Meetings

Photoalteration of Pesticides: Summary of Workshop

The abundance of pesticides and other persistent organic compounds in our environment provokes the question of the potential effect of light on these chemicals. Evidence originating in a number of laboratories suggests that photochemical reactions involving these materials may be more common than previously suspected. In recognition of these possibilities and their significance in terms of environmental contamination, a workshop was organized by the U.S. Atomic Energy Commission and the Agricultural Research Service of the U.S. Department of Agriculture on 6 to 8 April 1972 at the National Academy of Sciences, Washington, D.C.

The objectives of the workshop were to evaluate the magnitude of the phenomenon, including a definition of the contributory factors entering into photochemical alterations. Photochemical products may have altered toxicity, biological activity, or capacity to undergo degradation by comparison with the parent substance. The possibility of using such information for the improvement of future strategies of pesticide use was also an important aim.

About 30 invited participants were selected from several disciplines to assure as broad a technical exposure as possible and to stimulate communication between disciplines as diverse as molecular photochemistry and marine biology. Representatives of governmental agencies and industry were also in attendance.

The first session was concerned with the current status of pesticide photochemistry. J. Casida (University of California, Berkeley) discussed the photolability of different classes of insecticides and summarized reaction types. Reactions of compounds ranging from the relatively labile pyrethroids and juvenile hormone analogs to the more stable organophosphorus compounds, methylcarbamates, and chlorinated hydrocarbons were included. Photoalteration products are frequently less toxic to mammals and insects than the original compounds, with several important exceptions such as dieldrin. Often a complex mixture of products results from photoalteration: the structures and biological properties of these compounds are in many cases unknown. Approaches aimed at altering photostability include modification of molecular structure at a site remote from the toxophore and the use of photosensitizers to accelerate the rate of residue degradation.

J. D. Rosen (Rutgers University) categorized reaction types common to chemical classes of herbicides. The fission of aryl halogen bonds in halogenated herbicides is typical. The reaction product is a reactive aryl radical which yields further products by subsequent attack on solvent or neighboring molecules. Such reactions in "natural waters" could yield a variety of products since the reaction is dependent on the environment of the free radical. Surface factors are important; for example, in aqueous solution paraquat is unchanged by sunlight, but on leaves or on a layer of silica gel rapid photodecomposition is observed.

In his review of the status of the photochemistry of fungicides and plant growth substances, M. Zabik (Michigan State University) highlighted examples of the types of conversions that may occur, including oxidations, reductions, substitutions, dimer formation, and other reactions. The problem of pesticide residues in the environment is greatly magnified, because relatively few of these reactions are documented and current monitoring systems fail to detect their products. Zabik made a strong plea for greater standardization, development of model systems for comparative study, and the need for data on the quantum efficiency of these reactions.

C. L. Foy (Virginia Polytechnic Institute) discussed the ways in which pesticides encounter light during field application. The volatility of pesticides is a significant factor in determining their exposure to light. Many substances are applied as finely divided droplets from either aircraft or ground sprayers, thus providing significant transport of the pesticide through air and exposure to light. Evidence exists for changed photochemistry under plant canopies where the quality and intensity of the radiation is different from that above the canopy. Unfortunately, there are no complete balance sheets which can be used to evaluate the contribution of photochemistry relative to other pathways for the dissipation of pesticides in the environment.

E. P. Lichtenstein (University of Wisconsin) spoke on factors affecting the fate of pesticides. Soils are the major recipients of pesticides, and their dissipation is influenced by biological, chemical, and physical processes. The photodecomposition of aldrin on soil and of azinphosmethyl in water, the nature of the decomposition products, and their fate in soil and in crop plants were described.

E. F. Corcoran (University of Miami) considered the distribution of pesticide residues in the aquatic environment. Using the Mississippi River system as an example, he explained that a surprisingly small amount of pesticide used in the delta area reaches the Gulf. These observations may be explained in terms of the tendency of pesticides to absorb to hydrosoils and sediment. Because the current concentrations of pesticides in the oceans cannot be accounted for solely on the basis of river drainage, rainfall and atmospheric fallout contaminated through pesticide vapors or pesticides adsorbed on particulate material are suggested as the principal modes of entry. Solubilization and accumulation of chlorinated hydrocarbons in naturally occurring lipid films or oil spills at the ocean surface may render this a potentially important site for the localization of photochemical reactions.

P. H. Wendschuh (University of California, Riverside) discussed the photochemical fate of organic molecules in the atmosphere. The phenomenon of oxygen-enhanced light absorption was stressed as a means by which nonabsorbing molecular species may be induced to absorb light and subsequently to photodecompose. Photoreactive species are present in the atmosphere, but higher concentrations are present in the air surrounding urban areas. Thus there is a much greater probability of generating atmospheric photoalteration products of pesticides where smog is prevalent.

A. A. Lamola (Bell Telephone Laboratories) emphasized the use of light sources which can be measured with respect to the intensity and spectral distribution of natural radiation. Most pesticides have triplet levels in the visible region of the spectrum, and these can be excited by the absorption of light, although with low probability. There are a number of direct and sensitized mechanisms that can conceivably permit light absorption by pesticides in the environment. On the surfaces of soil particles, for example, charge-transfer processes may be very important. Electronic energy transfer is likely to be the least important process for pesticides in the environment. Mechanisms involving ground-state complex formation and excited complex formation, electron transfer, and "chemical" sensitization are much more likely to occur, and their operation will depend on the nature of the microenvironment.

C. S. Foote (University of California, Los Angeles) outlined mechanisms of photochemical oxidation reactions occurring in the presence of oxygen. Oxygen may function as an energy acceptor in a reaction with the photoexcited triplet state of an organic molecule to give singlet oxygen, a metastable excited species. The reaction pathways of singlet oxygen with olefins, dienes, heteroatoms, and phenol were outlined. Another significant oxidation reaction is the reaction of free radicals with oxygen to give a peroxy radical which often initiates a chain autoxidation process.

O. L. Chapman (Iowa State University) outlined the relationship of organic photochemistry to pesticide chemistry. Predictably, pesticide molecules might be expected to undergo a number of types of photochemical reactions. These include rearrangement of heterocyclic or aromatic systems, photo-Fries reactions, elimination processes, and rearrangements of aromatic or olefinic nitro compounds to nitrites. Photooxidation, photoreduction, photodimerization, halogen bond cleavage, and the enhancement of phenol acidity by light are among the types of photochemical reactions that may be significant in the natural environment.

Research in photodynamic action was summarized by J. D. Spikes (University of Utah). Photodynamic damage to biological macromolecules results by selectively sensitized photooxidation of component residues such as the guanine residues in DNA and several amino acid residues in proteins. The formation of a triplet-excited state of a dye is the first stage of photodynamic action, and, subsequently, singlet oxygen may be produced by the reaction of triplet dyestuff with molecular (triplet) oxygen. In a second pathway, the triplet dye may abstract a hydrogen atom from a substrate molecule to give a free radical that undergoes oxidation. Finally, other metastable states of the dye may be formed and react with substrate. Several examples of the practical importance of photodynamic reactions were cited. The possible role of photodynamic reactions in the photodegradation of pesticides in the environment was also discussed.

W. Klein (Radiation Biology Laboratories, Smithsonian Institution) discussed efforts to quantify the intensity and quality of the visible and ultraviolet radiation which reaches the earth and which would be available for photochemical reactions. He presented results which indicated that this radiation exposure is highly variable depending on season and cloud cover, as well as smog and haze.

A general discussion of the practical significance of pesticide photoalteration followed, with D. G. Crosby (University of California, Davis) as chairman. Several panels considered various aspects of the problem, and their conclusions and recommendations may be briefly summarized as follows:

The use of pesticides, especially synthetic pesticides, undoubtedly will continue for many years, but an accounting of the distribution of pesticides is very incomplete. A fundamental problem is the location and fate of residual pesticides. Present information indicates that most pesticides are altered by sunlight, but there is very little indication of the magnitude of photoalteration processes that affect pesticides. The principal concern is with the identity and the potential hazard of photoalteration products. Development of reliable information on the toxicology of the photoproducts is impeded by several considerations: (i) ignorance of the chemical nature of the photoproducts produced; (ii) a lack of standardized procedures for the investigation of photochemical reactions; and (iii) a lack of knowledge of the nature of the macro- and microenvironments to which pesticides are exposed in the field, including the intensity and spectral distribution of solar energy at the earth's surface, the effects of adsorption on soil or foliar surfaces, and the effects of sensitizers in the solid phase or in water.

The most likely sites in which photoalteration can occur appear to be the atmosphere, either in the vapor phase or on particulates, and organic films on the surface of water, soils, and plants. A case was made for the study of the distribution of pesticides and their photoalteration products throughout all components of the environment.

Regulation of pesticides will require protocols for standardized estimation and prediction of photoalteration. Before such protocols are closely defined, gaps in current knowledge must be filled. Furthermore, many of the potential alternative methods of pest control such as the use of microbial agents, insect juvenile hormones, pheromones, and chemosterilants are not exempt from photoalteration reactions.

There is a lack of communication between researchers in basic photochemistry and those concerned with pesticide use and development. There is enough common ground between these two groups to ensure fruitful exchanges of information, and this needs encouragement. It is also possible to be critical of industry and government because of their reluctance to make public research information that has been developed to ensure the registration of propietary compounds. Some clearinghouse of photochemical information generated, regardless of source, would be extremely beneficial for more rapid progress on these problems.

Despite the proportions of the problem delineated, a somewhat unanticipated piece of information which emerged from the meeting was that research support for the general area appeared to be decreasing. A more extensive summary of the proceedings is in preparation and will shortly be available on request from J. R. Plimmer.

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Forthcoming Events

July

15–19. American **Medical** Assoc., 106th annual mtg., New York, N.Y. (E. B. Howard, 535 N. Dearborn St., Chicago, Ill. 60610)

15–19. American **Veterinary Medical** Assoc., Philadelphia, Pa. (M. R. Clarkson, AVMA, 600 S. Michigan Ave., Chicago, Ill. 60605)

15–20. American Assoc. of **Clinical Chemists**, New York, N.Y. (J. S. King, Jr., AACC, P.O. Box 15053, Winston-Salem, N.C. 27103)

15–20. World Federation of **Culture**