

Effects of Light on the Organophosphorus Pesticides Bromophos and Iodofenphos and Their Main Degradation Products Examined in Rainwater and on Soil Surface in a Long-Term Study

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The photolysis of bromophos [*O,O*-dimethyl *O*-(4-bromo-2,5-dichlorophenyl) phosphorothioate], iodofenphos [*O,O*-dimethyl *O*-(2,5-dichloro-4-iodophenyl) phosphorothioate], and their main degradation products was studied under artificial sunlight. A day and night rhythm was simulated over a period of 96 days. Simultaneously, a parallel experiment was carried out in the dark to investigate the effect of all other parameters except photolysis. The degradation experiments were conducted in rainwater and on a standard soil surface. Both pesticides were readily decomposed. In all cases the rate of decomposition due to photolysis was higher for bromophos than for iodofenphos. The quantitative behavior of the two major degradation products 4-bromo-2,5-dichlorophenol and 2,5-dichloro-4-iodophenol was investigated in both media in complete darkness as well as in a day and night rhythm. By carrying out photolysis studies in water and on soil surface, we obtained useful information on the chemical behavior of the pesticides. Since the experiments were performed in the laboratory, they were not impaired by meteorological variations that would have occurred in field experiments.

Photodecomposition is only one of the various transformation processes determining the fate of pesticides in the environment. It may occur in water and air as well as on target organisms and on soil surface. Useful data on the photolysis of pesticides in water (Burkhard et al., 1975; Hautala, 1978; Koshy et al., 1983; Nilles and Zabik, 1974, 1975; Walter-Echols and Lichtenstein, 1983) are available, but published information on photochemical degradation on soil surface is relatively scarce (Burkhard and Guth, 1979; Liang and Lichtenstein, 1976; Nilles and Zabik, 1974, 1975; Smith et al., 1978).

Studies carried out under natural sunlight depend strongly on the meteorological variations of the environment (Nilles and Zabik, 1974, 1975; Liang and Lichtenstein, 1976; Smith et al., 1978). Other authors used mercury vapor arcs with a spectral energy distribution different from that of sunlight (Hautala, 1978) or applied germicidal lamps that are rich in radiation between 240 and 260 nm (Liang and Lichtenstein, 1976). The latter experiments are of limited practical value for investigations on the photochemical stability of pesticides since ultraviolet light with a wavelength below 290 nm does not reach the surface of the earth (Hirt et al., 1960). In one study the radiation source was a xenon burner (Burkhard and Guth, 1979). Its spectral energy distribution is very similar to that of sunlight, but the light intensity was much higher than the intensity of natural sunlight reaching the surface of the earth. No long-term investigations have been published so far on photolysis of organophosphorus pesticides.

In the present paper the photodecomposition of the organophosphorus pesticide bromophos, *O,O*-dimethyl *O*-(4-bromo-2,5-dichlorophenyl) phosphorothioate, and iodofenphos, *O,O*-dimethyl *O*-(2,5-dichloro-4-iodophenyl) phosphorothioate, in rainwater and on a standard soil surface was studied over a period of 96 days. Samples of pesticides in both media were exposed to artificial sunlight for 12 h and then kept in the dark for 12 h, thus simulating a day and night rhythm. A self-constructed radiation apparatus was used. With this experimental setup it was possible to work at any time of the year independent of climatic variations.

EXPERIMENTAL SECTION

Chemicals. Bromophos and iodofenphos were analytical standards obtained from U.S. Environmental Protection Agency, Research Triangle Park, NC, and were used as received. These chemicals were at least 99.9% pure as was determined by gas chromatography. The internal standard fenitrothion, *O,O*-dimethyl *O*-(3-methyl-4-nitrophenyl) phosphorothioate, was kindly supplied by Bayer, Leverkusen, FRG. The degradation products 2,5-dichloro-4-iodophenol and 4-bromo-2,5-dichlorophenol were purchased from Loba, Vienna, Austria. All solvents used for extractions and analysis were of analytical grade.

Water. The rainwater was collected during July 1982 in Vienna, Austria, and stored at 5 °C prior to use. The water samples were centrifuged for 1 h at 4000 rpm in a Heraeus-Christ Labofuge III to remove particles.

Soil. The standard soil was an insecticide-free loamy sand from Speyer, FRG (pH 5.8; organic carbon 2.6%, clay 8.8%, silt 6.4%, sand 84.8%; Speyer Standard Soil 2.2), that had been reactivated with water and sunlight 3 weeks before starting the degradation experiments, to compensate for the possible loss of microbial activity during transport. The reactivated soil contained 12% water.

Irradiation. Light from three TL 40/47 Philips daylight lamps, one TL 40/12 Philips UV-A lamp, and one TL 40/09 Philips UV-B lamp was used. The lamps were mounted in an alternate configuration. The spectral energy distribution of the system is shown in Figure 1. No ultraviolet light with a wavelength below 290 nm was emitted. The photolysis vessels were wide-necked quartz bottles, placed 30 cm below the radiation source. The total average energy output of the five photolamps was measured by a YSI-Kettering radiometer and determined to be $21 \text{ J m}^{-2} \text{ s}^{-1}$ at the sample surface. For comparison, the sunlight energy on a summer's day (100% overcast sky) in Vienna at ground level is very similar— $25 \text{ J m}^{-2} \text{ s}^{-1}$.

Exposure Procedure. The initial concentrations of bromophos and of iodofenphos in aqueous solutions (rain water) were 80 ppm each. At intervals of 3 days the amount of water that had evaporated was determined by weighing and was replaced in order to retain the original weight of the sample. The average solution temperature was $27 \pm 2 \text{ °C}$ during the experiments.

The reactivated soil was uniformly treated with the pesticides. Because of their relatively low solubility in

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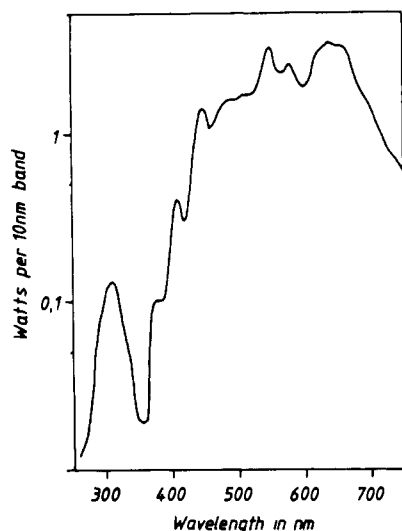


Figure 1. Spectral energy distribution for the irradiation system.

water, the pesticides were dissolved in small amounts of organic solvents. Consideration was given to the amounts and type of solvent used to avoid possible toxicity to the microbial organisms. Methanol was used. The quantities were in all cases below 1 mL, and a gentle stream of air was used to remove the methanol quickly. After removal of the organic solvent and a thorough mixing of the pesticide-treated soil, the initial concentrations of bromophos and iodofenphos were 180 ppm each. During the experiments, the water content of the soil was maintained at 12% and the average soil temperature was $25 \pm 2^\circ\text{C}$.

To study the influence of light, two series of experiments were conducted over a period of 96 days. Aliquots of each sample were collected after 1, 3, 6, 12, 24, 48, and 96 days. In the first one, pesticide-treated water and soil samples were stored under conditions of constant darkness to determine whether additional degradation processes, such as hydrolysis, thermal decomposition, or volatilization, occurred during the photolysis studies. In the second series of experiments, the otherwise identically treated samples were irradiated for 12 h and then kept in the dark for 12 h, simulating a day-night rhythm.

Extraction. The water samples were extracted with three portions of 10, 5, and 5 mL of methylene chloride. Residues on glass surfaces were removed quantitatively by rinsing with the same solvent. The combined methylene chloride extracts were dried with anhydrous sodium sulfate and then filtered through a Schleicher & Schuell black ribbon filter. The extracts were carefully reduced to a volume of 1 mL by using a vacuum rotary evaporator at 30°C . Then 2 mL of ethyl methyl ketone was added and concentrated again to 1 mL. Finally, the solution was adjusted to 2.5 mL by the addition of ethyl methyl ketone. Average recoveries for bromophos and iodofenphos were 71%.

The thoroughly mixed soil samples were exhaustively extracted with 200 mL of methylene chloride in a Soxhlet apparatus for 4 h. Then, the methylene chloride extracts were treated in the same manner as the water samples. The extraction efficiencies for bromophos and iodofenphos were 95% and 81%, respectively.

Chromatography. The quantitative analysis was performed by high-resolution capillary gas chromatography using a Varian 3700 gas chromatograph equipped with a flame ionization detector. A 30-m fused silica capillary column (0.256-mm i.d.) coated with SE-30 (0.25- μm film thickness) was used to separate the interesting compounds from the matrix. The oven temperature was 240°C (iso-

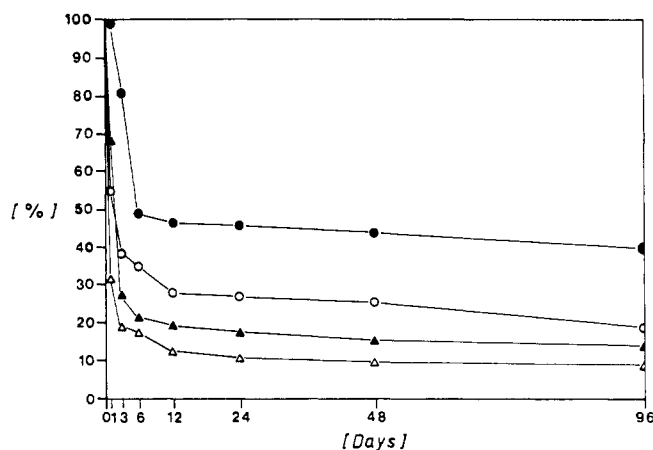


Figure 2. Percentages of bromophos (circles) and iodofenphos (triangles) remaining in illuminated (open symbols) and nonilluminated (closed symbols) rainwater samples.

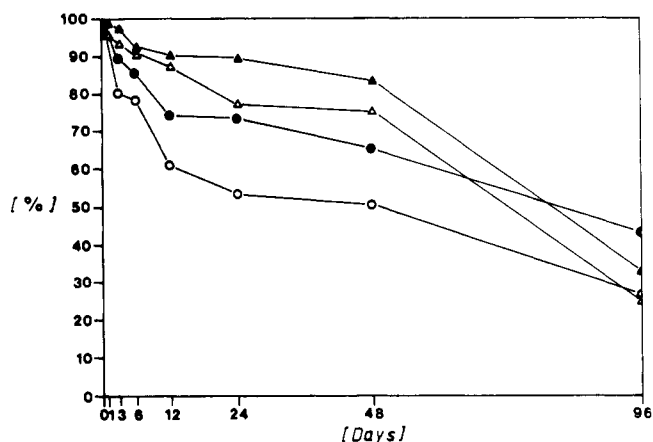


Figure 3. Percentages of bromophos (circles) and iodofenphos (triangles) remaining in illuminated (open symbols) and nonilluminated (closed symbols) standard soil.

Table I. Half-Lives (Days) of Bromophos and Iodofenphos in Rainwater and on Soil Surface

sample type	bromophos	iodofenphos
rainwater		
illuminated	1.5	0.4
nonilluminated	5.8	1.9
standard soil		
illuminated	48.3	70.5
nonilluminated	80.0	85.1

thermal), and the injector and detector temperatures were 250 and 270°C , respectively. A sample volume of $0.5\ \mu\text{L}$ was injected with a splitting ratio of 1:29. The helium carrier gas was held at a constant pressure to maintain the optimized linear velocity (\bar{u}) of $21\ \text{cm/s}$ at 240°C . The gas-liquid chromatographic retention index (standardized as defined by Kovats) for bromophos was 2012, for iodofenphos 2145, and for fenitrothion 1937 (internal standard for quantitative analysis).

All experiments were performed in the laboratory since studies run under field conditions can be influenced by environmental factors.

RESULTS AND DISCUSSION

Both compounds were rapidly degraded under the experimental conditions used. Figures 2 and 3 show the remaining amounts of the parent compounds (bromophos and iodofenphos) left in rainwater and soil surface after 1, 3, 6, 12, 24, 48, and 96 days. A 12-h rhythm of light and darkness was applied in one experiment. For comparison purposes a second experiment was carried out in the absence of light.

Table II. Photodecomposition of Bromophos and Iodofenphos in Rainwater and on Soil Surface

compound	days after application						
	1	3	6	12	24	48	96
Photolysis ^a in Rainwater at 27 °C (Percent)							
bromophos	43.3	42.6	13.9	18.6	18.9	18.5	21.0
iodofenphos	36.8	8.4	7.1	7.4	4.9	5.7	10.6
Photolysis ^a on Soil Surface at 25 °C (Percent)							
bromophos	4.1	8.8	7.4	13.3	20.8	15.0	15.9
iodofenphos	1.4	4.2	1.4	2.8	12.3	7.9	8.0

^a Difference between samples exposed to light and those kept in the dark.

Half-lives calculated from the decomposition curves are presented in Table I. In all experiments a decrease of the pesticide content was found after 24 h. After 96 days in both media in the light exposed as well as in the covered samples, the remaining amount of bromophos had decreased below 43% and of iodofenphos below 33%. The pesticides decomposed faster in samples kept under light irradiation than in those stored in complete darkness. The observed decomposition of the pesticides in the samples being stored in complete darkness indicates that other degradation processes also occurred under these experimental conditions. However, the difference between the amounts decomposed in the illuminated and covered samples can be considered to be the result of photodecomposition. These differences calculated for bromophos and iodofenphos are summarized Table II. The effect of temperature on the kinetics of photochemical decomposition is significant (Schaefer and Dupras, 1973). An attempt to keep the temperature constant during all the experiments was made. However, the average water temperature was slightly higher than the soil temperature due to the better absorption of the incident light. The lower degradation rate of bromophos and iodofenphos in moist standard soil in comparison to that in water may be due to the pesticides being less exposed to irradiation in the soil. In both media the rate of photolysis of bromophos was higher than that of iodofenphos.

With bromophos and iodofenphos, the same main degradation products 4-bromo-2,5-dichlorophenol and 2,5-dichloro-4-iodophenol, respectively, were found in both media regardless of the light conditions. Thus, the main decomposition reaction occurred by cleavage of the aryl ester bond. Figures 4 and 5 show the quantitative behavior of both phenols in water and on soil surface under the influence of light and in the dark. In the illuminated water samples the concentration of both phenols increased initially to a maximum after 6 days but then declined below 5% after 96 days. In the absence of light the concentrations of the phenols increased steadily, reaching their maxima after 96 days, 12 days after application of bromophos on the illuminated soil surface with 4-bromo-2,5-dichlorophenol reaching the highest concentration. On the other hand, in soil samples kept in the dark the maximum was reached after 24 days. This can be explained by the slower degradation velocity of the parent compound.

The behavior of 2,5-dichloro-4-iodophenol on the soil surface is quite different from that of the above-mentioned phenol. On soil samples—illuminated ones as well as those kept in the dark—the concentrations of the phenol increased steadily, reaching maxima of 39% and 35%, respectively, after 96 days.

There is a significant influence of light on the degradation rate of bromophos and iodofenphos in rainwater and on standard soil surface. Also, light influences strongly the behavior of the phenols, the main degradation products

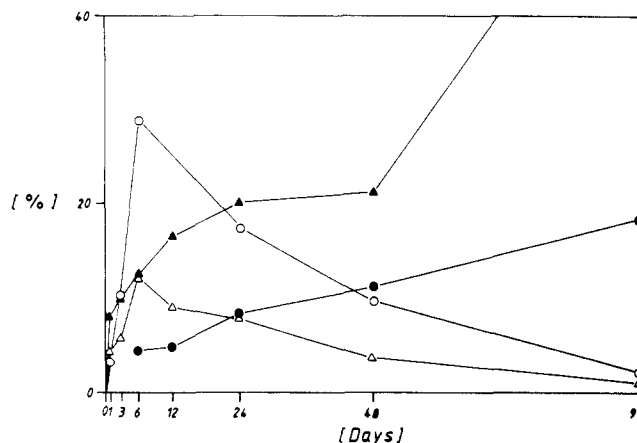


Figure 4. Percentages of 4-bromo-2,5-dichlorophenol (circles) and 2,5-dichloro-4-iodophenol (triangles) remaining in illuminated (open symbols) and nonilluminated (closed symbols) rainwater samples.

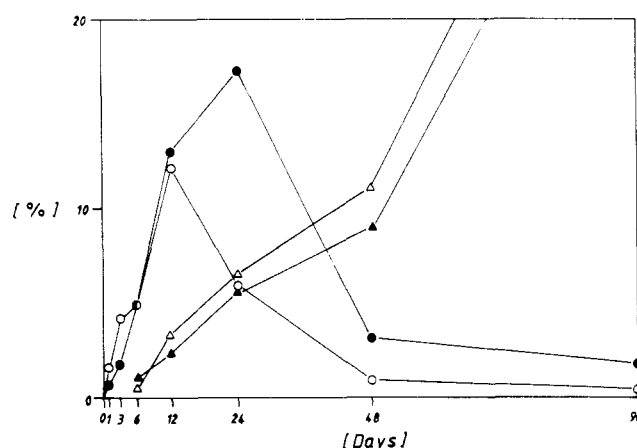


Figure 5. Percentages of 4-bromo-2,5-dichlorophenol (circles) and 2,5-dichloro-4-iodophenol (triangles) remaining in illuminated (open symbols) and nonilluminated (closed symbols) standard soil samples.

of the two pesticides.

Registry No. Bromophos, 2104-96-3; iodophos, 18181-70-9; 4-bromo-2,5-dichlorophenol, 1940-42-7; 2,5-dichloro-4-iodophenol, 7587-15-7.

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