1971 and should decline to ten percent of the peak value by 1993. Assuming that DDT use increases rather than decreases, the concentrations in the atmosphere and ocean should also increase.

Although this model is a step in the right direction in predicting environmental behavior of pesticides, there are a few problems with it. First, the approach taken was to base some rate estimates on DDT concentrations measured in the environment. Obviously this approach cannot be used for a pesticide that has not yet been introduced into the environment. Another problem is the difficulty in making reliable estimates of DDT concentrations in the atmosphere and ocean and in computing residence times. Thus, although the mathematical equations may themselves be correct, the numerical constants used to solve them may be seriously in error. Perhaps the greatest problem with this model, however, is that it predicts only average pesticide concentrations in the atmosphere and oceans. As the designers of this model point out, local fluctuations in concentration may be expected to be large. In particular, areas such as lakes, rivers, and estuaries near points of

application would possibly be more affected than the ocean by surface runoff and might at times have undesirably high pesticide concentrations not predicted by this model.

The United States Environmental Protection Agency is currently developing a model for predicting pesticide movement from soil to water (Nicholson, 1974). When completed, this model will be applied on a river basin scale in order to establish safe limits for pesticide application. Such a model should be useful in predicting localized impact of a pesticide on the environment.

FACTORS CONTROLLING ENVIRONMENTAL BEHAVIOR OF PESTICIDES

As indicated in the previous discussion, the currently available models of pesticide behavior have little or no predictive value. An effective model must consider sources of a pesticide, amount and rate of transfer through various parts of the environment, rates of physical, chemical, and biochemical transformations of both the parent compound and any environmentally significant degradation products, and the biological impact of the ultimate environmental concentrations. Some of the factors that may be significant in these processes are discussed here.

Pesticides may enter the environment through a number of different pathways (Westlake and Gunther, 1966), but the major sources are probably agricultural use, industrial and municipal sewage, and efforts to control aquatic weeds. Wastewater disposal and aquatic weed control generally involve direct introduction of pesticides into the aqueous environment, while pesticides applied for agricultural purposes must usually follow indirect routes to reach an aquatic system.

The method of application partly determines the fate of an agricultural pesticide. For example, Hindin, May, and Dunstan (1966) found that less than 35 percent of DDT and other pesticides applied by aircraft spraying reached the area being sprayed. Presumably, some of the remainder was carried into the atmosphere. Judging from the concentration of organochlorine pesticides found in rainwater in the United States (Cohen and Pinkerton, 1966) and Britain (Tarrant and Tatton, 1968) atmospheric transport of pesticides is considerable and has even been proposed as the major route by which DDT and related compounds reach the oceans (Risebrough, 1969; Woodwell, Craig, and Johnson, 1971). Other means of applying pesticides, such as direct application of herbicides to soil, probably result in less initial loss to the atmosphere.

Once a pesticide reaches the soil, a variety of fates may befall it. If it is systemic some of it will be taken up by the

crop and either degraded, volatilized, or transported away with the harvest. Uptake of non-systemic pesticides such as DDT is small, and loss by this route is usually considered insignificant (Hindin, May, and Dunstan, 1966). Another possibility is that the pesticide may be carried away by seepage and enter the groundwater. This is especially possible for compounds that are fairly water soluble and are not strongly sorbed by soil particles. For example, 2,4-D in manufacturing wastes is able to enter groundwater and result in contamination of wells (Walker, 1961). Compounds that have a low water solubility and tend to be sorbed do not migrate significantly into the groundwater. For example, Terriere et al. (1966) estimated that less than 0.1 percent of DDT applied to orchards entered groundwater and found that most of the pesticide was still in the top ten inches of soil.

Another means of removal from the point of application is direct surface runoff. This can occur with the pesticide dissolved in the runoff water, associated with suspended material in the water or both. Although the percentage of the pesticide applied that is lost through this route may be small, Hindin et al. (1966) estimate that less than 0.01 percent of DDT applied to a cornfield was lost in the runoff, it probably represents the major pathway by which agricultural pesticides enter lakes, streams, and rivers. The amount entering the environment by this avenue would be dependent on the solubility of the pesticide, the suspended solids concentration in the water, the sorption characteristics of the soil, and the amount of precipitation and runoff. The factors responsible for loss of the bulk of a pesticide from soil are probably losses to the atmosphere and degradation by soil microorganisms. These routes may account for up to 50 percent of DDT lost from soil (Terriere et al., 1966).

Movement into the atmosphere may occur both by direct volatilization, which is probably enhanced by covaporization with water, and by association with particulate materials carried off by wind. Pesticides in the atmosphere may then reenter the aqueous environment in the form of dustfall and precipitation at another location. Biological degradation may be complete or it may simply result in new compounds, as is the case in the formation of DDE from DDT and dieldrin from aldrin. The environmental behavior and significance of possible metabolites must therefore also be considered. Pesticides exhibit a wide range of degradability, from a few weeks for organophosphorus pesticides such as parathion to several years for chlorinated hydrocarbons such as DDT and dieldrin (Kearney, Nash, and Isensee, 1969). The relative importance of volatility and degradability would depend on the characteristics of a pesticide. For example, for a slowly degraded, volatile compound such as DDT, volatilization may dominate (Woodwell, Craig, and Johnson, 1971) while for a rapidly degraded compound such as parathion, degradation most likely dominates.

Once a pesticide reaches the aquatic environment, either through runoff, direct application, or atmospheric fallout, it can undergo a number of interactions with other components of the system. Perhaps the most important factor is the interaction of the pesticide with suspended matter and sediment. The nature of this interaction will depend on solubility of the pesticide and characteristics of the sediment such as organic content, clay content, and pH. Natural organic matter may play a major role in sorption of pesticides onto sediments. Sediments with high organic contents show increased tendencies to sorb lindane (Lotse et al., 1968) and the herbicides 2,3-D, 2,4,5-T, and 4-amino-3,5,6-trichloropicolinic acid (Hamaker, Goring, Youngson, 1966). Humic material may be responsible for this phenomena since phthalate esters have been found associated with a soil humic fraction (Ogner and Schnitzer, 1970) and humic material has been found capable of strongly sorbing DDT from solution (Wershaw, Burcar, and Goldberg, 1969). Another factor that may influence sorption is pH. While pH seems to have little influence on sorption of chlorinated hydrocarbons (Huang, 1971), it does have a marked effect on pesticides containing acidic functional groups. Hamaker, Goring, and Youngson (1966) found that sorption of 4-amino-3,5,6-trichloropicolinic acid increased sharply below the pK of this compound and at any pH the amount sorbed was related to the amount of unionized acid present.

A pesticide that is associated with suspended material will eventually enter the sediment. Once in the sediment, it may be rereleased into the water, taken up by organisms, altered or degraded by microorganisms or simply buried. Many sediments are anaerobic, a condition under which many compounds are not readily degraded. Some compounds, however, such as DDT and lindane, are degraded more readily under anaerobic than aerobic conditions (Hill and McCarty, 1967). Thus, the migration of compounds such as DDT into sediments is desirable because it places them in an environment that promotes their degradation.

Some pesticides may remain dissolved in the water rather than enter the sediments, and pesticides in sediments will probably also be present in the overlying water, at least in trace quantities. Pesticides present in water may have a number of fates. They may be sorbed by the sediments, degraded by microorganisms, taken up by organisms or diluted in the oceans. Degradation by microorganisms is probably not as likely to occur in water as it is in soil or sediment because of the lower concentration of microorganisms. However, some degradation will probably occur. Uptake and concentration by organisms, while potentially important to the organisms themselves is very small compared to the total amount of pesticides in the environment, at least in the case of DDT (Woodwell, Craig, and Johnson, 1971).

EVALUATION OF BIOLOGICAL IMPACT

Once environmental pesticide levels have been predicted, it becomes necessary to determine their significance to aquatic organisms. The usual method for accomplishing this is to perform some sort of bioassay. This involves measuring either short-term acute effects or long-term chronic effects of the pesticide on a test organism. The organism chosen for the test should be the most sensitive one that is significant to the aquatic system in question, and the organism should be at the most susceptible stage of its life cycle.

A reliable bioassay must take into account chemical factors which may affect the availability of a pesticide to an organism. Because of the low water solubility of many pesticides, they are added to bioassay water by first dissolving them in acetone or some other organic solvent. This represents an unnatural situation which could invalidate bioassay results. Natural factors that may affect bioassay results include suspended solids and dissolved organic matter since a pesticide associated with either of these may be more or less toxic than the same pesticide in the free, dissolved state.

The problem of toxicity is not simply one of acute lethal effects; it also must include chronic, long-range effects such as reducing the ability of an organism to withstand stresses or interfering with its reproductive capacity. For pesticides that are biologically concentrated, the problem is further complicated because it is necessary to predict not only the effects of pesticide levels in water and sediment but also the effects of the ultimate concentrations in organisms.

SUMMARY

Proposed EPA water quality criteria will require a much better understanding of environmental behavior of pesticides. Transport-transformation models offer potentially useful tools for predicting environmental behavior; however, existing models for aquatic systems have little predictive value. Research is needed into specific factors that control environmental behavior of pesticides in order to develop more effective models. These models will become effective management tools that can be used to determine whether a new pesticide is likely to cause significant problems in the aquatic environment. It is proposed that a pesticide regulatory agency should require all manufacturers of pesticides to develop transport transformation models for all new pesticides and that these models must be developed by the agency prior to approval for large-scale manufacturing use of the pesticide. It is further recommended that the

pesticide regulatory agency require the pesticide manufacturer to conduct the research necessary to determine how well the transport transformation model actually predicted environmental behavior at selected locations throughout the country. This requirement will ultimately lead to a significant improvement in the ability to model expected pesticide behavior, and thereby minimize the frequency with which national chemical crises such as caused by DDT occur in the future. Also, the studies on the actual fate of the pesticides used in the aquatic environment will provide the regulatory agency with the information needed to determine whether the new pesticide could be having a significant deleterious effect on aquatic ecosystems.

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