unfavorable. Although a mechanism involving radicals can be formulated to explain 6 and 7, it is considered too speculative for discussion here.

The relative rates of decomposition of 1b, 1c, 1d, 3, and 4 as thin films on glass exposed to sunlight were determined. After irradiating for 4 h in direct winter sunlight, the films were dissolved in tetrahydrofuran and chromatographed by TLC, and the amount of recovered starting compound measured by isolating from the TLC plate and measuring the yield by uv absorption. It was found that 4 and 5 decomposed in a few days, but at a significantly slower rate than the other derivatives.

In field trials of this general class of compounds, trace pesticide activity was found after 2–3 weeks (Metcalf, 1975). These data suggested that the photodecomposition products might possess insecticidal properties. There was no reason to believe that the aldehyde or aniline products would be toxic to insects, but 2 and its analogues do show some similarities in structure to compounds involved in the adrenergic nervous system, i.e. derivatives of mandelic acid. For this reason 2b and 2c were submitted for pesticide screening. The results of these tests showed no activity at 500 μg/g against houseflies or 1 ppm against mosquito larva. Another possibility was that an intermediate dichloroaziridine (Miller et al., 1974) was present in trace amounts and was toxic. Therefore, compound 8 was prepared. However, testing of 8 also showed a complete lack of activity at 500 μg/g against houseflies and

1 ppm against mosquito larva.

SUMMARY

It has been shown that the structure of the photolabile insecticides, 1, can be manipulated to control the lifetime and still retain activity. The success of the mechanistic approach is demonstrated in that a predictable change in reactivity was observed in going from a 4-chloro derivative (1c) to a 2,4-dichloro derivative (4).

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Light-Induced Transformations of Methoxychlor in Aquatic Systems

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The light-induced decomposition of methoxychlor was studied in hexane, distilled water, and several natural water samples. Product studies indicate that the primary photochemical process for methoxychlor is the same as that for DDT—cleavage of one of its carbon–chlorine bonds to form free-radical intermediates. Subsequent reactions of these intermediates with themselves, oxygen, or the solvent determine the nature of the products. In distilled water, the major product is 1,1-bis(p-methoxyphenyl)-2,2-dichloroethylene (DMDE), a DDE analogue. A procedure was developed for computing the direct photolysis rates of pesticides in the aquatic environment. Using this procedure, we estimated that the direct photolysis half-lives of methoxychlor and DDT near the surface of a water body are 4.5 months and greater than 150 years, respectively. Direct photolysis of both DMDE and DDE by sunlight was found to be very rapid. The photolysis rate of methoxychlor under sunlight was found to be much more rapid in several natural water samples (half-lives of 2 to 5 h) than in distilled water. These results indicate that photochemical processes other than direct photolysis cause rapid degradation of methoxychlor in some aquatic environments.

The banning of DDT (except for emergency use) by the U.S. Environmental Protection Agency has spurred the use of several substitutes (Metcalf, 1972). One of the most promising substitutes is methoxychlor, a pesticide that Metcalf (1972) has termed a "persistent yet biodegradable insecticide". The biological degradation has received considerable attention. Although the chemical structure

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of methoxychlor is similar to that of DDT, investigations by Kapoor, Metcalf, and their coworkers have indicated that methoxychlor is biodegraded much more rapidly (Kapoor et al., 1970; Metcalf et al., 1971). Biodegradation by higher trophic levels proceeds mainly via O-demethylation, but microbial degradation involves slow dehydrochlorination to bis(p-methoxyphenyl)-2,2-dichloroethylene (DMDE), a DDE analogue (Paris et al., 1975).

Only a few previous studies have dealt with the abiotic degradation of methoxychlor. Merna and Eisele (1973)

found that methoxychlor decomposes very slowly in distilled water at 20 °C (half-life > 200 days). Wolfe et al. (1975) also found that chemical decomposition is very slow; the half-life at 25 °C is about 500 days and is pH independent in the pH 5–9 range. Metcalf (1972) reported that methoxychlor is quite stable to photodegradation on surfaces. However, MacNeil and co-workers (1972) found that methoxychlor, sprayed as a film on Pyrex glass, was completely decomposed by exposure to sunlight for 2 months. Crosby (1969) reported that the photooxidation of methoxychlor is also rapid in aqueous alcohol.

We studied the products and rates of the direct photolysis of methoxychlor in water and saturated hydrocarbons. Direct photolysis is defined as photodecomposition that is initiated by direct absorption of light by a pesticide. The studies in hydrocarbons were prompted by findings that water-insoluble chlorinated organics concentrate in organic surface films (Seba and Corcoran, 1969; Duce et al., 1972). In the latter part of the paper, evidence is presented that photochemical processes other than direct photolysis are mainly responsible for the light-induced decomposition of methoxychlor in some natural waters.

EXPERIMENTAL SECTION

Materials. Water used in most of the experiments was distilled, passed through ion-exchange columns, and then redistilled twice. The final distillation was carried out from permanganate in an all-glass apparatus with retention of a middle cut. Natural water samples, collected from inland surface waters in the southeastern United States, were sterilized by passage through 0.22-μm Millipore filters. Acetonitrile was purified following the procedure of O'Donnell et al. (1965) and then distilled on a spinning band column with retention of a middle cut. Spectro grade hexane from Burdick and Jackson was used without further purification. Analytical grade thiophene-free benzene from Burdick and Jackson was used for extractions from water in the kinetic experiments. Chemical Samples Company cis-1,3-pentadiene was distilled immediately prior to use. Methoxychlor and several of its photoproducts were synthesized as described below. Other photoproducts were obtained from commercial sources.

Methoxychlor. Anhydrous aluminum trichloride (7.4 g) was added slowly to a cold (4 °C), magnetically stirred solution of 10.8 g (0.10 mol) of anisole and 7.3 g (0.050 mol) of freshly distilled chloral in 250 ml of alcohol-free chloroform. The resulting deep purple mixture was stirred at 4 °C for 30 min and then at room temperature for 12 additional hours. The reaction mixture was hydrolyzed by mixing with water and the chloroform layer was dried over sodium sulfate. Upon evaporation a pale yellow oil was obtained, which crystallized upon standing. The crude methoxychlor was chromatographed on Woelm neutral alumina and was recrystallized five times from 95% ethanol to yield colorless crystals (5.5 g) melting at 89–90 °C [lit. mp 87–88 °C (Cristol, 1945)].

1,1-Bis(p-methoxyphenyl)-2,2-dichloroethylene (DMDE). DMDE was prepared by dehydrochlorination of methoxychlor in a refluxing solution of 5% potassium hydroxide in 95% ethanol. The crude product was three times recrystallized from 15% water–ethanol to yield crystals melting at 111.0–111.5 °C [lit. mp 109 °C (Schneller and Smith, 1949)]. The mass spectrum was identical with that reported elsewhere (MacNeil et al., 1972).

1,1-Bis(p-methoxyphenyl)-2,2-dichloroethane (DMDD). Anhydrous aluminum trichloride (7.4 g) was slowly added to a stirred solution of 10.8 g of anisole (0.10 mol) and 4.4 g of dichloroacetal (0.050 mol) in alcohol-free

chloroform (250 ml) with cooling by an ice bath to maintain the temperature at 4 °C. The mixture was stirred at 4 °C for 20 min and then at room temperature for 5 h. Then water (250 ml) was added and the resulting mixture was vigorously stirred for 15 min. The chloroform layer was dried over sodium sulfate and solvent was removed to yield 12.2 g of crude product. The product was recrystallized once from methanol and once from 95% ethanol to yield pure crystals, mp 116–117 °C [lit. mp 114.5–115 °C (Cristol et al., 1952)]. The mass spectrum was the same as the spectrum of DMDD reported by MacNeil and co-workers (1972).

Apparatus. GLC analyses were performed on a Tracor MT-222 gas chromatograph equipped with flame and ^{63}Ni electron capture (EC) detectors. Spectra were obtained on the following instruments: NMR, Varian HA-100 NMR spectrometer; ir, Perkin-Elmer 621 infrared spectrophotometer; electronic absorption spectra, Perkin-Elmer Model 602 spectrophotometer; mass spectra, Finnigan 1015 SL quadrupole mass spectrometer coupled with a Varian Aerograph Model 1532-B GLC and a Systems Industries 150 data system. Quantum yields were measured in a photochemical apparatus described by Moses et al. (1969). Preparative-scale GLC was conducted on a Varian Aerograph Model 90-P gas chromatograph.

Product Studies. Direct photolysis studies employed Pyrex-filtered light (>280 nm) from a high-pressure mercury lamp. Solutions were analyzed after about 30% conversion to products.

Studies in hexane or water–acetonitrile were carried out under both air-saturated and degassed conditions; methoxychlor concentrations in these solvents were in the 10^{-4} to 10^{-3} M range. Degassing was accomplished by three freeze–pump–thaw cycles on a high vacuum rack. After irradiation, the solutions were concentrated and products isolated by preparative GLC; alternatively, solutions were directly analyzed by combined GLC–MS. Products were identified by comparison of their spectra with those of authentic samples. We also looked for methylated acidic products from the photolysis in water–acetonitrile following treatment of an ethereal solution of the products with diazomethane; no such products were found.

Product studies in water were conducted in triplicate by irradiating 4 l. of a 25-ppb solution of methoxychlor. The solution was extracted by 10% ether in chloroform and then acidified to pH 2 and extracted again. GLC–MS analysis indicated that the latter extract contained only some unreacted methoxychlor in trace amounts. The initial extract was dried, concentrated, and analyzed by combined GLC–MS. In addition to the products reported below, we also found hexachloroethane in all the extracts of photolyzed solutions, but not in extracts of dark controls. However, since we did not detect hexachloroethane by GLC analysis (EC detector) of benzene extracts of photolyzed solutions, it may have formed by reaction of one of the photoproducts with the chloroform in the extraction solvents.

In a control experiment, p,p'-dimethoxybenzophenone (MDCO) (1.0 × 10^{-7} M) in water was photolyzed exactly as above, and the reaction mixture was worked up following the same procedure. MDCO was readily detected in the concentrated organic extract; no p-methoxybenzaldehyde was formed. No MDCO was found in the concentrated organic extracts of photolyzed methoxychlor solutions.

Photolysis studies in air-saturated river-water samples were carried out under natural sunlight in stoppered quartz cells. Benzene extracts of the photolyzed solutions were

analyzed by GLC using the EC detector. DMDE was tentatively identified as a product by its retention time on nonpolar (3% SE-30) and polar (3% FFAP) columns; no DMDD was found. Irradiation of river-water samples containing no methoxychlor caused marked changes in the GLC profiles of benzene extracts, suggesting that photoalteration of the natural substances in the water had occurred. No GLC peaks with the retention times of methoxychlor or DMDE were present in extracts of unphotolyzed or photolyzed river-water samples.

Quantum Yields. Solutions of methoxychlor (3.00×10^{-3} M) in hexane and 1.1 M water in acetonitrile and the chemical actinometer were irradiated in parallel in the photochemical apparatus using filtered light from the mercury lamp. The light filter employed for studies in hexane and 1.1 M water in acetonitrile was similar to Filter V described by Muel and Malpiece (1969) (maximum transmission at 277 nm). A hexane solution of 2,4-D methyl ester [photolysis quantum yield (ϕ) = 0.13] was employed as actinometer (Zepp et al., 1975). Both methoxychlor and actinometer solutions absorbed >95% of the light.

The quantum yield for reaction of methoxychlor in pure water was obtained by comparing the photolysis rate for methoxychlor in water (30 ppb) with that for methoxychlor (30 ppb) in 1.1 M water in acetonitrile. We assumed that the rate of light absorption was the same in both solvents, since spectral studies showed that the absorption spectrum of methoxychlor is the same in 50% water–acetonitrile as in 1.1 M water in acetonitrile.

Quantum yields for DMDE were measured at 313 nm using a benzophenone–cis-1,3-pentadiene actinometer (Lamola and Hammond, 1965). Quantum yields for the photolysis in water were measured at 12 ppb using procedures described elsewhere (Zepp et al., 1975). Quadruplicate quantum yield measurements all agreed within experimental error.

Sunlight Studies. Sunlight studies were conducted during May and June on the roof of our laboratory. Samples were irradiated in tightly stoppered quartz cells that were positioned above a black cloth to minimize reflected light.

Calculations. Specific rates of sunlight absorption, k_a, were calculated by eq 1

$$k_a = \frac{1}{D}\Sigma \left[I_{d\lambda}(1 - 10^{-\alpha_\lambda l_d}) + I_{s\lambda}(1 - 10^{-\alpha_\lambda l_s}) \right]\epsilon_\lambda\alpha_\lambda^{-1} \qquad (1)$$

where D is the depth of the water, $I_{d\lambda}$ and $I_{s\lambda}$ are intensities of the vertical component of direct (d) radiation from the sun and sky (s) radiation, respectively, α_λ is the decadic absorption coefficient of the water or oil slick, ϵ_λ is the molar extinction coefficient of the pesticide, and l_d and l_s are pathlengths for direct and sky radiation in water and oil slick, respectively. Near the surface of a water body, k_a becomes independent of α_λ and can be expressed by eq 2.

$$k_a = (2.303/D)\Sigma\epsilon_\lambda(I_{d\lambda}l_d + I_{s\lambda}l_s) \qquad (2)$$

Bener's (1972) solar radiation data were employed for the calculations. The extinction coefficients for DDT and methoxychlor could not be measured in pure water due to solubility limitations. Therefore, we used extinction coefficients measured in water–acetonitrile in our calculations of k_a in water. Values of l_d and l_s were calculated according to eq 3 and 4 where n is the refractive index of water or oil slick and z is the solar zenith angle. Since we could find no data concerning refractive indices of oil slicks,

$$l_d = Dn/\sqrt{n^2 - \sin^2 z} \qquad (3)$$

$$l_s = 2n(n - \sqrt{n^2 - 1})D \qquad (4)$$

we assumed a value of 1.43, the refractive index of hexadecane (Weast, 1964). Calculations of the effect of the variation in atmosphere ozone amount (O_3) upon photolysis rates of DDT and methoxychlor were based mainly upon Table B in Bener's report (1972), which describes the effect of the reduction in O_3 upon the intensity of uv light at the earth's surface. All calculations were carried out by a Digital PDP-8E computer. Derivations of eq 1–4 will appear elsewhere (Zepp and Cline, 1976).

Solubility Studies. Excess methoxychlor was stirred in distilled water for 1 week prior to analysis. Also, water containing excess methoxychlor was warmed with stirring (at 50 °C) for 1 h and then stirred for 2 days at room temperature (25 ± 2 °C). Portions from these mixtures were centrifuged for 1 h at 15 000 rpm in a Sorvall RC-2 centrifuge set at 25 °C. Benzene extracts of solution taken from the upper halves of the centrifuge tubes were analyzed by GLC (EC detector). DMDE solubility studies were carried out in a similar fashion.

RESULTS AND DISCUSSION

Solubility Studies. Kapoor et al. (1970) have reported that the solubility of methoxychlor in water is 0.62 ppm (temperature unspecified), compared to 0.002 ppm (25 °C) for DDT. Our studies indicated that the solubility is 0.12 ppm at 25 °C. Factors that could cause such differences in reported solubilities are discussed in some detail by Gunther et al. (1968). We also found that the water solubility of the DDE analogue, 1,1-bis(p-methoxyphenyl)-2,2-dichloroethylene, 0.012 ppm at 25 °C, was lower than that of methoxychlor. All of our studies in water were conducted at concentrations lower than the solubility limits.

Products of Direct Photolysis. Several studies have established that methoxychlor, like DDT (Plimmer et al., 1970), is photodecomposed to a wide variety of products. Other investigators have reported that the major photoproducts in aqueous alcohol were p,p'-dimethoxybenzophenone (MDCO), p-methoxybenzoic acid (MBA), and p-methoxyphenol (MP) (Crosby, 1969; Fernandez, 1966). Photolysis of methoxychlor in butter oil (Bradley and Li, 1969) reportedly yielded the above products along with several dimeric products similar to those derived from photolysis of concentrated solutions of DDT (Fleck, 1949). MacNeil and co-workers (1972) found that 1,1-bis(p-methoxyphenyl)-2,2-dichloroethane (DMDD) and, to a lesser extent, 1,1-bis(p-methoxyphenyl)-2,2-dichloroethylene (DMDE) were the major volatile photoproducts in nitrogen-saturated heptane.

Given the multiplicity of products found in these studies we were not surprised to find that the photolysis of methoxychlor is highly dependent upon its reaction medium. In agreement with the above studies, we found that the major photoreaction in oxygen-free hexane involves stepwise replacement of chlorine by hydrogen to give DMDD initially; small amounts of DMDE were also formed (Figure 1). The presence of air altered the nature of the products; MDCO became the major product and DMDD, DMDE, and MP were minor products (Figure 1).

Direct photolysis of methoxychlor (25 ppb) in air-saturated distilled water by >280-nm light yielded DMDE as the major product (Figure 2). After partial reaction (~10% conversion of methoxychlor), DMDE accounted for 60% of the products. The yield decreased with increasing conversion because of subsequent photolysis of DMDE. After further reaction (30–50% conversion) we
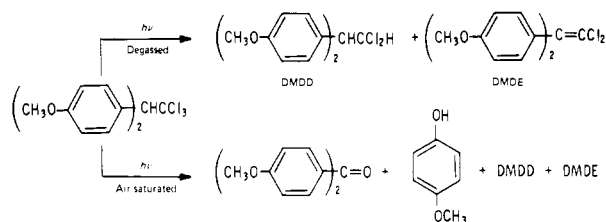
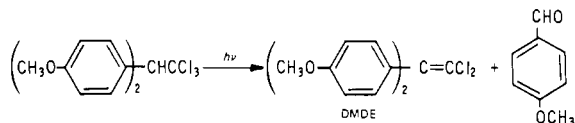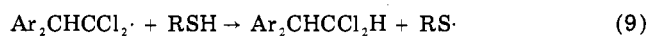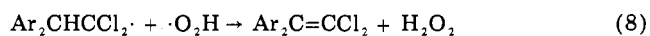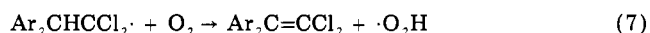Figure 1. Products from direct photolysis of methoxychlor in hydrocarbon solvents.
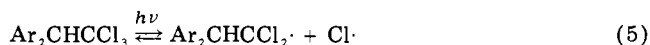

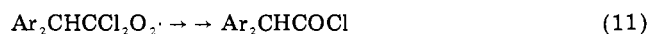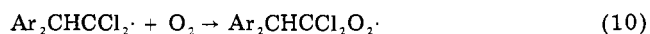Figure 2. Photoproducts of methoxychlor in pure water.

also found p-methoxybenzaldehyde but no MDCO in organic extracts of photolyzed solutions (Figure 2). Control experiments established that MDCO should have been detected if it were formed. Experiments were also conducted at higher methoxychlor concentrations (0.3 g/l.) in an air-saturated 1.1 M water in acetonitrile mixture; under these conditions DMDE (60% yield) and a yellow nonvolatile product were formed. In degassed water–acetonitrile, DMDE was the major product but its yield was lower ($\sim$20%). Addition of the free-radical scavenger, 2-mercaptoethanol (0.036 M), to the degassed water–acetonitrile mixture resulted in a sharp decrease in the yield of DMDE and formation of a new product, DMDD, the major product that formed in degassed hexane. Irradiation of DMDE in the presence of 2-mercaptoethanol produced no DMDD.

These results suggest that the primary photochemical process for methoxychlor is the same as that for DDT, homolysis of one of its carbon–chlorine bonds to form free-radical intermediates (eq 5) (Mosier et al., 1969; Plimmer et al., 1970). Subsequent chemical reactions of the free radicals with themselves, oxygen, or the solvent determine the nature of the products. Some possible reactions that account for the major products in water are shown in eq 5–9 where Ar represents a p-methoxyphenyl group and RSH is a thiol.

$$Ar_2CHCCl_3 \overset{h\nu}{\rightleftarrows} Ar_2CHCCl_2\cdot + Cl\cdot \tag{5}$$

$$Ar_2CHCCl_2\cdot + Cl\cdot \rightarrow Ar_2C{=}CCl_2 + HCl \tag{6}$$

$$Ar_2CHCCl_2\cdot + O_2 \rightarrow Ar_2C{=}CCl_2 + \cdot O_2H \tag{7}$$

$$Ar_2CHCCl_2\cdot + \cdot O_2H \rightarrow Ar_2C{=}CCl_2 + H_2O_2 \tag{8}$$

$$Ar_2CHCCl_2\cdot + RSH \rightarrow Ar_2CHCCl_2H + RS\cdot \tag{9}$$

The thiol scavenged the free-radical intermediate as shown in eq 9, forming DMDD and inhibiting DMDE formation. Plimmer and his co-workers (1970) suggested that the free-radical intermediate obtained from DDT photolysis reacts with oxygen according to eq 10 and 11:

$$Ar_2CHCCl_2\cdot + O_2 \rightarrow Ar_2CHCCl_2O_2\cdot \tag{10}$$

$$Ar_2CHCCl_2O_2\cdot \rightarrow \rightarrow Ar_2CHCOCl \tag{11}$$

In the case of methoxychlor in aqueous media, such a reaction sequence would ultimately lead to formation of bis(p-methoxyphenyl)acetic acid. We did not find this product, presumably because reactions such as those in eq 6–8 occur much more rapidly in the case of methoxychlor. Other studies have demonstrated that abstraction of benzylic hydrogen atoms by chlorine atoms and oxygen-free radicals is markedly accelerated by para methoxy relative to para chloro ring substituents (Pryor, 1968).

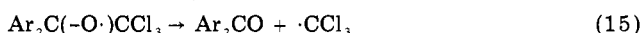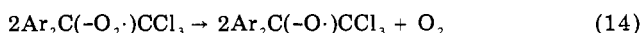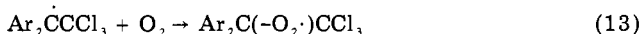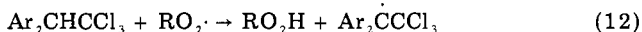Table I. Quantum Yields for Direct Photolysis of Methoxychlor

Solvent	Disappearance quantum yield[a]
n-Hexane[b]	0.12
1.1 M water in acetonitrile[b]	0.32
Water[c]	0.3

[a] Maximum transmittance of chemical filter was 277 nm. [b] Methoxychlor concentration was 0.00300 M. [c] Methoxychlor concentration was 30 ppb.

We made no detailed studies of the photooxidation of methoxychlor in hydrocarbons. The observed formation of dimethoxybenzophenone can be accounted for by a mechanism similar to one suggested by Plimmer et al. (1970) for photooxidation of DDT to dichlorobenzophenone (eq 12–15). The alkylperoxy radicals, $RO_2\cdot$, result

$$Ar_2CHCCl_3 + RO_2\cdot \rightarrow RO_2H + Ar_2\dot{C}CCl_3 \tag{12}$$

$$Ar_2\dot{C}CCl_3 + O_2 \rightarrow Ar_2C({-}O_2\cdot)CCl_3 \tag{13}$$

$$2Ar_2C({-}O_2\cdot)CCl_3 \rightarrow 2Ar_2C({-}O\cdot)CCl_3 + O_2 \tag{14}$$

$$Ar_2C({-}O\cdot)CCl_3 \rightarrow Ar_2CO + \cdot CCl_3 \tag{15}$$

from reaction of solvent-derived free radicals with oxygen.

Direct Photolysis Rates. The dearth of information concerning the rate of direct photolysis of methoxychlor under sunlight prompted us to examine the kinetics in some detail. Preliminary experiments under natural sunlight indicated that the photolysis of methoxychlor (30 ppb) in either hexane or distilled water was quite slow. Exposure to 48 h of midday (1000 to 1400 E.D.T.) sunlight (June, latitude 34°N) resulted in less than 10% decomposition in both solvents. Assuming first-order kinetics for the photolysis, these data indicated that at least 300 h of midday sunlight would be required to decompose half of the pesticide.

Kinetic data obtained from experiments under natural sunlight, although useful, cannot be extrapolated from one location to another. The intensity of solar ultraviolet radiation, particularly in the 300–320-nm region, is a function of latitude and season (Cutchis, 1974). We have developed a procedure to calculate by computer the direct photolysis rates of pesticides at different latitudes and seasons (Zepp and Cline, 1976). The calculations assume that the direct photolysis of pesticides in dilute solution obeys a first-order rate law (eq 16). The rate ($-d[P]/dt$),

$$-d[P]/dt = \phi k_a[P] \tag{16}$$

given by eq 16, is proportional to the disappearance quantum yield, ϕ, and the specific sunlight absorption rate, k_a. The disappearance quantum yield is the fraction of light absorbed by the pesticide that results in photoreaction. We have used this procedure to calculate direct photolysis rates of several pesticides and pesticide metabolites (Zepp and Cline, 1976; Zepp et al., 1975) and have found that the calculated rates are in reasonable agreement with rates measured under natural sunlight.

Quantum yields for direct photolysis of methoxychlor were measured in hexane, 1.1 M water in acetonitrile, and distilled water (Table I). The quantum yield in hexane was similar to the value of 0.16 previously reported for DDT in hexane (Mosier et al., 1969). The quantum yield in a degassed 1.1 M water in acetonitrile mixture was not decreased by the addition of 0.036 M 2-mercaptoethanol, a free-radical scavenger, or 0.004 M cis-1,3-pentadiene, a triplet-state quencher. The latter experiment indicated that dissolved substances in natural waters are too dilute (Hutchinson, 1957) to quench the photolysis by energy transfer processes (Turro, 1965). The low quantum yields
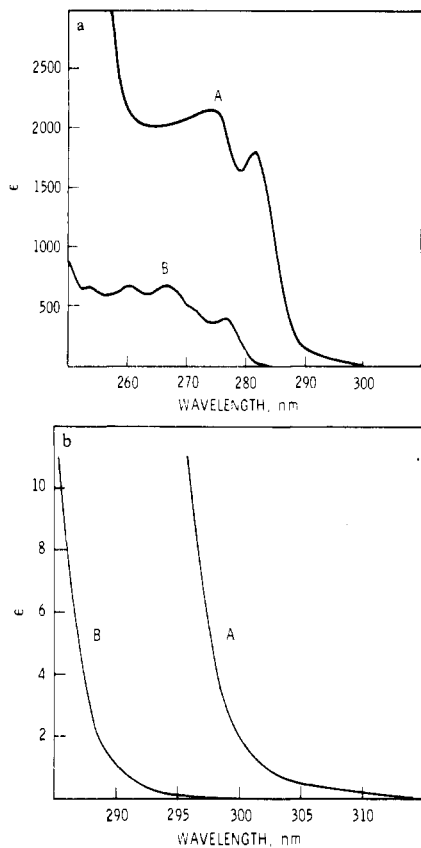
Figure 3. (a) Electronic absorption spectra of methoxychlor (A) and DDT (B) in hexane; (b) long-wavelength portion of spectra.

for DDT and methoxychlor may in part be due to recombination of the free radicals initially formed in the photolysis (eq 5, reverse reaction).

The magnitude of the specific sunlight absorption rates of pesticides depends upon the degree of spectral overlap between their electronic absorption spectra and the spectrum of sunlight at the earth's surface. The cutoff for solar radiation is about 295 nm (Bener, 1972). The spectra of carefully purified samples of DDT and methoxychlor in hexane are compared in Figure 3. In water–acetonitrile mixtures the extinction coefficients of methoxychlor at wavelengths >295 nm are slightly higher than in hexane; the reverse is true for DDT. However, even in the polar solvents, the extinction coefficients of methoxychlor were very low. Specific sunlight absorption rates for both compounds were calculated from the above spectral data and Bener's (1972) table of intensities of natural ultraviolet radiation.

Kinetic parameters for the direct photolysis of DDT and methoxychlor during midsummer in the central United States (latitude 40°N) are compared in Table II. The half-lives, $t_{1/2}$, in Table II represent the period of midday sunlight required to decompose the pesticides to half of their original concentration near the surface of a water body [$t_{1/2} = 0.693(k_a\phi)^{-1}$]. The quantum yield for direct photolysis of DDT in water was not available in the literature. However, according to the Stark–Einstein law (Calvert and Pitts, 1966), the quantum yield for a photochemical process does not exceed unity. Accordingly, the minimum half-life for direct photolysis of DDT in water was computed assuming a quantum yield of one; i.e., the half-life was assumed to equal or to be longer than $0.693(k_a)^{-1}$. The following conclusions were derived from examination of these parameters: direct photolysis of methoxychlor is at least 300 times more rapid than that

Table II. Kinetic Parameters for the Direct Photolysis of DDT and Methoxychlor in the Central United States[a]

Pesticide	Medium	$10^9 k_a$, s^{-1}	ϕ	$10^{10} k_a \phi$, s^{-1}	$t_{1/2}$, h
Methoxychlor	Hydrocarbon	390	0.12	470	4 100
	Water	870	0.3	2800	690
DDT	Hydrocarbon	4.3	0.16[b]	6.8	280 000
	Water	0.85	c	c	>227 000[d]

[a] Calculated for midday sunlight during midsummer at latitude 40°N. [b] Taken from Mosier et al. (1969). [c] Data not available. [d] Minimum half-life calculated assuming quantum yield of unity.
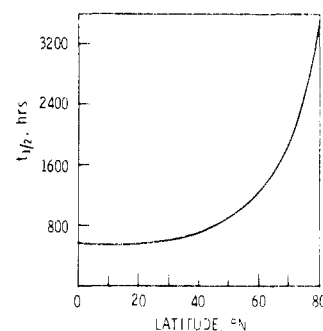

Figure 4. Midday half-lives for direct photolysis of methoxychlor in water during summer.

of DDT in water; direct photolysis of methoxychlor is nearly six times more rapid in aqueous than in hydrocarbon media; both DDT and methoxychlor are photolyzed very slowly by sunlight in pure water or hydrocarbons. The data in Table II pertain to midsummer, midday sunlight; the half-lives are longer during other seasons and in the morning or afternoon. Midday half-lives for methoxychlor and DDT, averaged over all seasons, are 1100 h and > 460 000 h, respectively, in water at latitude 40°N. Assuming conservatively that the average daily half-lives are 50% longer than the midday half-lives, the direct photolysis half-lives (in 12-h days) of methoxychlor and DDT in water are 4.5 months and greater than 150 years, respectively (latitude 40°N).

The calculated photolysis half-life of methoxychlor for midsummer is an increasing function of northern latitude (Figure 4). For example, the half-life in the central U.S. is approximately 30% longer than in the tropics.

Direct photolysis of the 1,1-diphenylethylene derivative, DMDE, was found to be much more rapid than that of methoxychlor. Quantum yields (313 nm) for photolysis of DMDE were found to be 0.20 in hexane and 0.30 in distilled water; Mosier et al. (1969) reported that the quantum yield for DDE in hexane is similar, 0.26 at 254 nm. The calculated midday half-lives for DMDE (summer, central United States) were 40 and 50 min in water and hydrocarbons, respectively. DDE also photolyzes much more rapidly than DDT in hydrocarbon media. The calculated midday half-life of DDE is about 5 h under the above conditions whereas that of DDT is 280 000 h. Photolysis rates measured under natural sunlight agreed closely with the calculated values. These results provide an interesting contrast to the findings of Moilanen and Crosby (Maugh, 1973) that DDT photolyzes more rapidly than DDE in the vapor phase.

The solar intensities employed in the above calculations are based upon average atmospheric ozone amounts (O_3) for a given latitude and season. In fact, natural variations of ±5% in O_3 occur over a period of years and O_3 varies longitudinally within a given latitude (London, 1963).
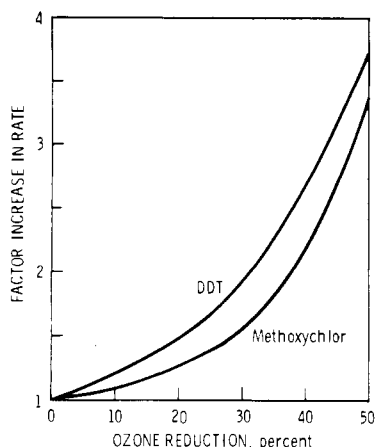
Figure 5. Effect of ozone reduction upon photolysis rates of DDT and methoxychlor.

Table III. Half-Lives for Photodecomposition of Methoxychlor (40 ppb) under Sunlight in Various River Waters[a]

Water	pH	Photolysis half-life, h[b]
Distilled	6.3	>300
Suwannee River	4.7	2.2
Tombigbee River	7.6	5.4
Alabama River	7.7	2.9
Withlacoochee River	8.2	c
South Georgia stream[d]	7.2	c
20 ppm of "humic acid" in distilled water[c]	5.2	7.3

[a] Solution in sealed quartz cells exposed to midday May sunlight, latitude 34°N. [b] Calculated assuming first-order kinetics, expressed as hours of midday sunlight. [c] No detectable photolysis after 2-h exposure. [d] Collected near Thomasville, Ga. [e] Humic acid obtained from Aldrich Chemical Company.

Recently, several scientists have expressed concern that certain human activities may be leading to depletion of stratospheric ozone (Hammond and Maugh, 1974). Our calculations indicate that variation in ozone amount affects the direct photolysis rate of DDT more than that of methoxychlor (Figure 5). Generally, each 5% reduction in ozone amount should result in about a 10% increase in rate for DDT and a 6% increase for methoxychlor.

Indirect Photolysis. Although the photolysis of methoxychlor in pure water is slow, we found that photolysis under sunlight was rapid in certain filter-sterilized natural waters (Table III). The natural waters were collected from rivers in South Carolina, Alabama, Georgia, and Florida; pH values ranged from 4.7 (Suwannee River) to 8.2 (Withlacoochee River). Dark controls showed no decomposition in all the water samples over the period of sunlight exposure.

Detailed product studies were not carried out. However, the GLC traces of organic extracts of the photolyzed solutions all had peaks with the same retention time as DMDE. In the Suwannee River water, DMDE formation almost completely accounted for methoxychlor disappearance at 30% conversion of the methoxychlor. DMDE photolyzed more slowly than methoxychlor in the Suwannee River water; its low photolysis rate was attributed to light screening by the ultraviolet-absorbing materials in the river water.

We found that methoxychlor photodecomposed rapidly in distilled water containing a commercially available derivative of decayed plant materials, Aldrich "humic acid" (Table III). We used this material because its electronic absorption spectrum was very similar to that of materials dissolved in our natural water samples and because it is likely to contain many of the same chemical moieties. The observed sunlight photolysis rate using 20 ppm of this model substance was roughly comparable to that found in several natural waters.

The above phenomena involve sunlight absorption by materials in the river water, followed by decomposition of the pesticide; we shall refer to this process as indirect (or "sensitized") photolysis. Indirect photolysis should *not* be viewed as acceleration of the *direct* photolysis process by materials in natural waters (see below). This point is important, because the products of indirect photolysis of pesticides are sometimes different than those of direct photolysis (Ross and Crosby, 1975; Ross, 1974; Zepp et al., 1974).

At present, we know very little about the mechanism(s) for indirect photolysis in natural waters. However, energy transfer photosensitization (Turro, 1965) cannot account for our results. The triplet state energy of methoxychlor, determined from its phosphorescence spectrum, was found to be 80 kcal mol^{-1}. Since triplet energy transfer occurs efficiently only when the triplet energy of the sensitizer equals or exceeds that of the energy acceptor (Turro, 1965) only high energy sensitizers can transfer energy to methoxychlor. Such sensitizers are present in natural waters, but they absorb only the short-wavelength ultraviolet component of sunlight, so their rates of sunlight absorption are not rapid compared to those of visible-absorbing substances such as humic materials. The quantum efficiencies of energy transfer under natural conditions are also decreased by the presence of competing energy acceptors such as dissolved oxygen. Moreover, studies using filtered light from a mercury lamp indicated that visible light (>400 nm) caused decomposition of methoxychlor in the Suwannee River water; the energy of visible light is <71 kcal mol^{-1} (Calvert and Pitts, 1966), far lower than the minimum energy required to electronically excite methoxychlor (80 kcal mol^{-1}).

We also investigated the possibility that singlet oxygen, an excited form of oxygen (Trozollo, 1970), may play a role in the light-induced decomposition of methoxychlor in natural waters. Our results indicated that both methoxychlor and DMDE are unreactive toward singlet oxygen (Zepp et al., 1974).

We did not investigate other possible mechanisms although the exciplex mechanism suggested by Miller and Narang (1970) for the amine-induced photolysis of DDT is one attractive possibility. Alternatively, decomposition of methoxychlor may result from attack by free radicals generated by photolysis of materials in the natural water. The latter is a common mechanism for indirect photolysis in the atmosphere (Altschuller and Bufalini, 1971). More detailed studies of the indirect photolysis of pesticides are presently underway in our laboratory.

CONCLUSIONS

Our results indicate that direct photolysis of methoxychlor in pure water or oil slick, although at least 300 times more rapid than DDT photolysis, is still a very slow environmental process. These results are not applicable to photolysis of methoxychlor films on solid surfaces, since films of pure compound absorb sunlight more rapidly than dilute solutions. The major photoproduct of methoxychlor photolysis in pure water is 1,1-bis(p-methoxyphenyl)-2,-2-dichloroethylene (DMDE). This product photodegrades rapidly in both aqueous and hydrocarbon media.

In contrast, we found that sunlight-induced decomposition of methoxychlor was rapid in several natural

waters. These results indicate that the rates of methoxychlor photolysis in pure water can be viewed only as minimum values for its rate of light-induced decomposition in natural waters.

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Factors Affecting the Stability of Dimilin in Water and the Persistence of Dimilin in Field Waters

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Dimilin (1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl)urea), a very promising new mosquito control agent, persists in water long enough to accomplish mosquito control but does not have long-term stability in water. Persistence of this compound in water appears to be limited due to hydrolysis and to adsorption onto organic matter. It is least stable when water temperature and pH are both relatively high. Its persistence is not greatly affected by sunlight or by microorganisms. Application of a 25% wettable powder formulation disperses the active ingredient throughout water, but application of technical material in ethanol or of a 2.07 lb of active ingredient/gal of flowable liquid formulation causes a much greater concentration in the upper water levels for up to 3 days.

Dimilin (1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl)urea) is a potent inhibitor of chitin synthesis in immature stages of insects (Post and Vincent, 1973) that has high biological activity against mosquitoes (Jakob, 1973; Schaefer et al.,

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1974; Hsieh and Steelman, 1974; Mulla et al., 1975). An extensive, operational evaluation of Dimilin demonstrated its commercial potential as a mosquito larvicide (Schaefer et al., 1975); although some nontarget organisms were reduced by these treatments, their populations recovered within a short period of time (Miura and Takahashi, 1975).

Since Dimilin is projected to be used as a commercial larvicide, determination of factors affecting its stability