Bull. Environ. Contam. Toxicol. (1989) 43:239–245

Bulletin of Environmental Contamination and Toxicology

Photodecomposition of Monocrotophos in Soil, on Plant Foliage, and in Water

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Concern about the wide spread use of pesticides and ultimate fate of these compounds in the environment has led to the extensive studies of their photolytic reactions. Photolysis is one of the various factors determining the fate of pesticide in the environment. A number of recent studies have examined the photolysis of pesticides in water and air as well as on plant and soil surfaces by sunlight and ultraviolet light irradiation (Draper and Crosby 1981; Wong and Crosby 1981).

Monocrotophos (3- dimethoxyphosphinyloxy)-N-methyl ciscrotonamide), a foliar insecticide mainly used for cotton, is active against a wide range of insects and mites and has contact, systemic and residual activity. As a part of our study to evaluate the environmental fate of pesticides, photolysis of monocrotophos under sunlight and untraviolet light was investigated under more realistic conditions, such as in soil, water and on plant foliage. The effect of soil type, soil moisture and surface area on the photo- decomposition of monocrotophos was also studied.

MATERIALS AND METHOD

Analytical grade (99.2% W/W) monocrotophos was supplied by CIBA GEIGY, India Ltd. Solvents used for extraction and analysis were distilled acetone, benzene, hexane, acetonitrile, chloroform and methanol.

Four soil types were used in this experiment. They were alluvial, black, red loamy soil and laterite soil (Properties in Table 1).

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Table 1 Characteristics of soils

Sampling site	Soil Type	Organic Matter	Particle Content				pH
			Coarse Sand	Fine Sand	Slit	Clay	(H_2O)
Bihar (India)	Alluvial	0.25	0.1	46.5	15.0	7.4	8.4
Maharashtra (India)	Black	0.33	1.7	15.4	21.7	56.2	8.1
Karnataka (S.India)	Red loamy	0.35	60.2	-	16.4	23/4	6.0
Kerala (S.India)	Laterite	0.47	58.3	13.6	6.5	21.82	4.8

Three different types of water were used in this experiment distilled water (pH 6.0), tap water (pH,7.8) and 2% aq acetone (pH 6.0).

Bean plants (Phaseolus vulgaris0 were grown for 2-3 weeks in small clay pots, until the stalk reached a length of 20-30 cm. Six bean plants per clay pot were used for each duplicate test.

Ultraviolet light was supplied by two 15 W germicidal lamps held 30 cm from the test substrate. The light produced by these lamps, was rich in irradiation at 2537^{0}A. Tests with sunlight were run on the cloudless April and May days between 9 A.M. and 5 P.M. on an area of a roof protected as much as possible from the wind. The temperature at the test surfaces varied between 35 to 42^{0}C in the sunlight and 25 to 30^{0}C under ultraviolet light.

All soils, plants, water and glass surface were treated with acetone solutions of monocrotophos in unlabelled form. When the insecticide was to be mixed with the soil the method of Lichtenstein and Schulz (1959) was employed. The application on the glass, soil, water and plant leaves involved dispensing various amounts of compound in acetone solution onto appropriate surface and allowing the solvent to evaporate, before the tests were began.

All soils were extracted by the method described by Lichtenstein (1973), which involves twice extraction with (1;10 methanol- acetone followed by a single extraction with (1:1:1) methanol- acetone-benzene. Residues on glass surfaces were removed quantitatively by rinsing with the methanol - acetone - benzene- solvents.

Bean leaves from each pot were removed and cut into 0.5 cm sections, which were then extracted three timesx with 20 ml aliquots of acetonitrile, solvent was concentrated on a vacuum evaporator to approximately 10 ml.

Gas liquid chromatography (g.l.c.) was used for the analysis of monocrotophos in extracts. It was carried out using a Hewlett Packard model 5890 A chromatograph fitted with 530 u.i.d. capillary column with 3% OV-17 material with a flame ionisation detector (f.i.d.). The oven temperature was programmed from 150-180^{0} at a rate of 5^{0} C/min and carrier gas used was nitrogen at a flow rate of 80ML min^{-1}.Injector and detector ports were maintained at 250 and 275^{0}C respectively.

To test the effect of light in the photodecomposition of monocrotophos on soil and plant leaf surface. it was first deposited on glass surface for comparison purposes. For this 100 ug of monocrotophos was deposited on the inner bottom surface (64cm^{2}), of each of two glass petridishes. These petridishes were then exposed out door to sunlight. Controls were handled the same way except that they were covered with a aluminium foil to exclude light. After the 8th exposure period, monocrotophos residues were removed and analysed by gas liquid chromatography (g.l.c.).

The effect of different soils on the photodecomposition of monocrotophos was studied with alluvial, black, red loam and laterite soil (Table 1). Of each air dried soil, 350 g of it was treated and mixed with 700 ug of monocrotophos as described . Six 50 g portion of the treated soil, each containing 100 ug of monocrotophos, were placed in petridishes with bottom surface area of 268cm^{2}. Two dishes containing either the alluvial, black, red loamy or laterite soil were then exposed to sunlight, to ultraviolet light or kept in the dark for 8th as described. Controls, wothout soil (glass surface with an area of 268 cm^{2}) were prepared with 100 ug of monocrotophos and exposed to sunlight, ultraviolet light or kept in the dark. After exposure for 8h, the soils were removed from the dishes and extracted as described.

The effect of soil moisture and surface area on the photodecomposition of monocrotophos were studied with sandyloam soil in dry, moist and water logged conditions. Air dried soil was treated with a 2 ppm solution of monocrotophos as described. Fifty gram portions of the treated soil were then placed into six beakers with a bottom surface area of 16 cm^{2}. Two of the treated soils were kept dry, two were kept moist and two were flooded until 1.5 cm of water covered the soil surface.Two beakers without soil or water, containing a deposit of 100 ug of monocrotophos

served as control.These eight beakers were then exposed for 8h to ultraviolet as described. Simultaneously eight beakers prepared as described above, were exposed for 8h to sunlight and another eight were kept in the dark. The same experiment was repeated with a 17 times larger surface area 268cm^{2}. At the e3nd of exposure of soil and glass sufraces, extraction and analysis were carried out as described above. Water logged soil was dried by distillation under high vacuum and extracted with methanol - acetone and benzene.

The degradation of monocrotophos due to irradiation was studied with leaves of bean plants. For that purpose four pots each containing four bean plants (20-30 cm stalk) were utilized. Monocrotophos (100 ug) in 1 ml of acetone was distributed as evenly as possible with a microsyringe over the upper epidermis of 12 bean leaves per plant. Thus a total of 48 bean leaves were treated with monocrotophos. All experiments were performed in subdued light. After the solvent had evaporated, two pots each of treated bean plants were taken outdoor and placed in the light at 35^{0}C for 8h. In addition, two pots each with treated bean plants were covered with black cloth to exclude light and placed next to uncovered pot.

After 8h exposure period, 12 bean leaves from each pot were removed and extracted as described. Quantitative analysis was done by gas liquid chromatography.

Sandy loam soil (0.35% , organic matter 21.2% silt, 60.2% sand and 18.6% clay and 7.2 pH) was utilized for rate studies. The thin layer soil plates (10x10 cm, 50 um thickness) were prepared with fine powdered soil, sieved through a 2mm sieve according to the method of Helling and Turner (1968). Onto each soil plate, 1 ml solution of monocorotophos in chloroform or acetone was evenly applied by spraying to give a concentration of 7 ug cm^{-2} and exposed to sunlight during the month of April New Delhi (India) for 30 days. Samples were taken after 0,3,5,7,14,21 and 28 days interval. The thin layer of soil was scrapped from the glass plate and extracted twice by shaking for 10min. with 6 ml of ethylacetate. The solvent was concentrated to 1 ml and solution analyzed by glc.

Monocrotophos (0.2mg litre^{-1}) dissolved in the selected water (distilled water , tap water and 20 g litre^{-1} aqueous acetone) in one litre closed pyrex flask was exposed to natural sunlight for 30 days (8h day^{-1} April). Sunlight intensity at wavelengths between 300 and 400 nm was approximately 720, 1780 and 350 uW cm^{-2} at the beginning, middle and end of the day, respectively.

A control sample was kept in the dark by covering the flasks with aluminium foil to confirm that a given photoproduct was derived only by photochemical reactions. Samples were withdrawn after 0,3,5,7,14,21 and 28 days intervals. The aqueous solution was extracted with chloroform and the solvent was concentrated to 1 ml and analyzed by glc.

RESULTS AND DISCUSSION

For comparison purposes the degradation of monocrotophos on glass surface with sunlight was studied. Results showed that no degradation of monocrotophos occurred in the dark, since 98% of the applied (100%) monocrotophos was recovered backas analyzed by gas liquid chromatography. Whereas on exposure to sunlight for 8h, 72.8% of the applied monocrotophos could be recovered, indicating photodecomposition of monocrotophos and formation of other photolysis products.

Alluvial, laterite, red loamy and black soils treated with monocrotophos were irradiated with ultraviolet and sunlight as described, utilizing glass surface as control. Results obtained are summarized in Table 2.

Table 2 Effect of soil types on photodecomposition of monocrotophos

	Monocrotophos Exposed to Light on 268cm^2 Surface[a]				
Exposure for 8h to	Glass surface	Alluvial soil pH=8.4	Black soil pH=8.1	Red loamy soil	Laterite soil pH=4.8
		% Recovery of monocrotophos			
UV (254 nm)	62±2	40.4±2	49.6±1	54.9±2	60.1±3
Sunlight	72.8±1	52.4±3	58.1±2	60.0±1	62.0±1
Dark	98.1	96.3	96.1	96.0	96.0

(a) Monocrotophos (100 ug) was applied to glass surface or mixed with 50 g of air dried soil. Results are average of duplicate experiment. Analysis was done by glc.

In the absence of light no degradation of monocrotophos had occurred.Practically all (over 96%) of the applied (100%) monocrotophos was recovered from the glass or soil extracts. Irradiation of mono-

crotophos on glass or a soil surface for 8h, had pronounced effect. On a glass surface recovery of monocrotophos was 62% with ultraviot light and 72.8% with sunlight. Photodegradation of monocrotophos was found to be greater on soil surfaces then on a glass surface which could be due to soil properties such as organic matter. The order of photodegradation on four different soil were :-

Alluvial < lack < Redloamy < Laterite

A sandy loam soil, treated with monocrotophos as described was used ina dry, moist and waterlogged condition to study the effect of soil moisture and soil surface on the photodegradation of monocrotophos.

Results summarized in Table 3 indicated that in the absence of light, no degracation of monocrotophos occurred under all experimental conditions.

Table 3 Effect of soil moisture and soil surface area on photodecomposition of monocrotophos

Exposure of 8h to	Monocrotophos Exposed to Light(a)							
	Glass Surface (Dry) 16 cm^2	Sandy Loam Soil						
		268cm^2	Dry		Moist		Flooded	
			16 cm2	268 cm^2	16 cm^2	268 cm^2	16 cm^2	268 cm^2
UV Light	75.0	58.3	70.9	47.8	67.3	42.2	62.3	38.7
Sunlight	87.1	72.8	78.3	55.4	76.3	49.8	71.8	43.5
Dark	97.5	97.3	98.1	98.0	97.5	98.1	98.1	98.0

(a) Monocrotophos (100 ug) was applied to the glass surface and soil surfaces.After that soil was kept dry,, moist, and water logged. Results are average of duplicate results.

With insecticide deposited on a glass surface and exposure to light, an increased loss of monocrotophos was noticed, when the insecticide was applied to a larger surface area, the extend of loss was greater with ultraviolet light than with sunlight. Thus light apparently is less effective when monocrotophos is applied to a small surface area of glass or dry sandy loam soil. This explains the increase in the rate of degradation with increase in area.

Soil moisture, however, was an important factory, contributing to the fate of monocrotophos due to irradiation with UV light or sunlight especially when area had been enlarged by a factor of 16 to 268cm^2. Similar results were found with the flooded soil. Thus rate of photodegradation was greater on flooded and moist soil than dry loam soil.

Photodegradation of monocrotophos on bean leaves was studied as described above over an 8h exposure period to sunlight. Results summarised indicated a pronounced effect of sunlight on the degradation of monocrotophos. Of the applied monocrotophos 94% was recovered from the bean plant, when kept in the dark and in sunlight however a total of 68% was recovered. This figure was 72.0% with the glass surface.

The rate of photodegradation of monocrotophos in tap water on exposure to light was compared with that in sterilised distilled water and water containing 20 g/litre acetone as a sensitizer under identical conditions. The rate of degradation varied, depending upon the type of aqueous solution being fastest in the presence of acetone. The rate of degradation of monocrotophos in tap water was approximately twice that in distilled water under sunlight.

Thus results presented in this study clearly indicates the effect of various environmental factors have to be considered, whenb the photodegradation of Agrochemicals is being investigated.

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Received January 10, 1989; accepted February 1, 1989