DDT: An Unrecognized Source of Polychlorinated Biphenyls

Polychlorinated biphenyls (PCB's) are disturbingly widespread in the earth's biosphere. They have been found in newly developed real estate lakes, at isolated geological field stations, and in polar bears and seals north of the Arctic Circle—at a large number of sites, in short, where a relatively involatile industrial chemical shouldn't appear. Their ubiquity, if not their concentrations, resembles that of the much more widely used, more volatile pesticide, DDT.

Now it appears that this similarity of distribution is far from coincidental. Kenneth W. Moilanen and Donald G. Crosby of the University of California at Davis last month told the 165th national meeting of the American Chemical Society that DDT vapor can be converted to PCB's by irradiation with ultraviolet light of the same wavelengths present in sunlight in the lower atmosphere. This finding, if confirmed, promises to change much scientific thought about the fate of pesticides in the environment.

DDT Was Thought Inert

DDT [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane] in solution or as a thin film is essentially inert to sunlight, although it is readily decomposed by ultraviolet light of shorter wavelengths. Many scientists have assumed that the vapor-phase photochemistry of DDT would be similar to that in solution, so that atmospheric degradation of DDT by sunlight would be unimportant in comparison to transport, even though the mean residence time of DDT in the atmosphere is estimated to be approximately 4 years.

DDT in water is also inert, but in soil it is converted by some microorganisms to the more volatile and more persistent pesticide relative DDE [1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene]. Since DDE is even more inert than DDT, large quantities of both chemicals should be accumulating in the biosphere. Yet global models of pesticide transport and monitoring of pesticide residues can account for only a small fraction of the approximately 2.8 billion kilograms of DDT that have been dispersed since the early 1940's, and scientists have been unable to explain this discrepancy. Moilanen and Crosby conclude that much of the DDT and DDE may have been converted to other chemicals whose presence in the environment would not necessarily be suspicious because there are other sources.

The two workers used a special reactor incorporating a collimated beam of light designed to minimize reactions occurring on the reactor walls. Control experiments were performed with both a dark reactor and one in which a convex mirror permitted light to strike the reactor walls, so that the effects of wall reactions and reactions occurring in the absence of light could be recognized and taken into account.

When DDT vapor in the presence of a large excess of air was irradiated with light in the region 290 to 310 nm, they found that the DDT was converted very slowly to DDD [1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane] and about 15 times more rapidly to DDE. After 4 days of irradiation, as much as 34 percent of the DDT was converted to DDE and about 2 percent was converted to DDD. Further experiments showed that DDD is inert to ultraviolet radiation, but that under the same conditions DDE is converted to at least nine other products, including 4,4′-dichlorobenzophenone and several chlorinated biphenyls. The photodegradation of DDE is, however, much slower than its formation from DDT.

The conversion of DDT to DDD requires the presence of a hydrogen donor because it involves replacement of a chlorine atom with a hydrogen atom; this conversion might thus be a surface reaction occurring on the reactor walls, since the extent of the reaction is probably limited not by the amount of light that reaches the reactor walls, but by the very limited number of hydrogen donors present in the reactor. In the atmosphere, then, this transformation could be enhanced by the presence of particulates and of other hydrocarbons. Apparently DDD is not degraded further in the atmosphere.

The conversion of DDT to DDE, in contrast, is probably a unimolecular reaction in which a molecule of hydrogen chloride is expelled. The DDE itself breaks down by either of two pathways. In the least important route, two molecules of DDE apparently interact directly to form small quantities of di-, tri-, and tetrachlorobiphenyls and even smaller quantities of other, as yet unidentified, chlorinated compounds.

In the more important pathway, DDE is converted at a moderate rate to DDMU [1-chloro-2,2-bis(*p*-chlorophenyl)ethylene]. This reaction, like the formation of DDD, requires a hydrogen donor, and there is some possibility that it is also a surface reaction. In the photolysis of thin films of DDE, however, a major product is 3,6-dichlorofluorenone, which is inert to further irradiation. Moilanen and Crosby found the dichlorofluorenone only when light was allowed to reach the reactor walls, so there is a strong possibility that conversion of DDE to DDMU is, in fact, a vapor-phase reaction. In either case, the degradation of DDE would be accelerated by the presence of other hydrocarbons in the atmosphere.

DDMU, in turn, is converted at a moderate rate to 4,4′-dichlorobenzophenone by interaction with oxygen. The dichlorobenzophenone is relatively stable to irradiation, but it is converted at a finite rate to 4,4′-dichlorobiphenyl. All of the biphenyls are themselves resistant to further irradiation in the vapor phase, and would thus be expected to accumulate in the biosphere.

Replace One Contaminant with Another

Extrapolated to the atmosphere, then, Moilanen and Crosby's overall scheme (Fig. 1) predicts that DDT vapor is converted to small amounts of DDD, which should accumulate in the biosphere, and to a great deal more DDE, which should degrade more slowly than DDT. DDE vapor, in turn, is converted at a moderate rate to dichlorobenzophenone (via DDMU), and then at a much slower rate to dichlorobiphenyl. Some of the DDE is also converted to 3,6-dichlorofluorenone, whose environmental fate is unknown, and to small amounts of di-, tri-, and tetrachlorobiphenyls. The principal result is thus replacement of one environmental contaminant (DDT) with another (PCB's).

Part of this scheme resembles the photochemical decomposition of solid DDT or of DDT in hexane as described in 1969 by W. D. Guenzi of the U.S. Department of Agriculture in Fort Collins, Colorado; but Guenzi did not ob-

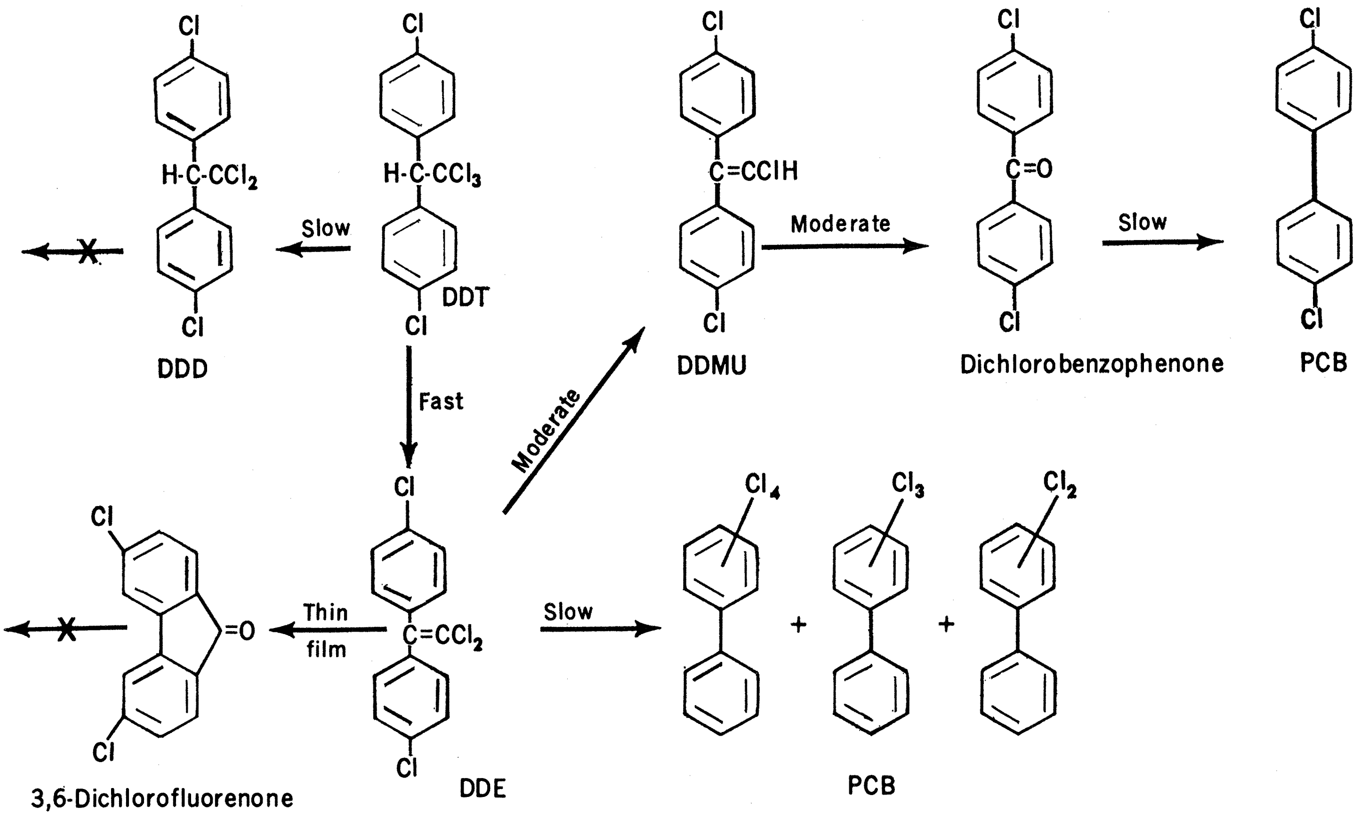

Fig. 1. Proposed scheme for the degradation of DDT vapor in sunlight. [Source: K. W. Moilanen and D. G. Crosby, University of California at Davis]

serve the formation of DDMU or of PCB's. Most important, his work was performed at 253 nm, a wavelength that is not present in sunlight in the lower atmosphere, and there has been little previous evidence of photodecomposition of DDT and DDE at the wavelengths used by Moilanen and Crosby. Evidence supporting the existence of the DDT and DDE reaction pathways in the atmosphere may, moreover, be difficult to acquire because of the presence of competing pathways to some of the decomposition products.

DDT in the soil, for example, is converted to DDE and DDD by several microorganisms, although at a very slow rate; since DDE and DDD have higher vapor pressures than DDT, however, they are preferentially released from the soil, according to Mark M. Cliath and William F. Spencer of the University of California, Riverside. They reported last fall that DDE comprises as much as 80 percent of the organochlorine chemicals in the air above freshly plowed fields that had previously been sprayed with DDT. It has recently been recognized, in fact, that DDE is now among the most abundant organochlorine contaminants in the biosphere. Even if only a small portion of this DDE were produced photochemically, however, all of it in the atmosphere would still be susceptible to further photochemical degradation.

Some Products Not Detected

Dichlorobenzophenone and DDMU have apparently not been detected in atmospheric samples, but that may be simply because no one is looking for them. Dichlorobenzophenone, moreover, is a common metabolite of many plants and animals, Crosby says, and its presence in tissues would not be suspicious.

And finally, most investigators who have detected PCB's in the environment have measured only the total amount of PCB's present and have not attempted the more difficult task of assaying the relative amounts of highly chlorinated and partially chlorinated biphenyls. There is thus little evidence to indicate whether environmental PCB's are enriched in the less highly chlorinated isomers, as would be expected if photodegradation of DDT is a major source.

Much work remains, then, before the full significance of Moilanen and Crosby's results can be assessed. As a first step, they will soon begin to study the effects of particulates and other hydrocarbons on the photochemistry of DDT and DDE. In association with J. M. Seiber, they also plan this coming winter to analyze air samples from test fields where DDT has been freshly applied (some experimental applications of DDT are still permitted, even though its use as a pesticide was banned at the end of 1972) to look for the presence of DDMU and dichlorobenzophenone. They do not expect to find PCB's in the air samples because the concentrations should be too low, but they hope that other groups will begin to examine oil slicks, biota, and other sites where PCB's are concentrated in the environment to determine whether the PCB's are, in fact, enriched in the less highly chlorinated compounds. Only when all of these results have been obtained, Crosby says, will they be confident that their laboratory work can be extrapolated to reactions in the atmosphere.—Thomas H. Maugh II

Additional Reading

1. A. R. Mosier, W. D. Guenzi, L. L. Miller, *Science* **164**, 1083 (1969).
2. G. M. Woodwell, P. P. Craig, H. A. Johnson, *ibid.* **174**, 1101 (1971).
3. M. M. Cliath and W. F. Spencer, *Environ. Sci. Technol.* **6**, 910 (1972).
4. *Degradation of Synthetic Organic Molecules in the Biosphere*, Proceedings of a Conference, San Francisco, Calif., 12 to 13 June 1971 (National Academy of Sciences, Washington, D.C., 1972).